

Hydrothermal synthesis of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ /graphene composites as anode materials for lithium-ion batteries

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Abstract: A potential Lithium-ion battery anode material $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 0.15$) has been synthesized via a facile hydrothermal method with short processing time and low temperature. The XRD and FE-SEM results indicate that samples with Na-doped are well-crystallized and have more homogeneous particle distributions with smaller overall particle size in the range of 300-600nm. Electrochemical tests reveal that Na-doped samples exhibit impressive specific capacity and cycle stability compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at high rate. The $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ electrode deliver an initial specific discharge capacity of 169mAh/g at 0.5C and maintained at 150.4mAh/g even after 40 cycles with the reversible retention of 88.99%. Finally, a simple solvothermal reduction method was used to fabricate $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /graphene ($\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /G) composite. Galvanostatic charge-discharge tests demonstrate that this sample has remarkable capacities of 197.4mAh/g and 175.5mAh/g at 0.2C and 0.5C rate, respectively. This indicates that the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /G composite is a promising anode material for using in lithium-ion batteries.

Key words: $\text{Li}_4\text{Ti}_5\text{O}_{12}$; Na-doping; graphene; hydrothermal synthesis.

1. Introduction

Lithium-ion batteries are a new generation battery that have been rapidly developed over the past few decades. Compared to other second generation batteries, lithium-ion batteries have numerous merits, such as high energy densities, long cycle lifetime, high lithium insertion potential, safety and environmentally friendly, which allows them to be widely used in a range of devices from portable electronics to electric vehicles[1-2]. In contrast with the current commercial graphite anode materials, lithium titanate is a new generation anode material with excellent electrochemical and dynamic properties. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has outstanding cycle performance and favorable stable structure due to the zero strain during Li-ion insertion/extraction and not distort in dimensional or volume

at high charge/discharge rates. It offers a long voltage-plateau around 1.55V versus Li/Li^+ compatible with polymer electrolytes and high-voltage cathodes, therefore providing an electrode system with much improved safety characteristics and excellent reversibility. However, there are limits to its commercial application due to its intrinsically poor electrical conductivity, sluggish lithium-ion diffusion coefficient and unsatisfactory specific capacity [3-5].

In order to overcome these serious blemishes of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material, researchers have done a lot of work about these issues. Summarizing the previous reports: three approaches have been used to improve electrochemical performance: (1) explore the effective synthesis route to get nano-sized particles. Nanoscale particles can shorten the Li-ion diffusion distance and significantly broaden contact between electrode and electrolytes [6-11]. (2) introduce the

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favorable conductive material into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, such as a carbon materials or metal powder [10-14]. Recently, Chen et al successfully synthesized a mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material that had grown on the graphite oxide (rGO=18wt%). This material possesses impressive high-rate performance with an initial discharge capacity of 132mAh/g at 40C [15]. (3) modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with metal or non-metal ions at Li, Ti or O sites to enhance its electronic conductivity, such as Nb^{5+} , Ni^{2+} , Cu^{2+} , Ta^{5+} , Br^- .

Graphene (G), a two-dimensional macromolecular sheet of carbon atoms with a honeycomb structure, is well known as a novel material in lithium-ion batteries. Two-dimensional graphene sheets with excellent electronic conductivity and mechanical properties have gained interest as a prominent conductive additive for hybrid nano-structured electrodes [16]. Introducing graphene into the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material via mixing, coating or by growing the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles directly on graphene had obtained great progress [14-15]. Zhu et al. [17] synthesized a composite material by implanting graphene into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers. Compared to the original $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, this graphene composite presents superior electronic conductivity, long-term cycling stability and outstanding rate performance.

This paper proposes to employ a facial hydrothermal method to synthesize the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material using LiOH and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ as starting materials. Compared to the conventional high temperature solid-state method, this facile hydrothermal route can gain more tiny particles with well crystallinity, and more particles evenly distributed. However, pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ does not meet the requirements for a competent anode electrode. Herein, different mole ratios of Na have been substituted for Li, and the effect of Na-doping on the electrochemical performance has been investigated. The end result was in order to select the optimum content of Na-doping to improve high-rate performance and electronic conductivity. To our knowledge, modified spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with low content of sodium using hydrothermal method has not been reported until now. Finally, a simple solvothermal reduction method was used to fabricate the optimal anode material $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /graphene ($\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /G) use ethanol as the reductant. This approach can remove the oxygen-containing functional groups (uniformly distribute in the surface of graphite oxide) gradually compared to a chemical reduction method, and has the additional benefit of not producing any toxic byproducts. The composite of

$\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /G fabricated by the solvothermal reduction method has smaller overall particle size and larger specific surface area, and can form a conductive network by means of using two-dimensional structure of graphene, which greatly increase the electronic conductivity and diffusivity of the Li-ion. Electrochemical tests show it has outstanding electrochemical performances, which reveal that this material is a promising anode material for lithium-ion batteries.

2. Experimental

2.1 Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with Na-doping

All raw materials involved in this work were received without any further processing. Pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized via a hydrothermal method with LiOH.H₂O and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ as raw materials. Initially, 17mL tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) was dissolved into ethanol under vigorously stirred to form a clear solution. A certain quantity of lithium hydroxide monohydrate was dissolved in deionized water to form a 2mol/L LiOH solution. Followed, the LiOH solution was added into the base solution drop and drop with constant stirring. Then, the ivory solution was transferred into a Teflon-lined autoclave and held at 180°C for 24h. Until the solution cooled to room temperature naturally, washed the precursor with deionized water and ethanol for several times via centrifuging, and lastly dried in an oven for approximately 12h. Finally, the as-prepared precursor was calcinated in a muffle at 700°C for 8 h with a temperate ramp rate of 4°C min⁻¹ to obtain $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder. Excess LiOH.H₂O (8mol%) was added to compensate the Li source loss in the high temperature calcination process.

In order to obtain the Na-doped samples, LiOH and NaOH solution were added into the base solution simultaneously while undergoing vigorous stirring using a magnetic stirrer, other steps were performed as above. $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ (x=0, 0.05, 0.1, 0.15) samples were gained by adjusting the doping content of NaOH.

2.2 Synthesis of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ /G composite

Graphite oxide nanosheets were synthesized by a modified Hummers method using the natural graphite powders as raw material. A 2.0g/L graphene oxide solution

(GO) was prepared by dispersing graphite oxide powder into an ethanol solvent with ultrasonication for 0.5 h. In order to prepare the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composite, 1g $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ was dissolved in 20mL ethanol and vigorously stirred for 30min, then the previously prepared GO solution was transferred into the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ solution slowly with 3wt% content of GO. The mixture was next transferred into Teflon-lined autoclave and maintained at 120 °C for 12h. A gray $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composite powder was obtained by washing and drying the resulting product.

2.3 Material characterization and electrochemical measurements

The crystalline structure of the prepared samples was identified by X-ray powder diffraction measurements with Cu K α radiation. A Field emission scanning electron microscope (FE-SEM, SU8020) and Energy Dispersive Spectrometer (EDS) were used to observe the particle morphology and analyze composition of the samples.

In order to test the electrochemical performance of the as-prepared anode materials, anode material, acetylene black, and polyvinylidene fluoride (PVDF) binder at a weight ratio of 8:1:1 was mixed and dissolved in appropriate content of N-methylpyrrolidone (NMP) to form homogeneous slurry. The prepared slurry was then brushed onto a thin aluminum foil substrate using a doctor-blade and dried in a vacuum oven at 120 °C for 12h, then cut into slices with a diameter of 14mm to obtain a working electrode. Pure lithium foil was used as the counter electrode. The cells were assembled in an argon-filled glove box and were tested using CR2032 coin-type half cells. Celgard2400 microporous polyethylene membrane was used as the separator, and 1M LiPF_6 dissolved in dimethyl carbonate (DEC)/ethylene carbonate (EC) (1:1 by volume) as the electrolyte. The charge/discharge test was carried out on a CT3008W cell test instrument with a potential range of 1.0-2.5 V under different current densities at room temperature.

3. Results and discussion

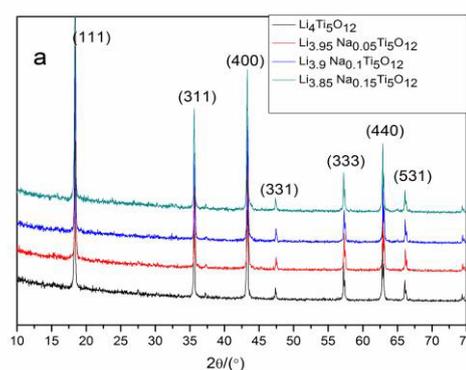
3.1 The effect of Na-doping on crystal structure, morphology and electrochemical performance

The precursor of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared through a

hydrothermal reaction and calcined at low-temperature to obtain the Na-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. The XRD patterns of the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample with and without Na-doping are depicted in Fig.1(a). The diffraction peaks of all investigated samples can be attributed to expected reflections of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a space group of Fd-3m [5]. No impurity peaks were observed, which reveal that a small amount of Na^+ ions have entered the lattice of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without causing large changes in its structural characteristics. In order to clearly understand the effects of Na-doping in crystal structure, the enlarged peak of (111) plane in the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ samples are shown in Fig.1 (b).

It is easily observed that the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ samples undergo a slight shift toward lower degrees, which demonstrates that the lattice parameter increases due to the Na-doping. This is likely attribute to the larger size of the Na^+ ion (0.102nm) replace the site of Li^+ ion (0.076nm). In addition, the lattice parameter increase is beneficial to enhance the specific capacities of materials.

FE-SEM images of pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ are shown in Fig.2. Although all samples are aggregated due to the final calcination process, the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ sample has more homogeneous particle products and more narrow particle-size distributions compared to pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The sample is well crystallized with a particle size in the rang of 300-600nm. In order to gain more information, EDS was carried out to confirm that Na was present in the Na-doped materials. The three different colored bright spots correspond to the presence of Ti, O and Na in Fig.3, respectively. Combined with the above phase analysis, Na^+ ions can be considered conclusively to have entered the lattice structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It can also be noted that all elements are uniformly distributed within the sample.



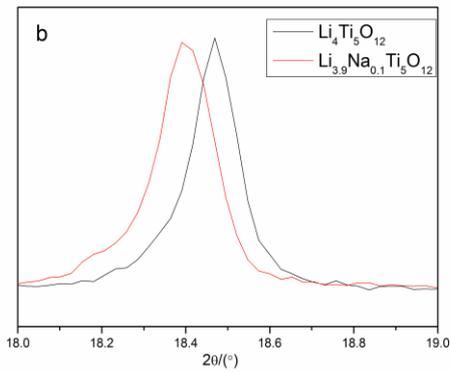


Fig1 (a) XRD patterns of the $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.05, 0.1, 0.15$) materials; (b) Enlarged (111) peaks of the $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.1$) materials

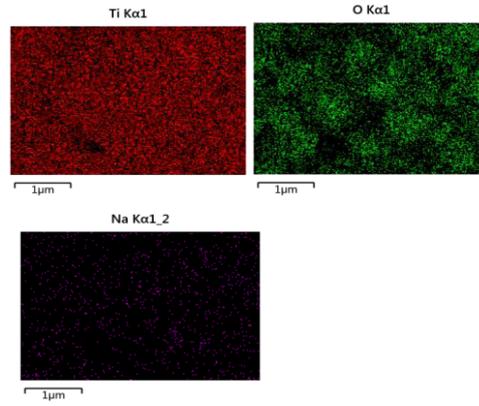


Fig.3 EDS element mapping of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$

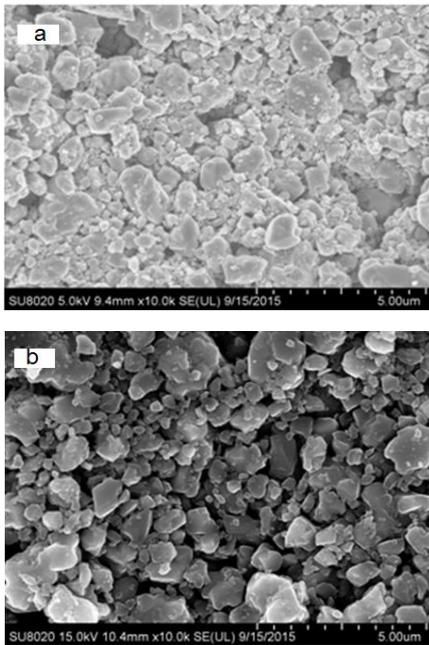
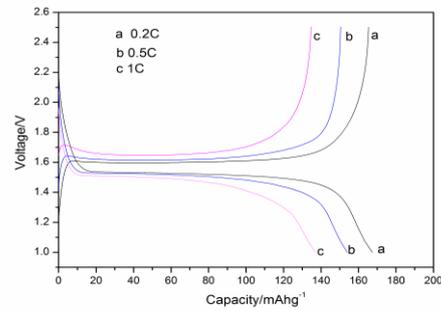
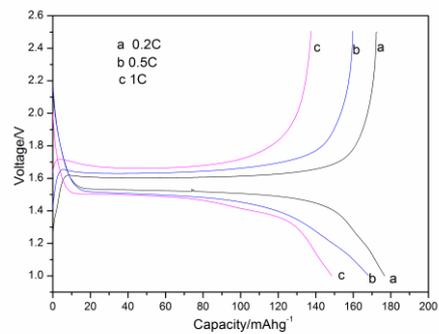


Fig.2 FE-SEM images of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.1$): (a) $x=0$, (b) $x=0.1$

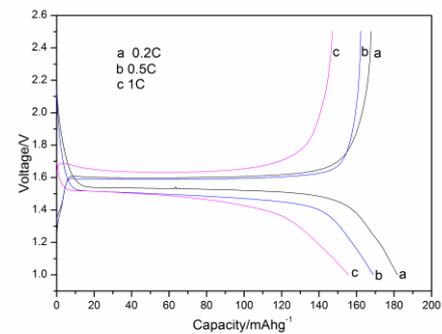
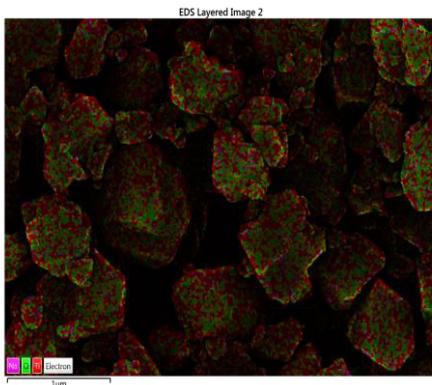
a



b



c



d

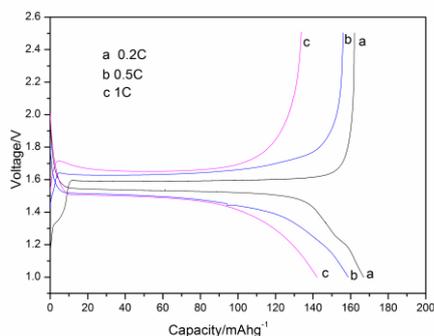


Fig.4 Initial charge/discharge curves of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.05, 0.1, 0.15$) samples at 0.2C, 0.5C, 1C rates: (a) $x=0$, (b) $x=0.05$, (c) $x=0.1$, (d) $x=0.15$

The specific capacities of all samples were tested through the galvanostatic charge/discharge method by a CT3008W cell test instrument. The initial charge/discharge curves of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.05, 0.1, 0.15$) samples at different current rates are shown in Fig.4. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode exhibits a two-phase transition between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$ during Li-ion insertion/extraction reactions. All anode electrodes with and without Na-doping have a stable voltage platform at current rates of 0.2C or 0.5C, and the voltage platform occupies 80% of the discharge curve with $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This reveals that a stable $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material can be successfully synthesized by means of a facile hydrothermal method. In addition, the results consistently confirm that Na-doping does not alter the structure of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

The initial specific discharge capacity of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.05, 0.1, 0.15$) electrodes at 0.2C rate were measured as 167.4, 176.7, 181.9 and 166.9mAh/g, respectively. All samples have a high capacity and close to or higher than theoretic capacity. This may be due to the Li-ions have enough time to move between anode and cathode electrodes and the reaction motivation can keep pace with the charge current at low rate, resulting in a lower electrode polarization and higher capacity

The specific capacities of the samples decrease when the charge/discharge current density increases, the effect is particularly noticeable in the pristine sample. Fig.4 shows that the initial specific discharge capacities of $\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($x=0, 0.05, 0.1, 0.15$) electrodes at 0.5C rate are 154.0, 168.3,

169.0 and 158.6mAh/g, respectively, with the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ electrode has the highest capacity among all samples. When the discharge rate increases to 1C, the capacity of the pristine electrode decreases to 137.1mAh/g, but the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ sample retains at 155.7mAh/g, a significant improvement over the pristine sample. This reveals that Na-doping plays an important role in the improvement of reversible capacities at high rates. This may be due to the comparatively large size of the Na^+ ions (0.102nm) replace the Li^+ ions (0.076nm) and lead to the lattice parameter increase, which in turn may lead to an increased in electronic/ionic conductivity and reversible specific capacity. However, the large ion radius of Na^+ ions substitute Li^+ ions may hinder the ion insertion. When the concentration of Na^+ is too low or too high, hindering effects may play a relatively leading role. Therefore, it is important to achieve the appropriate ratio to enhance the electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

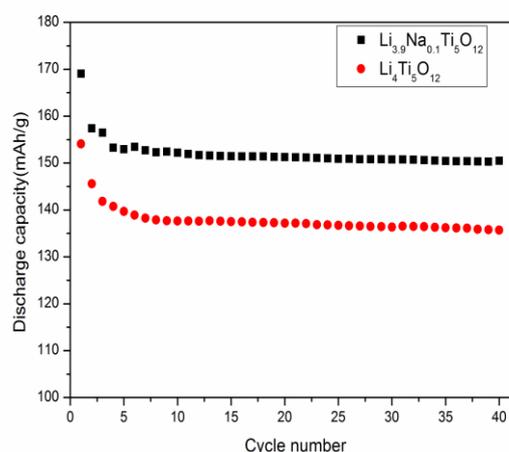


Fig.5 Cycling performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ samples at 0.5C-rate

Cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ samples at a current rate of 0.5C are shown in Fig.5. The initial discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ have sharply decreased in comparison to the second discharge process, but their capacities become increasingly steady after cycling several times. This phenomenon may be due to the fact that the first cycle is an activation process or a certain degrees of electrolyte decomposing during the charge/discharge process. The result reveals that the initial discharge capacity of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ electrode maintains at 169.0mAh/g at 0.5C, and the reversible capacity is retained

at 150.4mAh/g even after 40 cycles with a capacity retention of 88.99%, higher than the pristine samples of 135.6mAh/g. Based on the above results, Na-doping has been found to result in outstanding cycling stability and excellent high-rate capability.

3.2 Crystal structure, morphology and electrochemical performance of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ sample

The XRD patterns of the pristine sample, $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ samples are depicted in Fig.6. The XRD patterns of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ with 3wt%GO are completely consistent with $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As no graphene peaks were found, this indicates that the addition of graphene has not altered the crystal structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, perhaps the GO content is below the limit of detection by XRD.

Fig.7 shows the SEM images of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composites at different magnifications. Graphene sheets are uniformly distributed among the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ particles and efficiently hindered particle regrowth, which lead to the composite have homogeneous powder and narrow particle-size distribution. In addition, the presence of graphene can magnify the contact of interparticle and increase electronic/ionic conductivities, which is great

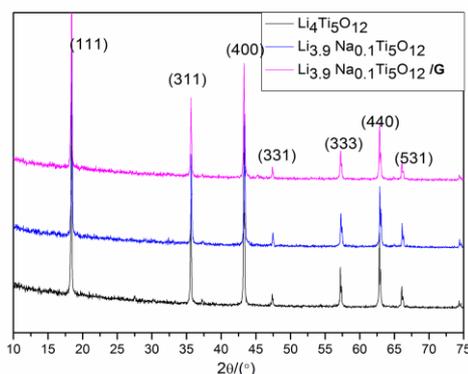


Fig.6 XRD patterns of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ samples.

importance in improving electrochemical performance. The following graph (Fig.8) shows the initial charge/discharge curves of the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ sample at 0.2C, 0.5C, 1C, 2C rate, the electrochemical performance has greatly improved compared to the pristine and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ samples. This composite exhibits lower potential separation and outstanding reversible capacity no matter what on low

or high current rates, possibly due to the addition of graphene. $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composites with a 3wt% of GO have a remarkable reversible capacity of 197.4mAh/g at 0.2C rate, significantly higher than the pristine electrode (167.4mAh/g). The specific capacity decreases

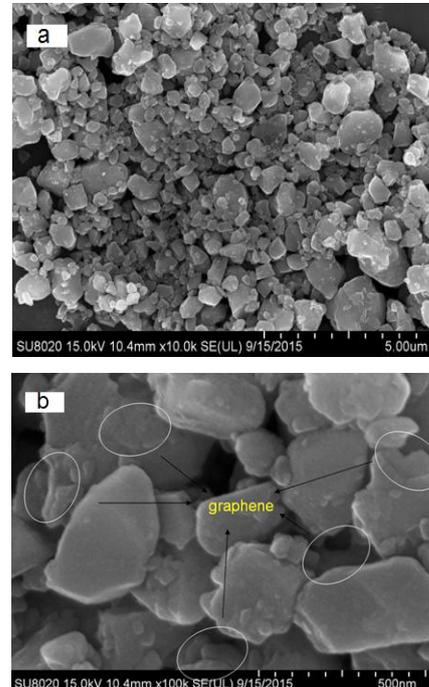


Fig.7 FE-SEM images of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composites (a,b) at different magnification

as the charge/discharge current rate increases, but even at 0.5C, 1C, 2C current rate, it still can present a discharge capacities of 175.5, 158.8 and 145.3mAh/g, respectively. Furthermore, the cycle performance is also improved due to the introduced of graphene, as described in Fig.9. The irreversible capacity has a large loss after the first cycle. However, it becomes more and more stable after several cycles, with the trend of cycle performance consistent with the pristine sample. The initial specific discharge capacity of the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ electrode is 158.8mAh/g at 1C rate, and maintains at 146.3mAh/g even after 40 cycles, with the reversible capacity retention is 92.13%, higher than the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ sample at 87.73%. The results indicate that the cycling performance and capacity have greatly improved due to addition of graphene. Graphene with remarkable specific surface area and extraordinary electronic conductivity can greatly enlarge the contact of interparticles in the composite and change the intrinsic poor electronic and ionic conductivities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In addition, the addition of graphene may effectively create numerous new Li^+ storage

sites. This may be the reason why the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ composite has such excellent long-term cycling performance and impressive capacity.

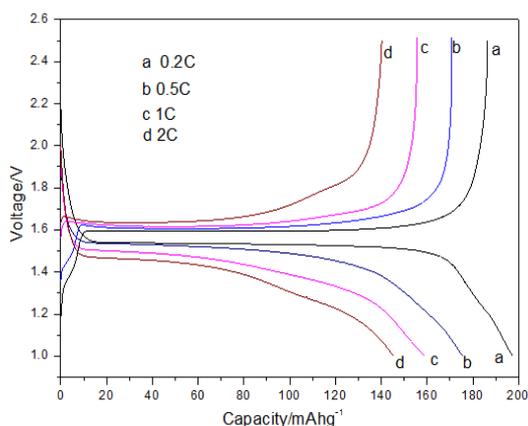


Fig.8 Initial charge/discharge curves of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ samples at 0.2C, 0.5C, 1C, 2C rates

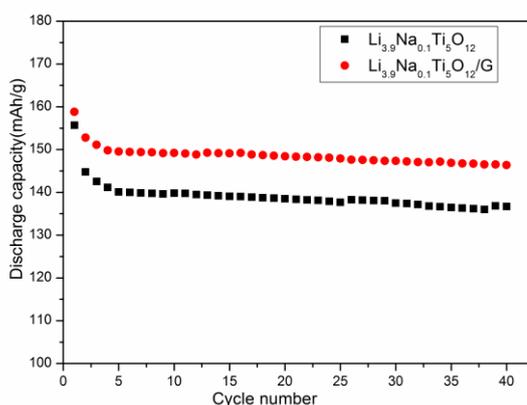


Fig.9 Cycling performance of the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ samples at 1 C rate

4. Conclusions

$\text{Li}_{4-x}\text{Na}_x\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 0.15$) samples were successfully synthesized by a facile hydrothermal method. The results show that doping with Na^+ ions do not alter the structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and the resulting samples are well crystallized with a particle size in the range of 300-600nm. The Na-doped samples have higher specific capacities and excellent cycling stability, with the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ electrode showing particularly good electrochemical properties among the four samples. The initial specific capacity of $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}$ electrode is 169.0mAh/g at 0.5C, and maintains at 150.4mAh/g even after 40 cycles. Finally, graphene was introduced to the composite by means of a simple solvothermal reduction method with ethanol as the

solvent. This approach does not produce poisonous materials and has high efficiency. The initial specific discharge capacity of the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ electrode is 158.8mAh/g at 1C rate, and maintains at 146.3mAh/g even after 40cycles. The experiment results that the $\text{Li}_{3.9}\text{Na}_{0.1}\text{Ti}_5\text{O}_{12}/\text{G}$ (3wt%) composites exhibit extraordinary electronic conductivity, faster lithium ion diffusivity, high-rate capability and long-term cycling stability, which makes it more practical in applications for lithium ion batteries.

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