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# Fast Solution Combustion Synthesis of Porous NaFeTi<sub>3</sub>O<sub>8</sub> with Superior Sodium Storage Properties

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In this work, NaFeTi<sub>3</sub>O<sub>8</sub> with three-dimensional porous net-like sheet morphology is firstly prepared by a simple and effective solution combustion method. Encouragingly, when being assessed as an anode electrode for sodium ion batteries, the NaFeTi<sub>3</sub>O<sub>8</sub> net-like sheet composite exhibits superior electrochemical properties. We also study the effect of the combustion fuel glycine. The results indicate that the NaFeTi<sub>3</sub>O<sub>8</sub> composite tends to be porous with glycine as the combustion fuel, which displays more excellent long cyclic stability (discharge capacity of 91 mA h g<sup>-1</sup> after 1000 cycles at the current density of 0.5 A g<sup>-1</sup>) and superior rate performance (84.4 mA h g<sup>-1</sup> even at 1.6 A g<sup>-1</sup>) than that of NaFeTi<sub>3</sub>O<sub>8</sub> without glycine as the combustion agent. The enhanced electrochemical properties could be ascribed to the unique porous morphology, which achieves better electrolyte infiltration and faster ion diffusion.

Keywords: Ti-based materials, NaFeTi<sub>3</sub>O<sub>8</sub>, solution combustion method, sodium ion batteries



### **1. INTRODUCTION**

The lithium-ion batteries (LIBs) as one of the most successful energy storage technologies have been widely used in portable electronics devices.<sup>[1]</sup> However, the lack of lithium resources will limit their further applications in the future.<sup>[2,3]</sup> The sodium has asimilar physical and chemical properties and electrochemical behaviors to the lithium, since the ionic radius of sodium is about 1.02 Å, slightly larger than the lithium (0.76 Å) and the operating voltage is low (–2.71 V, Li<sup>+</sup>/Li working voltage is –3.04 V).<sup>[4,5]</sup> With

other advantages such as rich-storage and low-cost, the sodium is considered as the most likely substitute for lithium.<sup>[6,7]</sup> Therefore, the sodium-ion batteries (SIBs) has aroused widespread concern and been expected to be applied in the large-scale energy storage devices.<sup>[3,8,9]</sup>

Up to now, among the tested anode materials for the SIBs, the carbon materials,<sup>[10-13]</sup> alloys,<sup>[14-18]</sup> metal oxides,<sup>[19-23]</sup> metal sulfides,<sup>[24-26]</sup> amorphous phosphorus<sup>[27]</sup> and metal phosphides<sup>[28,29]</sup> exhibit high specific capacities but with large volume change during charge and discharge, which makes them improper for long-life batteries. The Ti-based materials,<sup>[30,31]</sup> such as the spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,<sup>[32]</sup> anatase TiO<sub>2</sub><sup>[33,34]</sup> and Na<sub>x</sub>Ti<sub>y</sub>O<sup>[35-37]</sup> based on insertion/extraction mechanism have attracted much attentions due to their advantages of small volume change, good rate performance,

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environmental friendliness and good safety. However, the Ti-based materials mainly composed of solid-state,<sup>[38]</sup> sol-gel,<sup>[39]</sup> hydrothermal method.<sup>[40]</sup> which are unsuitable for industrial production, because a long time and higher calcination temperature are necessary for the solid-state method, the sol-gel process is complex and time-consuming and the hydrothermal reactions under high pressure and temperature conditions are dangerous, high-cost and low yield. There is a significant and urgent demand to look for simple, effective and energy-saving method to synthesize Ti-based oxides with stable structure, higher capacity and coulomb efficiency.

The solution combustion method has been well applied to prepare the Ti-based anode materials of LIBs, [41-43] but has not ever used in Na-Ti-O materials for anode materials of SIBs. Compared with the conventional synthesis methods, this route has three advantages: (1) the preparation process is easy to control; (2) the heating time is extremely short; (3) the product has a porous morphology with a high surface area, which is beneficial to the electrolyte infiltration and ion diffusion. Herein, NaFeTi<sub>3</sub>O<sub>8</sub> materials with good crystallinity were successfully fabricated by the simple and fast solution combustion method. As the anode material of the SIBs, the performance of NaFeTi<sub>3</sub>O<sub>8</sub> electrode was first tested by Junke Hou et al.<sup>[38]</sup> The results show that the NaFeTi<sub>3</sub>O<sub>8</sub> materials synthesized by solution combustion method have an excellent cyclic stability and superior rate performance, delivering a reversible discharge capacity of 432.4 mA h g<sup>-1</sup> at the current density rate of 50 mA  $g^{-1}$  with the coulomb efficiency of 72.4%. It is worth noted that even at the high current rate of 1.6 A g<sup>-1</sup> the discharge capacity retains 84.4 mA h  $g^{-1}$  yet, and the discharge capacity of 91 mA h  $g^{-1}$ still maintains after 1000 cycles at current density of  $0.5 \text{ A g}^{-1}$ .

# 2. EXPERIMENTAL PROCEDURE

The preparation process of NaFeTi<sub>3</sub>O<sub>8</sub> material is as follows: a dilute ammonia solution (pH = 10, 12 mL) was dropped slowly into tetrabutyltitanate Ti(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub> (12 mmol) with strong stirring to precipitate TiO(OH)<sub>2</sub> at low temperature, followed by adding nitric acid (4 mL) to form the precursor [TiO(NO<sub>3</sub>)<sub>2</sub>] aqueous solution. Then the precursor solution was mixed uniformly with 0.34 g NaNO<sub>3</sub> (4 mmol), 1.62 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (4 mmol) and 2.00 g glycine by ultrasound. Afterward the mixed solution was placed in an alumina crucible and sintered at 800 °C for 20 min in a muffle furnace, and then cooled down naturally in air. Finally, as-prepared product was obtained, which was marked as NaFeTi<sub>3</sub>O<sub>8</sub>-glycine. The contrast sample was prepared by the same process without glycine, marked as NaFeTi<sub>3</sub>O<sub>8</sub>-none.

#### 2.1 Materials characterizations

The field emission scanning electron microscope (LEO 1530, HITACHI S-4800) was used to characterize the morphology of the as-prepared material. TEM images were obtained by using the high-resolution transmission electron microscopy (FEI, TECNAI G2 F30). The X-ray diffraction (XRD) patterns was recorded with Philips X'pert Pro Super X-ray diffractometer and CuK $\alpha$  radiation. The Brunauere-Emmette-Teller (BET) method was used to attain the nitrogen adsorption and desorption isotherms on micromeritics surface area and a porosity analyzer (ASAP 2020) was used to measure specific surface area of porous NaFeTi<sub>3</sub>O<sub>8</sub>-glycine.

#### 2.2 Electrochemical performance characterization

The testing NaFeTi<sub>3</sub>O<sub>8</sub> electrodes were prepared by mixing the as-synthesized material, acetylene black, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) (70:20:5:5, w/w/w) uniformly with water into a slurry, which was then spread on copper foil and dried at 80 °C for 24 h in a vacuum oven. The CR2032-type coin cells were constructed by assembling and sealing as-prepared NaFeTi<sub>3</sub>O<sub>8</sub> electrodes with the pure sodium metal as a counter electrode, the glass fiber (GF/A, Whatman) as a separator, and the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) at the volume ratio of 1:1 with 1 mol  $L^{-1}$  NaClO<sub>4</sub> dissolved as a electrolyte in an argon-filled glove box. The fabricated cells were electrochemically cycled between 3.0 and 0.01 V using a CT2001A cell test instrument (LAND Electronic Co.) Cyclic voltammograms (CVs) were carried out at a scan rate of 0.1 mV s<sup>-1</sup> in 0.01-3.0 V. The electrochemical impedance spectra (EIS) of the NaFeTi<sub>3</sub>O<sub>8</sub> electrodes discharged to different voltages were measured in the frequency range of 10 mHz-100 kHz by using twoelectrode coil cells via the Autolab PGSTAT 101 cell test instrument with Zplot software by imposing an alternate current with an amplitude of 10 mV on the electrode.

### **3. RESULTS AND DISCUSSION**

The X-ray diffraction (XRD) pattern (Fig. 1a) illustrates that the diffraction peaks of both the NaFeTi<sub>3</sub>O<sub>8</sub>-glycineand NaFeTi<sub>3</sub>O<sub>8</sub>-none materials consist well with the PDF standard card (PDF No. 01-070-0637) and belong to the monoclinic system (space group: C12/m1). The main characteristic peaks at 14.3°, 15.1°, 24.5°, 28.8° and 29.6° are corresponding to (001), (200), (110), (002) and (111) plane, respectively. The framework of NaFeTi<sub>3</sub>O<sub>8</sub> reported by Ishiguro *et al.*<sup>[44]</sup> is shown in Fig. 1b, from which it can be seen that O atoms pack in the octahedral structure, while Ti/ Fe atoms arranged in disorder in the octahedral center and the M/O octahedral arranged edge with edge, so that the Na<sup>+</sup>



**Fig. 1.** (a) XRD patterns of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and NaFeTi<sub>3</sub>O<sub>8</sub>none materials; (b) The structural model of NaFeTi<sub>3</sub>O<sub>8</sub> on the (010) projection.



Fig. 2. SEM images of (a, c) NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and (b, d) NaFeTi<sub>3</sub>O<sub>8</sub>none; (e) HR-TEM image and (f) the corresponding SAED patterns of NaFeTi<sub>3</sub>O<sub>8</sub>-glycine material.



Fig. 3. Nitrogen adsorption-desorption isotherms at 77 K of NaFeTi $_3O_8$ -glycine material.

channels are formatted along the b-axis direction. To observe the unit cell structure of NaFeTi<sub>3</sub>O<sub>8</sub>, two immobilization sites for sodium ion insertion. The theoretical specific capacity of NaFeTi<sub>3</sub>O<sub>8</sub> is calculated to be 153 mA h g<sup>-1</sup>. The sodium ion insertion process can be described as: NaFeTi<sub>3</sub>O<sub>8</sub> + x Na<sup>+</sup>  $\rightarrow$  Na<sub>1+x</sub>FeTi<sub>3</sub>O<sub>8</sub> ( $x \le 2$ )

The scanning electron microscope (SEM) images (Figs. 2a and 2c) describe the morphology of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine material with three-dimensional porous net-like sheet made of primary particles with a diameter of about 200-300 nm, while the NaFeTi<sub>3</sub>O<sub>8</sub>-none material (Figs. 2b and 2d) are blocks stacked by nanoparticles. This is due to the combustion of glycine in the reaction to produce a lot of gas and format many irregular channels. From the HRTEM image (Fig. 3f) lattice stripes of (110) and (310) can be observed. The corresponding SAED patterns of Fig. 3f are presented in Fig. 3f.

Charactering by galvanostatic cycling, it can be seen from the charge-discharge profiles (Fig. 4) that the NaFeTi<sub>3</sub>O<sub>8</sub>glycineand NaFeTi<sub>3</sub>O<sub>8</sub>-none electrodes have similar electrochemical behaviors. The first discharge platform at 0.2 V is irreversible. After several cycles, the discharge platform gradually stabilized at about 1.5 V and 0.5 V and the charging platform at 0.9 V and 1.9 V. The first discharge platform is at 0.2 V. After several cycles, the discharge platform gradually stabilized at about 1.5 V and 0.5 V and the charging platform at 0.9 V and 1.9 V.

Based on the nitrogen adsorption-desorption isotherms (Fig. 3), the specific surface area of the material is calculated to be  $4.35 \text{ m}^2 \text{ g}^{-1}$ , while average particle size is 380 nm and pore width 22 nm, which is quiet considerable compared with the materials synthesized by traditional solid-state method. Because the porous structure with a large surface area is beneficial for the electrolyte infiltration and reducing the sodium ion diffusion distance so as to improve the

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Fig. 4. Electrochemical measurements of (a) NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and (b) NaFeTi<sub>3</sub>O<sub>8</sub>-none electrodes charge-discharge profiles at low current density of 50 mA  $g^{-1}$ .



Fig. 5. Cyclic voltammograms of (a) NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and (b) NaFeTi<sub>3</sub>O<sub>8</sub>-none at a scan rate of 0.1 mV s<sup>-1</sup> in 0.01-3.0 V.

Table 1. The cycling performance for NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and NaFeTi<sub>3</sub>O<sub>8</sub>-none at different current densities.

Current density (mA g <sup>-1</sup> )	50	100	200	400	800	1600	50
NaFeTi <sub>3</sub> O <sub>8</sub> -glycine	419.4	231.8	174.9	142.3	113.1	84.4	204.6
NaFeTi <sub>3</sub> O <sub>8</sub> -none	228.3	76.0	49.4	33.2	19.4	6.5	79.5

electrochemical performance.

Figure 6 shows the electrochemical properties comparison of two electrode materials. When discharging at the current density of 50 mA g<sup>-1</sup>, the discharge capacity of the first cycle of NaFeTi<sub>3</sub>O<sub>8</sub>-glycine is 432.4 mA h g<sup>-1</sup> with the coulomb efficiency 72.4% and the capacity of the second cycle is 320.8 mA h g<sup>-1</sup>. After 200 cycles the discharge capacity still maintains 162.1 mA h g<sup>-1</sup>. For the NaFeTi<sub>3</sub>O<sub>8</sub>-none, the first discharge capacity of the first cycle is only 223.2 mA h g<sup>-1</sup> with the coulomb efficiency 64.4% and the second is 152.6 mA h g<sup>-1</sup>. And the discharge capacity maintains only 78.8 mA h g<sup>-1</sup>. Meanwhile, more excellent rate performance of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine material is obvious in Fig. 6b. The discharge capacities of two materials at different current densities are listed in Table 1. Moreover, the long cyclic performance of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycineelectrode at a high current density is tested. The result can be obtained in Fig. 6c. The discharge capacity of the 1000th cycle maintains 91 mA h g<sup>-1</sup> at the current rate of 500 mA g<sup>-1</sup> with the small current density of 50 mA g<sup>-1</sup> activation in the first five cycles.

In order to confirm the ability to insert sodium ions of NaFeTi<sub>3</sub>O<sub>8</sub> material as an anode material of the SIBs, we take the discharge process states into consideration, which are marked in Fig. 7a. Furthermore, the state marked as C-3.0 V that the electrode is charged to 3.0 V is also measured to compare the change of material structure before and after discharging and charging. The peaks at  $42.3^{\circ}$  and  $50.4^{\circ}$  in Fig. 7b belong to the Cu current collector and the Cu peaks are used as a reference to determine the change of other peak





**Fig. 6.** Electrochemical measurements of NaFeTi<sub>3</sub>O<sub>8</sub>-glycine and NaFeTi<sub>3</sub>O<sub>8</sub>-none electrodes: (a) charge-discharge performance at low current density of 50 mA  $g^{-1}$ ; (c) rate performance at various current densities; (c) long cycling performance at the current density of 500 mA  $g^{-1}$  of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine electrode.



**Fig. 7.** (a) The corresponding electrochemical plot during the first discharge process at different states; (b) *ex-situ* XRD patterns of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine electrode at a series of potentials in the initial discharge process; (c) the (110), (002) and (111) peaks area of NaFeTi<sub>3</sub>O<sub>8</sub>; (d) *ex-situ* Nyquist of the NaFeTi<sub>3</sub>O<sub>8</sub>-glycine electrode at a series of potentials in the initial discharge process.

	OCP	D-1.0V	D-0.8V	D-0.5V	D-0.2V	D-0.15V	D-0.1V			
(110)	3.6332	3.6344	3.6370	3.6406	3.6421	3.6383	3.6417			
(002)	3.0993	3.1027	3.1012	3.1043	3.1055	3.1060	3.1083			
(111)	3.0203	3.0204	3.0231	3.0239	3.0242	3.0247	3.0259			

Table 2. The change of the crystalline interplanar spacing (d) for the (110), (002) and (111) during the initial discharge. (Å)

positions to avoid the test system errors. It is clear that the crystal structure of NaFeTi<sub>3</sub>O<sub>8</sub> electrode remain essentially unchanged in the first discharge process, but the peak intensities decrease significantly after the state of D-0.15V, which may be attributed to the pulverization of electrodes.<sup>[45,46]</sup> What is need to pay attention to is that the peak positions of NaFeTi<sub>3</sub>O<sub>8</sub> electrode at C-3.0V are corresponded to the OCP electrode structure, which can be a direct proof that the NaFeTi<sub>3</sub>O<sub>8</sub> material has certain structural stability and excellent reversibility for sodium storage. Another phenomenon is that there is such a small shift towards lower angles for the peaks corresponding to the (110), (002) and (111) in Fig. 7c. According to the Bragg's law and Philips X'pert phase analysis software, the crystalline interplanar spacings of the (110), (002) and (111) are displayed in Table 2. It is clear from the table that the crystalline interplanar spacings are increasing during the discharge process, which may be attributed to the sodium ion intercalation. These results indicate that significant stability of the structure of NaFeTi<sub>3</sub>O<sub>8</sub> is retained during sodium ion intercalation/ deintercalation from the electrode materials.

The electrochemical impedance spectra (EIS) deliver the kinetic information of the electrode reaction. Based on the ex-situ EIS measured at the states corresponding to Fig. 6a, the equivalent circuit parameter values obtained from fitting results by the Zplot software are listed in Table S1. At OCP and D-1.0V, a semicircle appears in the high frequency (HF) range followed by a slightly inclined line in the low frequency (LF) range in the Nyquist plot of NaFeTi<sub>3</sub>O<sub>8</sub> anode. After D-0.8V, there is another depressed semicircle in the mediate frequency (MF) region and the diameter increases gradually with the continual discharging. It is generally suggested that the resistance in the HF region may belong to the reaction resistance of new phase like SEI film<sup>[47,48]</sup> and the resistance in MF region may reflect the charge transfer resistance of sodium ion insertion.<sup>[49]</sup> Zhao et  $al.^{[50]}$  have reported the similar effect for their Mg<sub>0.5</sub>Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> electrodes in the LIB and SIB cells. It must be noted that the diameter of the depressed MF semicircle increases rapidly at D-0.1V. As reported before, the SEI layer would form in NaClO<sub>4</sub>-ethylene carbonate electrolyte at low potential state.<sup>[50,51]</sup> And the SEI layer would limit the diffusion of sodium ion and increase impedance.<sup>[52]</sup> Taking the irreversible peak at 0.2 V of the first cycle in CV curve into account, the electrolyte decomposition and irreversible sites for sodium ion insertion in the crystal lattice defects may

emergence, which can be considered as the formation of the new phase like SEI film.<sup>[53]</sup> It can be speculated that the increased depressed MF semicircle may be related with the SEI film, which limits the sodium ion diffusion and caused an increased impedances.<sup>[52,54]</sup> In addition, when be charged to 3.0V, the semicircle in MF region disappears, leaving only the HF transfer resistance, similar to the OCP state, which is another proof that the NaFeTi<sub>3</sub>O<sub>8</sub> material is reversible in the charge-discharge process.

# 4. CONCLUSIONS

In summary, the NaFeTi<sub>3</sub>O<sub>8</sub> with three-dimensional porous net-like sheet has been firstly prepared by a simple and effective solution combustion method. The porous NaFeTi<sub>3</sub>O<sub>8</sub> maintains a reversible discharge capacity of 91 mA h g<sup>-1</sup> after 1000 cycles at the current density of 0.5 A  $g^{-1}$  and even at the high current density of 1.6 A  $g^{-1}$ , the NaFeTi<sub>3</sub>O<sub>8</sub> still holds a discharge capacity of 84.4 mA h g<sup>-1</sup>. The ex-situ XRD results display that the NaFeTi<sub>3</sub>O<sub>8</sub> shows good structural stability and reversibility as a sodium storage materials. Therefore, since it has the advantages of both excellent cyclic capacity and superior rate performance, we believe that the NaFeTi<sub>3</sub>O<sub>8</sub> material has a potential to be applied to anode material for the long-cycling and high-rate sodium ion batteries. And the solution combustion method is promising to be used for synthesis of titanium-based materials.

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