Rapid Communication

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

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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.

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 materials 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$_x$CoO$_2$,[3] 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

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 $Li_4Ti_5O_{12}$ is also proposed.

2. Experiment

The $Li_4Ti_5O_{12}$ was synthesized by spray-drying method: stoichiometric nano-sized anatase and Li_2CO_3 were mixed by ball-milling with polyvinyl butyral (6 wt%) in ethanol. The obtained white slurry was dried in the spray-dryer 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 $NaClO_4$ 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 $Li_4Ti_5O_{12}$ (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, $Li_4Ti_5O_{12}$ 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 $Li_4Ti_5O_{12}$ is well crystallized into a pure phase as shown in Fig. 1. The morphology of obtained $Li_4Ti_5O_{12}$ 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 $Li_4Ti_5O_{12}$.[14−21]
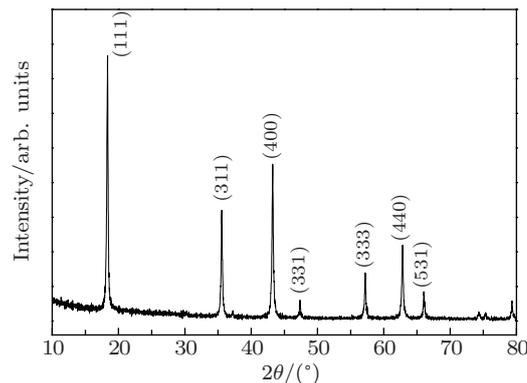
Fig. 1. XRD pattern of the as-prepared $Li_4Ti_5O_{12}$.
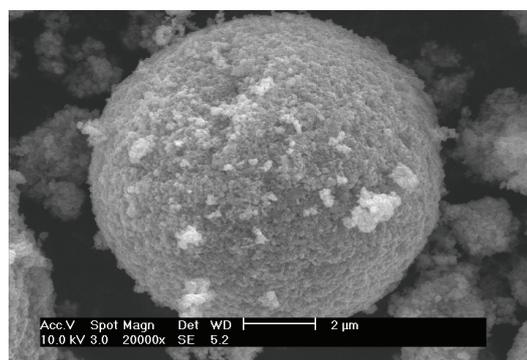
Fig. 2. The SEM image of the as-prepared $Li_4Ti_5O_{12}$.

Figure 3(a) shows the first two cycles of the $Li_4Ti_5O_{12}$ electrode in $NaClO_4$/PC electrolyte at a current rate of C/10 (C/10 means 3-mol Na insertion into $Li_4Ti_5O_{12}$ per formula unit in 10 h). $Li_4Ti_5O_{12}$ shows an initial discharge capacity of 182 mAh/g with a voltage plateau at around 0.80 V versus Na^+/Na, suggesting about 3-mol Na insertion into $Li_4Ti_5O_{12}$ per formula unit, which is similar to the case of Li insertion. Note that the average Na storage voltage is about 1.0 V versus Na^+/Na, about 0.55 V lower than 1.55 V of Li storage in $Li_4Ti_5O_{12}$, which is favorable for improving the energy density in a full battery. The initial charge curve indicates two slightly sloped regions between 0.7 V–1.3 V with a reversible capacity of around 145 mAh/g in the voltage range of 0.7 V–3.0 V. The shapes of the first and second discharge curves are slightly different as the first discharge plateau tends to become a sloped curve between 0.7 V and 0.9 V in the following discharge process. The redox behavior is revealed further by cyclic voltammogram (CV) curves (Fig. 3(b)). One peak centred at 0.70 V is observed in the initial reduction process, while two peaks centred at 0.95 V and 1.06 V can be observed in the initial oxidation process. In the second oxidation process, the two oxidation peaks tend to merge into one broad

peak, which might be caused by the increased polarization.
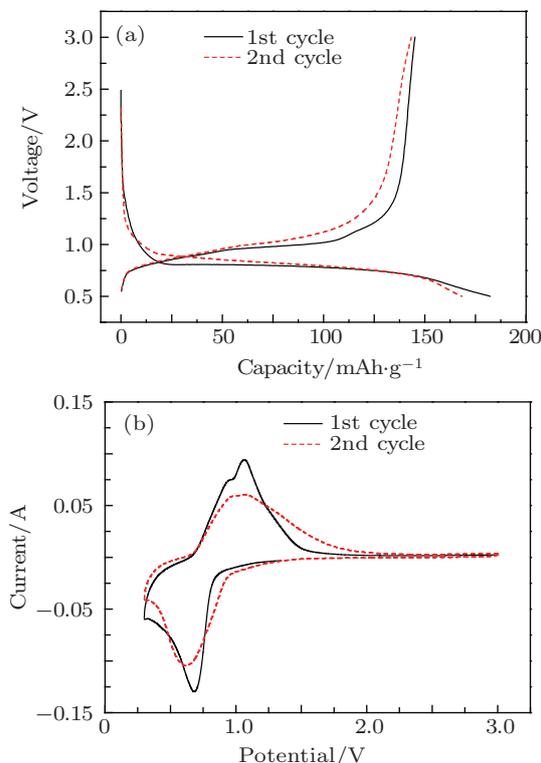
Fig. 3. (colour online) (a) The discharge/charge profiles of the 1st and 2nd cycles of the $Li_4Ti_5O_{12}$ electrode in $NaClO_4$/PC electrolyte at a current rate of C/10; (b) cyclic voltammetry (CV) curves of the $Li_4Ti_5O_{12}$ electrode versus Na^+/Na at a scan rate of 0.08 mV/s in a voltage range of 0.3 V–3.0 V.

Both results are different with those of lithium storage in $Li_4Ti_5O_{12}$, implying different phase evolution mechanisms. It is well known that there is no obvious change in XRD pattern during Li insertion/deinsertion into/from $Li_4Ti_5O_{12}$, showing a "zero-strain" characteristic for Li insertion.[22−25] In order to know the feature of Na storage in $Li_4Ti_5O_{12}$, *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 $Li_4Ti_5O_{12}$ (111), (311), (400), (333), (440), appear, but at lower degrees, and increase in intensity along with Na insertion. Meanwhile, the peak intensity of $Li_4Ti_5O_{12}$ 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 "$Li_4Ti_5O_{12}$"

and the other belongs to Na-containing phase, which is different from the mechanism of Li insertion where only one phase of $Li_7Ti_5O_{12}$ can be obtained after three lithium insertions. Here we propose a possible Na storage mechanism in $Li_4Ti_5O_{12}$. According to the Li storage mechanism in $Li_4Ti_5O_{12}$ 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 $Li_4Ti_5O_{12}$ to the rock-salt $Li_7Ti_5O_{12}$. Combining this with the *ex-situ* XRD result, it is reasonable to deduce that the final two phases are $LiNa_6Ti_5O_{12}$ and $Li_7Ti_5O_{12}$. Upon Na insertion into the vacancy of 16c site in $Li_4Ti_5O_{12}$, the Li at 8a site would migrate into 16c site. Due to the different sizes of Na^+ and Li^+ ions, the resulting product would be separated into $LiNa_6Ti_5O_{12}$ with larger lattice parameters and $Li_7Ti_5O_{12}$ with smaller lattice parameters (Note that the XRD pattern of $Li_7Ti_5O_{12}$ is very similar to that of $Li_4Ti_5O_{12}$). The proposed Na storage mechanism in $Li_4Ti_5O_{12}$ may be described as

$$3Na + Li_4Ti_5O_{12} \leftrightarrow 1/2\ LiNa_6Ti_5O_{12}$$
$$+ 1/2\ Li_7Ti_5O_{12}.$$
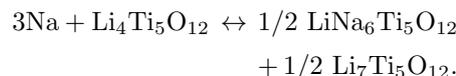
At the final charge stage *E*, the peaks at low degrees disappear and XRD pattern shows phase-pure $Li_4Ti_5O_{12}$, indicating the highly reversible Na insertion/deinsertion process. It is interesting to note that this mechanism is totally different from a typical two-phase reaction. Of course, more work will be performed to clarify this interesting mechanism. If this assumption is true, the clarification of Na insertion in $Li_4Ti_5O_{12}$ should be beneficial for understanding the Li storage mechanism in $Li_4Ti_5O_{12}$, which is still not very clear at atomic level.
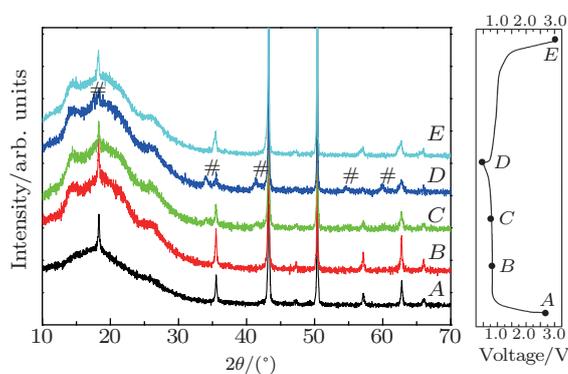
Fig. 4. (colour online) *Ex-situ* XRD patterns of the $Li_4Ti_5O_{12}$ electrode during the first cycle (# refers to a new phase; the broad hump between 10° and 30° is coming from Kapton film used to cover the electrode). *A–D*: The first Na-insertion. *E*: The first Na-extraction.

4. Conclusion

In this preliminary study, Na-storage behaviour in $Li_4Ti_5O_{12}$ 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.[26] It is found from galvanostatic voltage profile, CV curve, and *ex situ* XRD that Na-storage mechanism in $Li_4Ti_5O_{12}$ is relevant but different from that of Li-storage in $Li_4Ti_5O_{12}$: instead of forming a single phase $Li_4Na_3Ti_5O_{12}$ as expected, the final product after three Na insertions might be a mixture of $LiNa_6Ti_5O_{12}$ and $Li_7Ti_5O_{12}$. This is very interesting and the structure evolution mechanism will be clarified in the near future.

Acknowledgement

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