



Short communication

Advanced electrochemical performance of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ as a reversible anode material down to 0 V

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ABSTRACT

$\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were successfully prepared by a solid-state method. XRD reveals that both samples have high phase purity. Raman spectroscopy indicates that the Ti–O vibration have a blue shift. SEM shows that $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has a slightly smaller particle size and a more regular morphological structure with narrow size distribution than those of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Galvanostatic charge–discharge testing indicates both samples have nearly equal initial capacities at different discharge voltage ranges (0–2 and 0.5–2 V), but $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has a higher cycling performance than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. CV suggests that $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has lower electrode polarization and high lithium ion diffusivity in solid-state body of sample, implying that the vanadium doping is beneficial to the reversible intercalation and deintercalation of Li^+ . The novel $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ materials may find promising applications in lithium ion batteries and electrochemical cells due to the excellent electrochemical performance and simple synthesis route.

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1. Introduction

Recently, there has been considerable interest in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a potential anode for use in lithium ion batteries [1–10]. It has many advantages compared to the currently used graphite. It has a good reversibility but no structural change (zero-strain insertion material) in the charge–discharge process, and it offers a stable operating voltage of approximately 1.5 V vs. lithium. Unfortunately, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibits poor electronic and lithium ionic conductivities, thereby limiting its performance. To improve the conductivities, several effective ways have been proposed, including synthesis of nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [9], doping with metal ions (V^{5+} , Ta^{5+} , Mn^{4+} , Fe^{3+} , Al^{3+} , Ga^{3+} , Co^{3+} , Cr^{3+} , Ni^{2+} , Ag^+ , and Mg^{2+}) in Li or Ti sites [2–8], incorporation of second phase with high electronic conductivity. Although Kubiak et al. [2] have reported V-doped $\text{Li}_{4.25}\text{Ti}_{4.75}\text{V}_{0.25}\text{O}_{12}$, its discharge capacity is only 74 mAh g^{-1} discharged to 1 V. To our knowledge, no investigation was systematically reported on the electrochemical characteristics of V-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0 V. It is important to study the electrochemical behaviors of anode materials at lower voltage because the capacity of anode materials at lower voltage can offer a higher cell voltage and discharge capacity for lithium-ion batteries. It is

the purpose of this paper to investigate the effects of V doping on the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0 V. The result reveals the improved reversible capacity and cycle performance of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ discharged to 0 V, as well as simple synthesis route and low synthesis cost, are expected to show a potential commercial application.

2. Experiment

TiO_2 -anatase, Li_2CO_3 and V_2O_5 were mixed, and then calcined at 850 °C for 24 h in air to prepare well-crystallized spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$. XRD was performed on Rigaku D/MAX-2400 X-ray diffractometer with $\text{Cu K}\alpha_1$ ($10^\circ < 2\theta < 90^\circ$) monochromated radiation in order to identify the crystalline phase. Raman measurements were performed on a SPEX-1403 Raman spectrometer. The laser light source was the 488 nm line of an Ar^+ laser excited at 400 mW. All the powder samples were pressed into pellets before measurements. The particle morphologies were examined with a scanning electron microscope (Hitachi, S-4000). Charge–discharge performance was characterized galvanostatically on Land 2000T (China) tester at 0.2C charge–discharge rate between 0 and 2 V (vs. Li/Li^+). Cyclic voltamograms of both electrodes were measured on an electrochemical workstation (CHI 660A) between 0 and 3 V (vs. Li/Li^+). The lithium titanium spinels were adopted as the work electrode; the counter electrode and reference electrode were Li foil. The electrode was prepared by pasting a slurry containing 82 wt.% active material, 10 wt.% carbon black, and 8 wt.% polyvinylidene

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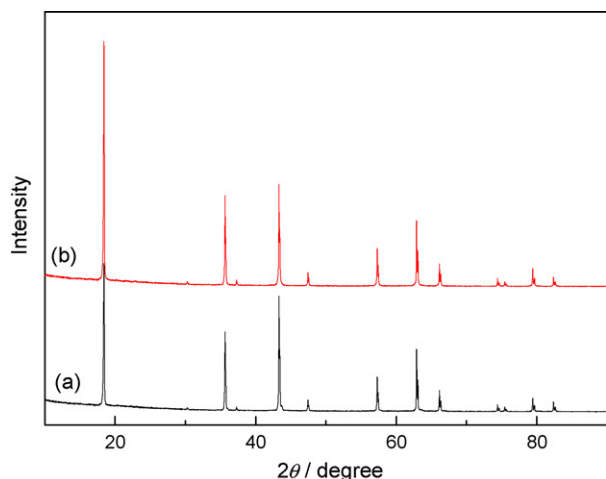


Fig. 1. XRD patterns of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$.

fluoride dissolved in *N*-methylpyrrolone onto a titanium foil. After coating, the film was dried in a vacuum oven at 100°C for 12 h, pressed, and then cut into a sheet. Before using, the sheet was dried in a vacuum chamber at 120°C for 10 h.

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. All the peak signatures of the XRD patterns conform to JCPDS card No-26-1198 without any impurity, suggesting that they are both single-phase spinel compounds. The lattice parameters were calculated through the least square program method from the diffraction data of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and were found to be about 8.3581 and 8.3585 Å, respectively. This indicates that the vanadium ions are successively substituted for titanium in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ host structure, and the sharp peaks in the patterns show good crystallinity of both electrode materials.

$\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were investigated by Raman spectroscopy as plotted in Fig. 2. As shown in Fig. 2, five vibration peaks were observed at 235 (234), 272 (272), 346 (344), 425 (429) and 672 (676) cm^{-1} , respectively. The values within brackets belong to $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$. These RS features are in good agreement with the feature of the spinel structure ($A_{1g} + E_g + 3F_{2g}$) [11–13]. Two strong bands at 235 and 672 cm^{-1} are assigned to the characteristic modes F_{2g} and A_{1g} , respectively. The band at 425 cm^{-1} with a medium strength is associated with the E_g mode, while the other two weaker bands appeared at 272 and 346 cm^{-1} are attributed to F_{2g} [11–13]. This observation demonstrated the formation of phase-pure of both materials, which is consistent with

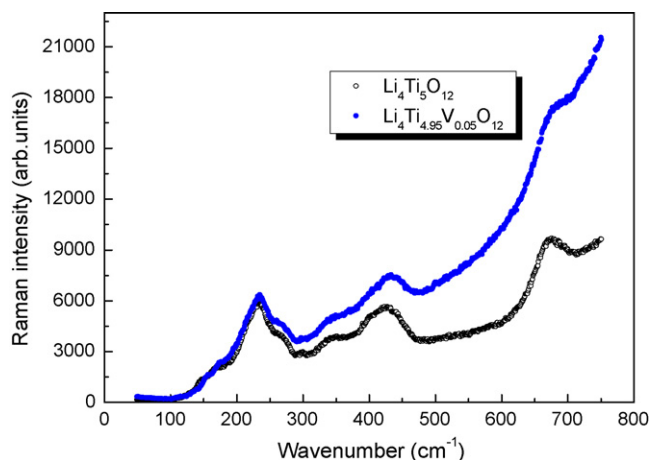


Fig. 2. Raman spectra of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ recorded with the 488 nm line of an argon-ion laser excited at 400 mW.

the XRD results in Fig. 1. The Raman bands corresponding to the Ti–O vibration have a blue shift from 672 to 676 cm^{-1} due to the doping vanadium ions, and this may enhance the cation–oxygen bonding, leading to a blue shift.

Fig. 3 shows SEM images of these materials. $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ powders have a uniform, nearly cubic structural morphology with narrow size distribution under $1\ \mu\text{m}$. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders have a wide particle size distribution ranging from 0.5 to $1.5\ \mu\text{m}$. The result suggests that Ti ions are successively substituted for V in the $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ host structure. The small particle size of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ results in sufficient contact between active materials and electrolyte and resulting in favorable diffusion and transmission of Li^+ in the electrode.

The initial charge–discharge curves in a potential range from 0 to 2 V and 0.5 to 2 V of $\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$ ($x=0, 0.05$) are shown in Fig. 4, and the cycling performances are plotted in Fig. 5. It is clear that both samples have nearly equal initial capacities at different discharge voltage range, but $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has a higher cycling performance than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is related to the presence of the dopant ions. It can be noticed that discharge capacities of $\text{Li}_4\text{Ti}_{5-x}\text{V}_x\text{O}_{12}$ ($x=0, 0.05$) exceed their theoretical capacities of $298\ \text{mAh g}^{-1}$ and have high irreversible capacities. These can be contributed from the CB lithiation in this low voltage range and the side reactions such as solid electrolyte interface (SEI) layer formation [14,15]. The discharge capacity reaches $218.4\ \text{mAh g}^{-1}$ after 50 cycles for the $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ while it decreases to $197\ \text{mAh g}^{-1}$ for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0 V. In addition, the V-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 1.0 V is also higher the discharge capacity than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the reported values by Kubiak et al. [2]. This indi-

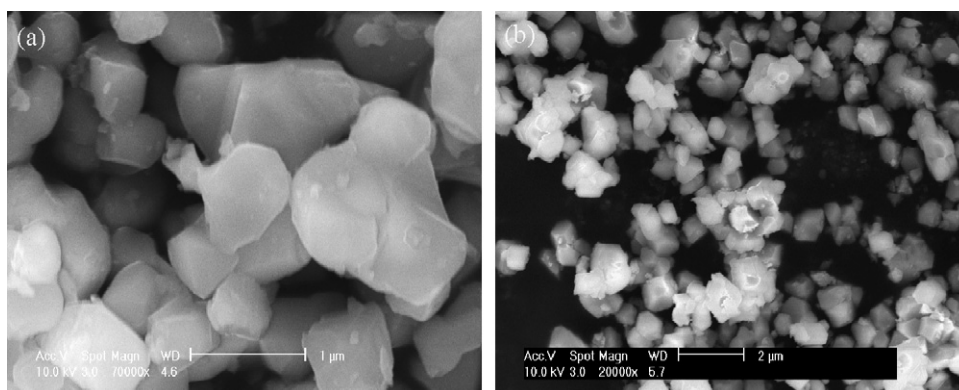


Fig. 3. SEM pictures of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$.

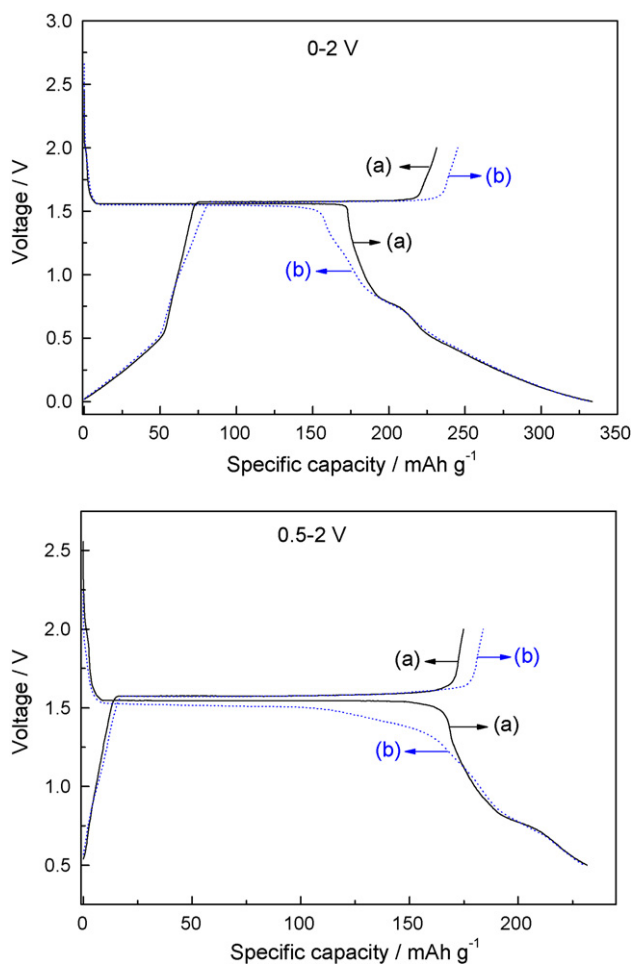


Fig. 4. Initial charge–discharge curve of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (b) $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ discharged to 0 and 0.5 V.

ates that the change of discharge voltage for $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ extended from 0.5 to 0 V does not affect the cycling stability, and the reversible capacity is improved. It may be concluded that the doping V stabilizes the spinel structure by assisting retention of the local symmetry during cycling. If the V substitute spinel $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ was prepared, titanium might exist as Ti^{3+} while vanadium would exist as V^{5+} . V substituted spinel should have improved electronic conductivity due to the introduction of Ti^{3+} . In addition, it has been reported that the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be increased by a substitution of Ti^{4+} site by M^{5+} ion (i.e., V^{5+} in the paper), which should lead to an increase in electron concentration [16]. The good cycling performance of V-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be attributed to the high electron concentration and cation–oxygen bonding. The good cycling performance and high discharge capacity, as well as simple synthesis route and low synthesis cost of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ spinel are expected to show a better commercial application (Fig. 5).

The electrochemical behaviors of both samples were characterized by cyclic voltammograms with coin cell as shown in Fig. 6. The figure clearly demonstrates that there are two pairs of redox peaks for each sample in the voltage range of 1.0–2.3 V and below 0.6 V, implying that V-doping does not change the electrochemical reaction process of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in this voltage range. The couple of peaks at high potential could be attributed to the redox of $\text{Ti}^{4+}/\text{Ti}^{3+}$ [17]. The reduction and oxidation peaks below 0.6 V caused by a multi step restore of Ti^{4+} [18] were obvious and repeatable during the subsequent cycles, indicating that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ possesses reversible capacity under 0.6 V. The poten-

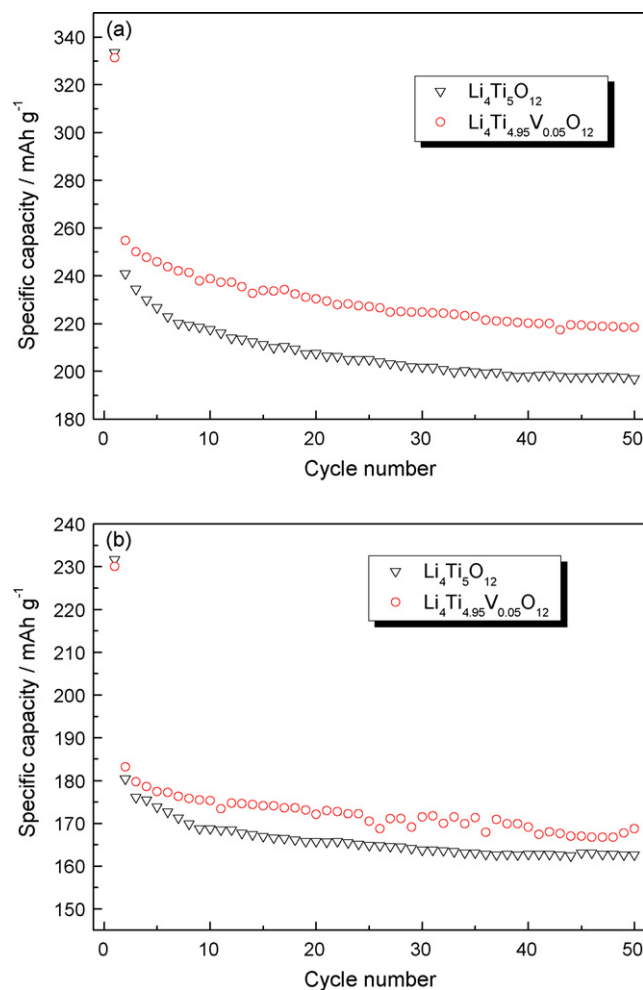


Fig. 5. Cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ discharged to (a) 0 V and (b) 0.5 V.

tial differences between anodic and cathodic peaks for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ are 297 and 255 mV, respectively, suggesting the lower electrode polarization and high lithium ion diffusivity in solid-state body of sample $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$. These phenomena confirms that the doping of vanadium is beneficial to the reversible intercalation and de-intercalation of Li^+ .

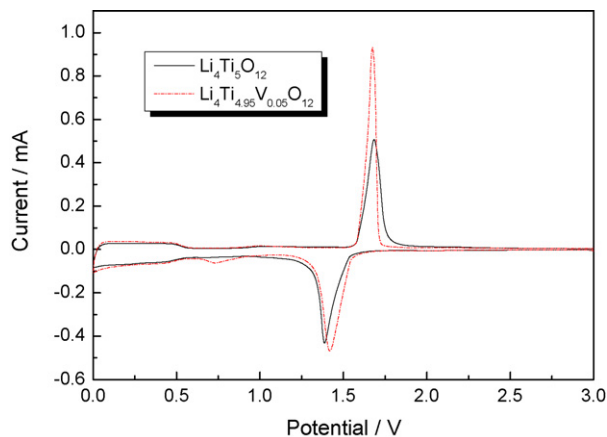


Fig. 6. Cyclic voltammograms of cells using the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ sample as electrode materials.

4. Conclusions

$\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were successfully prepared by a solid-state method. Both samples have good crystallinity and high phase purity. $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has a slightly smaller particle size and a more regular morphological structure with narrow size distribution than those of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The discharge capacity reaches 218.4 mAh g^{-1} after 50 cycles for the $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ while it decreases to 197 mAh g^{-1} for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ discharged to 0 V. $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ has lower electrode polarization and high lithium ion diffusivity in solid-state body of sample, implying that vanadium doping is beneficial to the reversible intercalation and de-intercalation of Li^+ . The good cycling performance and high discharge capacity, as well as simple synthesis route and low synthesis cost of $\text{Li}_4\text{Ti}_{4.95}\text{V}_{0.05}\text{O}_{12}$ spinel are expected to show a better commercial application.

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