Spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$) as novel anode material for room-temperature sodium-ion battery*

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(Received 6 January 2012; revised manuscript received 16 January 2012)

This is the first time that a novel anode material, spinel Li$_4$Ti$_5$O$_{12}$ which is well known as a “zero-strain” anode material for lithium storage, has been introduced for sodium-ion battery. The Li$_4$Ti$_5$O$_{12}$ shows an average Na storage voltage of about 1.0 V and a reversible capacity of about 145 mAh/g, thereby making it a promising anode for sodium-ion battery. Ex-situ X-ray diffraction (XRD) is used to investigate the structure change in the Na insertion/deinsertion process. Based on this, a possible Na storage mechanism is proposed.

Keywords: spinel, lithium titanate, Li$_4$Ti$_5$O$_{12}$, sodium-ion battery

PACS: 82.45.Yz, 82.47.Aa, 82.47.Cb, 84.60.–h

DOI: 10.1088/1674-1056/21/2/028201

1. Introduction

Since its commercialization in the early 1990s, lithium-ion battery has dominated the power supply of portable electric devices.[1] Recently, it has been considered as the most promising candidate for electric vehicles (EVs). If it is gradually used in EVs in large scale, the problems of the exhaustible lithium resources must be kept in mind.[2] Particularly, for the application in the large-scale energy storage for smart grid and solar/wind energy which requires low-cost, these problems would be a big challenge. Among all other alkali metals and alkaline-earth metals, sodium is the best alternative, for its many physical and chemical properties are similar to those of lithium. Most importantly, the sodium resources might be in principle inexhaustible compared with lithium; therefore the low cost of sodium salts would pave the way for its large-scale application. The standard potential of Na$^+$/Na redox is $-2.71$ V versus normal hydrogen electrode (NHE) which is slightly higher than that of Li$^+/Li$ ($-3.0$ V versus NHE). It has also been demonstrated by both experimental results and theoretical calculations that sodium-containing cathode mater-

als exhibit $0.3$ V–$0.5$ V lower storage voltage than their lithium-containing counterparts.[3–8] This may give rise to a decrease in energy density, but the loss of energy density can be compensated by the low-cost advantage.

Recently, many cathode materials for sodium-ion battery have been identified, such as Na$_2$CoO$_2$,[5] Na$_3$V$_2$(PO$_4$)$_3$,[4] NaNi$_0.5$Mn$_0.5$O$_2$,[5] Na$_0.44$MnO$_2$,[6,7] Na$_2$MPO$_4$F,[8] and so on. However, there are very few studies of possible anode materials.[9] Hard carbon has been reported as anode material for sodium-ion battery and shows good cycling performance.[10–12] However, like the case in lithium-ion battery, the low insertion voltage involves the problems of solid electrolyte interphase (SEI) formation and sodium metal deposition, which cause the low Coulombic efficiency and safety concern. Very recently, transition metal oxide Na$_2$Ti$_3$O$_7$ has been studied as an anode material for sodium-ion battery with poor cycleability.[13] Here, in this paper, we introduce for the first time a new anode, spinel Li$_4$Ti$_5$O$_{12}$ which is well known as a “zero-strain” anode material for lithium insertion, for sodium-ion battery. It is very interesting to note that the Li$_4$Ti$_5$O$_{12}$ host can accommodate not only Li but also Na. The reversible capacity for Na storage is

*Project supported by the National High Technology Research and Development Program of China (Grant No. 2009A033101), the National Basic Research Program of China (Grant No. 2010CB833102), the National Natural Science Foundation of China (Grant No. 50972164), the Chinese Academy of Sciences Project (Grant No. KJCX2-YW-W26), and the Hundred-Talent Project of the Chinese Academy of Sciences.

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028201-1
around 145 mAh/g with a relatively high (de)insertion voltage (between 0.5 V–1.3 V) versus Na⁺/Na. A possible Na storage mechanism in Li₄Ti₅O₁₂ is also proposed.

2. Experiment

The Li₄Ti₅O₁₂ was synthesized by spray-drying method: stoichiometric nano-sized anatase and Li₂CO₃ were mixed by ball-milling with polyvinyl butyral (6 wt%) in ethanol. The obtained white slurry was dried in the spray-drier at 110 °C, and then, the precursor was heat-treated at 800 °C for 20 h. The structure of material was characterized by an X’Pert Pro MPD X-ray diffractometer (Philips, Netherlands) using Cu Kα radiation (1.5405 Å, 1 Å=0.1 nm). The morphology of the material was observed using a scanning electron microscope (SEM) (Hitachi S-4800).

The salt NaClO₄ and the solvent propylene carbonate (PC) were purchased from Alfa and Guo Tai Hua Rong (China), respectively. The concentration of the electrolyte was 1 mol/L. The electrolyte was used until the water concentration is below 10 ppm by removing water using molecular sieve. The working electrode was prepared by spreading the slurry of the active materials Li₄Ti₅O₁₂ (80 wt%), acetylene black (10 wt%), and binder polyvinylidene fluoride (10 wt%) on Cu foil. The electrode was dried at 100 °C in vacuum for 10 h prior to use. The Swagelok-type cells were assembled with pure sodium foil as the counter electrode, Li₄Ti₅O₁₂ as working electrode and a glass fiber as separator in argon-filled glove box. The charge and discharge measurements were carried out on a Land BT2000 battery test system (Wuhan, China). Cyclic voltammetry (CV) was measured using Autolab PGSTAT302N (Metrohm, Switzerland). All electrochemical measurements were carried out at 25 °C.

3. Results and discussion

From the X-ray diffraction (XRD) pattern of the obtained white powder, it can be found that the synthesized Li₄Ti₅O₁₂ is well crystallized into a pure phase as shown in Fig. 1. The morphology of obtained Li₄Ti₅O₁₂ sample is shown in Fig. 2, the particles are micrometer-sized porous spheres, each of which is composed of several ten nanometer-sized primary particles. It has been demonstrated that such a structure can effectively enhance the electrochemical reactivity of Li₄Ti₅O₁₂.[14–21]
peak, which might be caused by the increased polarization.

![Graph](image)

**Fig. 3.** (colour online) (a) The discharge/charge profiles of the 1st and 2nd cycles of the Li$_4$Ti$_5$O$_{12}$ electrode in NaClO$_4$/PC electrolyte at a current rate of C/10; (b) cyclic voltammetry (CV) curves of the Li$_4$Ti$_5$O$_{12}$ electrode versus Na$^+$/Na at a scan rate of 0.08 mV/s in a voltage range of 0.3 V–3.0 V.

Both results are different with those of lithium storage in Li$_4$Ti$_5$O$_{12}$, implying different phase evolution mechanisms. It is well known that there is no obvious change in XRD pattern during Li insertion/deinsertion into/from Li$_4$Ti$_5$O$_{12}$, showing a "zero-strain" characteristic for Li insertion.$^{[22–25]}$ In order to know the feature of Na storage in Li$_4$Ti$_5$O$_{12}$, ex-situ XRD was carried out (see Fig. 4). Four points were investigated in the discharge/charge process of the first cycle: discharging to 58 mAh/g (B: corresponding to one-Na insertion), discharging to 117 mAh/g (C: corresponding to two-Na insertion), discharging to 0.5 V (D: corresponding to three-Na insertion) and charging to 3.0 V (E). At the stage C, several new peaks, corresponding to the peaks of Li$_4$Ti$_5$O$_{12}$ (111), (311), (400), (333), (440), appear, but at lower degrees, and increase in intensity along with Na insertion. Meanwhile, the peak intensity of Li$_4$Ti$_5$O$_{12}$ decreases. At the final discharge stage D, corresponding to three-Na insertion, it is likely to find that two phases co-exist, one belongs to "Li$_4$Ti$_5$O$_{12}$" and the other belongs to Na-containing phase, which is different from the mechanism of Li insertion where only one phase of Li$_7$Ti$_3$O$_{12}$ can be obtained after three lithium insertions. Here we propose a possible Na storage mechanism in Li$_4$Ti$_5$O$_{12}$. According to the Li storage mechanism in Li$_4$Ti$_5$O$_{12}$ through a typical two-phase reaction, the inserted Li will occupy the 16c site, simultaneously accompanied by Li$^+$ ion migration from the 8a sites into the 16c site, owing to the repelling effect, leading to a phase transition from the spinel Li$_4$Ti$_5$O$_{12}$ to the rock-salt Li$_7$Ti$_3$O$_{12}$. Combining this with the ex-situ XRD result, it is reasonable to deduce that the final two phases are LiNa$_6$Ti$_5$O$_{12}$ and Li$_7$Ti$_3$O$_{12}$. Upon Na insertion into the vacancy of 16c site in Li$_4$Ti$_5$O$_{12}$, the Li in 8a site would migrate into 16c site. Due to the different sizes of Na$^+$ and Li$^+$ ions, the resulting product would be separated into LiNa$_6$Ti$_5$O$_{12}$ with larger lattice parameters and Li$_7$Ti$_3$O$_{12}$ with smaller lattice parameters (Note that the XRD pattern of Li$_7$Ti$_3$O$_{12}$ is very similar to that of Li$_4$Ti$_5$O$_{12}$). The proposed Na storage mechanism in Li$_4$Ti$_5$O$_{12}$ may be described as

$$3\text{Na} + \text{Li}_4\text{Ti}_5\text{O}_{12} \leftrightarrow \frac{1}{2}\text{Li}_6\text{Na}_6\text{Ti}_5\text{O}_{12} + \frac{1}{2}\text{Li}_7\text{Ti}_3\text{O}_{12}.$$  

At the final charge stage E, the peaks at low degrees disappear and XRD pattern shows phase-pure Li$_4$Ti$_5$O$_{12}$, indicating the highly reversible Na insertion/deinsertion process. It is interesting to note that this mechanism is totally different from a typical two-phase reaction. Of course, more work will be performed to clarify this interesting mechanism. If this assumption is true, the clarification of Na insertion in Li$_4$Ti$_5$O$_{12}$ should be beneficial for understanding the Li storage mechanism in Li$_4$Ti$_5$O$_{12}$, which is still not very clear at atomic level.

![XRD Pattern](image)

**Fig. 4.** (colour online) Ex-situ XRD patterns of the Li$_4$Ti$_5$O$_{12}$ electrode during the first cycle (# refers to a new phase; the broad hump between 10° and 30° is coming from Kapton film used to cover the electrode). A–D: The first Na-insertion. E: The first Na-extraction.
4. Conclusion

In this preliminary study, Na-storage behaviour in Li$_4$Ti$_5$O$_{12}$ is reported for the first time. The average Na-storage voltage is about 1.0 V and a reversible capacity of around 145 mAh/g is achieved. These properties make it a promising anode material for high safety stationary sodium-ion battery. The storage performance could be further improved by carbon coating and optimizing the electrolyte and the binder.\textsuperscript{[26]} It is found from galvanostatic voltage profile, CV curve, and \textit{ex situ} XRD that Na-storage mechanism in Li$_4$Ti$_5$O$_{12}$ is relevant but different from that of Li-storage in Li$_4$Ti$_5$O$_{12}$: instead of forming a single phase Li$_4$Na$_3$Ti$_5$O$_{12}$ as expected, the final product after three Na insertions might be a mixture of LiNa$_6$Ti$_5$O$_{12}$ and Li$_7$Ti$_5$O$_{12}$. This is very interesting and the structure evolution mechanism will be clarified in the near future.

Acknowledgement

The authors thank Prof. Xue-Jie Huang and Mr. Yang Sun for fruitful discussion.

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