Tantalum-doped lithium titanate with enhanced performance for lithium-ion batteries

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A series of Tantalum-doped lithium titanate (Ta-doped Li4Ti5O12) samples have been successfully synthesized by one step solid-state method using TiO2, Li2CO3, and Ta2O5 as raw materials. The Li4Ti5O12 with only 0.1 at% Ta doping (Li4Ti4.995Ta0.005O12) exhibits higher rate capability and better cyclic stability than the pristine Li4Ti5O12. Li4Ti4.995Ta0.005O12 could deliver 95.1 mAh g\(^{-1}\) at 10C with much lower overpotential (216.1 mV) while the pristine Li4Ti5O12 delivers only 50.4 mAh g\(^{-1}\) at 10C with higher overpotential of 392.2 mV. As indicated by XRD, HRTEM and electrochemical characterizations, Ta doping in Li4Ti5O12 would enlarge the lattice parameter of the Li4Ti5O12, and facilitate the Li\(^{+}\) diffusion during the charge/discharge process. In addition, the higher charge compensation of the stoichiometric reduction of Ti\(^{4+}\) to Ti\(^{3+}\) by introducing Ta increases the electronic conductivity of Li4Ti5O12. The improved ionic conductivity and electronic conductivity are beneficial to the electrochemical performance of Li4Ti5O12. As a result, Ta doping is a new strategy for enhancing the electrochemical performance of Li4Ti5O12.

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the practical applications on high power devices. So far, numerous strategies have been reported for enhancing the rate capability of Li4Ti5O12 including nanostructure design, surface coating and ion doping on the Li site, the Ti site or the O site of Li4Ti5O12. The Li4Ti5O12 with nanostructures could greatly increase the interfacial area of the electrolyte and electrode, drastically shorten the ion/electron diffusion pathways and enhance charge transfer [10–12]. Surface coating by conductive materials, such as carbon layer, high dense TiN layer, graphene etc, on the surface of Li4Ti5O12 can enhance the electronic conductivity and then have a significant enhancement in the rate capability of Li4Ti5O12 [13–15]. Another way to improve electrochemical performance of Li4Ti5O12 is ion doping. Doping with ions as Al3+, La3+, W5+, Sc3+, Nb5+, Ta5+ etc to replace partially lithium, titanium or oxygen are proved to be effective to improve the rate capacity and cycling stability of Li4Ti5O12. Considering the industrial applications for the requirements of simplicity, economy and efficiency, doping method combined with solid-state method would not complex the synthesis process, is most easily to industrialization. Among various doping ions, Nb5+ and Ta5+ with a valence 5+ and similar ionic radii as Ti4+ are considering to be reasonable solubility in Ti sites. From previous literatures, M5+ doped (M = Nb, Ta) had been widely proved for improving physical and chemical properties of TiO2 owing to the significant effects of the metal ion dopants on their inner electronic and crystalline structure. Yang et al. fabricated mono-disperse rutile TiO2 with cross-bridge morphology via a simple Ta-doping method. The modified sample exhibits improved electron conduction with cross-medal morphologies via a simple Ta-doping crystalline structure. Yang et al. fabricated mono-disperse rutile effects of the metal ion dopants on their inner electronic and electronic conductivity. Our group previously has proved that niobium (Nb5+) or oxygen are proved to be effective to improve the rate capability [23]. Furthermore, Ta doping in Ti site of Li4Ti5O12 was found to benefit the electronic conductivity of Li4Ti5O12. Wolfenstein [24] tested the conductivities of LTO and Ta-doped Li4Ti5O12, but did not give the electrochemical performance results. Hu [25] and Zhang [26] reported the synthesis Li4Ti4.95Ta0.05O12 in reducing atmosphere (H2/Ar) and tested the electrochemical performance. However, the electrochemical performance of Ta-doped Li4Ti5O12 synthesized in oxidizing atmosphere which deducts the effect of reducing atmosphere on the reducing of Ti4+ to Ti3+ have not been reported.

Herein, we synthesized a series of Ta-doped Li4Ti5O12 with different Ta contents by a straightforward solid-state method in air which is widely used in industry, and studied their electrochemical performance. Based on the analysis of XRD and HRTEM, only 0.1 at% Ta doping in the lattice of the Li4Ti5O12 (Li4Ti4.95Ta0.05O12) could enlarge the lattice parameter of the Li4Ti5O12 which would improve the lithium ion diffusivity during the charge/discharge process. In addition, the higher charge compensation of the stoichiometric reduction of Ti4+ to Ti3+ by the introduction of Ta also increases the electronic conductivity of the Li4Ti5O12. As a result, the Ta-doped Li4Ti5O12 shows improved electrochemical performance, especially the high rate capability.

Table 1  
<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter (Å)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li4Ti5O12</td>
<td>8.3590</td>
<td>584.07</td>
</tr>
<tr>
<td>Li4Ta0.005Ta0.005O12</td>
<td>8.3614</td>
<td>584.57</td>
</tr>
<tr>
<td>Li4Ta0.01Ta0.01O12</td>
<td>8.3641</td>
<td>584.15</td>
</tr>
<tr>
<td>Li4Ta0.02Ta0.02O12</td>
<td>8.3619</td>
<td>584.68</td>
</tr>
<tr>
<td>Li4Ta0.05Ta0.05O12</td>
<td>8.3607</td>
<td>584.42</td>
</tr>
</tbody>
</table>
Fig. 2. SEM images of the as-prepared Li$_4$Ti$_{x-x}$Ta$_x$O$_{12}$ samples: (a) $x = 0$, (b) $x = 0.005$, (c) $x = 0.0125$, (d) $x = 0.025$, (e) $x = 0.05$.

Fig. 3. (a) EDS spectrum of the Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$ powder. (b)-(d) The corresponding EDS elements mapping of Ti, O and Ta elements.
as the milling medium by planetary ball milling (QM-3SP04) at a speed of 300 rpm for 10 h to obtain the slurry. The Ta-doping samples (Li$_4$Ti$_{5-x}$Ta$_x$O$_{12}$, $x = 0.005, 0.0125, 0.025, 0.05$) were yielded by the same way with different $x$ values and Ta$_2$O$_5$ (A.R.) were used as tantalum. Subsequently, the slurry was dried at 80 °C for 40 min to obtain the precursors. The well-milled precursors were further calcinated at 850 °C for 12 h with the heat rate of 2 °C min$^{-1}$ in muffle furnace. Excess Li was added to compensate for lithium volatilization during the high temperature heating process.

Phase analysis was conducted by X-ray diffraction (XRD, Bruker D8 Advance) using Cu-Kα radiation (10$^\circ$ ≤ 2θ ≤ 80$^\circ$) operated at 40.0 KV and 40 mA. The microstructures of the sintered particles was were observed by scanning electron microscopy (SEM, Nano430) and transmission electron microscopy (TEM, FEI, Tecnai G2 F30 S-Twin). X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos Axis Ultra DLD using the mono Al Kα radiation (1486.6 eV) under a pressure of 5 × 10$^{-9}$ torr.

2.2. Electrochemical measurements

The electrochemical properties of the pristine Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_{5-x}$Ta$_x$O$_{12}$ were investigated using coin-cells (CR2025). In order to make working electrodes, slurry containing 75 wt.% active materials (the bare Li$_4$Ti$_5$O$_{12}$ or the Li$_4$Ti$_{5-x}$Ta$_x$O$_{12}$), 15 wt.% carbon black, and 10 wt.% polyvinylidene (PVDF) were dispersed in N-methyle-2-pyrrolidone (NMP). Then the slurry was coated on copper foil. Highly pure lithium foil was used as the counter electrode while celgard 2325 membrane was used as a separator. The electrolyte is 1 mol L$^{-1}$ LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume). The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were less than 1 ppm. The cells were galvanostatically discharged and charged using a battery testing system (Neware Electronic Co., China) between 1.0 and 2.5 V. Electrochemical impedance spectra (EIS) of the pristine Li$_4$Ti$_5$O$_{12}$ and the Li$_4$Ti$_{5-x}$Ta$_x$O$_{12}$ electrodes were measured on the electrochemical workstation (Zahner IM6ex). The frequency range was set from 100 kHz to 10 mHz and the potential amplitude was 5 mV.

3. Results and discussion

The phase structures of the Li$_4$Ti$_{5-x}$Ta$_x$O$_{12}$ ($x = 0–0.05$) powders were investigated by powder X-ray diffraction (PXRD), as shown in Fig. 1. All the strong diffraction peaks can be perfectly indexed for a single-phase cubic spinel structure (JCPDS card No. 49-0207, space group Fd-3m (227)). When $x = 0.025$ and 0.05, the tiny diffraction peaks at 22.7°, 34.6°, 40.5°, 53.3° can be indexed to Li$_2$Ti$_3$O$_7$. While $x = 0.0125$ and 0.005, no impurity peaks was detected and the other diffraction peaks can be indexed to (111), (311), (400), (331), (333), (440), (513), (533), (622), (444) planes of the cubic Li$_4$Ti$_5$O$_{12}$.
denoting that moderate amount doping of Ta\(^{5+}\) do enter the lattice of Li\(_4\)Ti\(_5\)O\(_{12}\) without causing any changes of the basic Li\(_4\)Ti\(_5\)O\(_{12}\) structure. For clear observation (on the right of Fig. 1), the (111) peaks of the Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\) \((0 \leq x \leq 0.05)\) shift to smaller angles when \(x\) increases from 0 to 0.0125, suggesting that the Ta-doped samples have larger lattice constants than the pristine Li\(_4\)Ti\(_5\)O\(_{12}\) [23]. The peak shift degrees of the Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\) for \(x = 0.025\) and 0.05 decrease with Ta doping concentration increasing. The main reason may be due to the impurity segregation [27,28]. When \(x = 0.025\) and 0.05, the second phase of Li\(_2\)Ti\(_3\)O\(_7\) was detected in the Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\), the dopant (Ta\(^{5+}\)) was not completely incorporated into the lattice, and caused the lattice constant decreased. Moreover, lattice parameters and unit cell volumes of the Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\) \((x = 0–0.05)\) samples are calculated according to the Rietveld method using TOPAS software, the results are listed in Table 1. An increase in lattice parameter with the increase of Ta content is found. The lattice parameter of Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\) is increasing from 8.3590 Å to 8.3641 Å when Ta content (\(x\)) increases from 0 to 0.0125. And the cell volume also increases from 584.07 Å\(^3\) to 585.15 Å\(^3\). Here, the increase of the lattice parameter may be ascribe to two reasons: i) the larger Ta\(^{5+}\) (\(r = 0.64\) Å) occupied the site of the Ti\(^{4+}\) (\(r = 0.61\) Å), and ii) Ta doped on the Ti site cause the transition of a certain amount of Ti\(^{4+}\) to Ti\(^{3+}\) (0.67 Å) as charge compensation [23,24]. While the amount of Ta reached 1 at\% (Li\(_4\)Ti\(_{4.95}\)Ta\(_{0.05}\)O\(_{12}\)), the lattice parameter and the cell volume are decrease compared with Li\(_4\)Ti\(_{4.975}\)Ta\(_{0.025}\)O\(_{12}\) due to the formation of impurity Li\(_2\)Ti\(_3\)O\(_7\) compound. The lattice parameter of the Li\(_4\)Ti\(_{4.95}\)Ta\(_{0.05}\)O\(_{12}\) is larger than the pristine Li\(_4\)Ti\(_5\)O\(_{12}\), while smaller than those of other Ta-doped samples. As we known, the variation in the lattice parameter of Li\(_4\)Ti\(_5\)O\(_{12}\) is very small with less than 0.3% unit cell volume change during discharge process (Li insertion), and the Li insertion into the 16c sites is accompanied by Li ion at 8a sites migrate to 16c sites [29,30]. As a result, the enlarged lattice and the expansive channels reduced the block for the Li ion diffusion and intercalation process, which is beneficial for fast lithium ions transfer without lattice stability damaged and increasing the ionic conductivity of Li\(_4\)Ti\(_3\)O\(_{12}\).

The morphologies of the pristine Li\(_4\)Ti\(_5\)O\(_{12}\) and the Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\) were investigated by SEM. As shown in Fig. 2, there is no obvious change in the particle size of Li\(_4\)Ti\(_5\)O\(_{12}\), all samples are well crystalline and the particle size distributions are all ranging from 0.5 to 1.0 \(\mu\)m. The doping of Ta does not influence the structure and morphology of Li\(_4\)Ti\(_5\)O\(_{12}\) samples. The method of Ta doping combined with solid-state reaction would not affect the tap density of the Li\(_4\)Ti\(_5\)O\(_{12}\) which is very important for practical applications in industry. Meanwhile, the corresponding energy-dispersive X-ray (EDX) spectrum of Li\(_4\)Ti\(_{4.995}\)Ta\(_{0.005}\)O\(_{12}\) powder is employed (Fig. 3). As shown in Fig. 3a, the diffraction peaks of Ti, O and Ta were observed. Fig. 3b–d shows the mapping images of Ti, O and Ta elements. All elements show the similar distributions which means that Ta element evenly distributed in the powder of Li\(_4\)Ti\(_{4.995}\)Ta\(_{0.005}\)O\(_{12}\).

X-ray photoelectron spectroscopy (XPS) analysis is used to provide more information on the valence of Ti in Li\(_4\)Ti\(_{5-x}\)Ta\(_x\)O\(_{12}\). The binding energies in the XPS analysis are corrected with reference to the C1s peak (284.6 eV). Fig. 4 shows the XPS spectra of Ti2p of Li\(_4\)Ti\(_5\)O\(_{12}\) and Li\(_4\)Ti\(_{4.995}\)Ta\(_{0.005}\)O\(_{12}\) samples. As indicated in Fig. 4a, two strong peaks located at around 458.4 eV and 464.1 eV are

Fig. 5. (a)–(b) TEM and (c)–(d) HR-TEM images of the Li\(_4\)Ti\(_5\)O\(_{12}\) and the Li\(_4\)Ti\(_{4.995}\)Ta\(_{0.005}\)O\(_{12}\) powders.
assigned to Ti 2p3/2 and Ti 2p1/2, respectively [31,32]. After Ta doping in Li4Ti5O12, two new Ti2p peaks were observed at 457.9 eV and 462.9 eV as shown in Fig. 4b, which may be assigned to the presence of Ti3+. The Ti3+ is attributed to the stoichiometric reduction of Ti4+ to Ti3+ for each Ta introduced which would enhance the electronic conductivity of Li4Ti5O12 [20].

Room temperature electron paramagnetic resonance (EPR) spectra are also recorded to detect the generation of Ti3+ after Ta5+ doped in Li4Ti5O12, shown in Fig. 4c. It has been reported that paramagnetic Ti3+ center has a g-value of 1.94–1.99 [33–35]. The obvious signals at g = 1.990 for Li4Ti4.995Ta0.005O12 and Li4Ti4.95-Ta0.05O12 is ascribed to Ti3+, indicating the successful doping modification of Ta on Li4Ti5O12. The results is consistent with the XPS results.

The morphologies and structures of the pristine Li4Ti5O12 and Li4Ti4.995Ta0.005O12 were further clarified by TEM, HRTEM and SAED characterizations (Fig. 5). Both samples show similar smooth surfaces (Fig. 5a–b). HRTEM is used to characterize the structures and the lattice distances of the Li4Ti5O12 and Li4Ti4.95Ta0.005O12. The interplanar spacing corresponding to the (111) plane of the Li4Ti5O12 was measured to be 0.483 nm, while that of the Li4Ti4.95Ta0.005O12 increases to 0.485 nm. The above results further validate that Ta5+ doping in the lattice of Li4Ti5O12 increases the lattice constant of Li4Ti5O12, which is in accordance with the XRD results. The enlarged interplanar spacing is beneficial for lithium ion diffusion to achieve better rate capability of Li4Ti5O12. The selective area electron diffraction (SAED) pattern results demonstrate that both samples show good crystalline quality (insert of Fig. 5c–d).

The rate capability is a very beneficial feature for high power applications such as electric vehicles. Based on above results, Ta doping in the lattice of Li4Ti5O12 could facilitate the Li ion diffusion and enhance the charge compensation of Li4Ti5O12. It can be expected that those characteristics will benefit electrochemical performance of Li4Ti5-xTa0.12 at high current density compared with the pristine Li4Ti5O12. As shown in Fig. 6a, the rate capabilities of the Li4Ti4.995Ta0.005O12 samples (x = 0.005, 0.0125, 0.025) exhibit a higher discharge capacity than Li4Ti5O12. Apparently, the Li4Ti4.995Ta0.005O12 shows the best rate performance among those samples. For the Li4Ti4.995Ta0.005O12, even at the high current density of 10C and 20C, a reversible capacity of 95.1 and 62.3 mAh g–1 can still be delivered. However, the reversible capacity of the Li4Ti5O12 is only 50.4 and 17.4 mAh g–1 at the current density of 10C and 20C, respectively. The capacity of Li4Ti4.995Ta0.005O12 is 1.9 and 3.6 times of the capacity of the pristine Li4Ti5O12 at the rate of 10C and 20C. However, when x = 0.05, due to the formation of impurity (Li2Ti3O7), the Li4Ti4.95Ta0.05O12 delivers a
low discharge capacity at the low rates and but still shows the similar discharge capacity at the rate of 10C, 20C compared with the pristine Li4Ti5O12. Hence, Ta content in Ta-doped Li4Ti5O12 particles must be carefully controlled to avoid the generation of impurities, and then do not lead to poor electrochemical performance. In addition, the specific capacities of all the Li4Ti5-xTaxO12 samples can recover to the initial value when the current rate is reduced back to 0.2C, indicating that the Li4Ti5-xTaxO12 electrode shows an excellent cycling performance. The improved electrochemical performance of the Li4Ti4.995Ta0.005O12 may be attributed to the following reasons. Firstly, the enlarged lattice parameter and the expansive channels by Ta doping are beneficial for fast lithium ions transfer and increasing the ionic conductivity of Li4Ti5-xTaxO12. Secondly, an enhanced charge compensation due to Ta5+ replaces Ti4+ site in Li4Ti5O12, improves the electronic conductivity compared with the pristine Li4Ti5O12. Thirdly, the stoichiometric reduction of Ti4+ to Ti3+ for each Ta doping induces the formation of mixed value of Ti3+/Ti4+, which helps fast electron transfer at the discharge/charge process.

Fig. 6b illustrates the cycling performances of the pristine Li4Ti5O12 and the Li4Ti5-xTaxO12 at the rate of 5C. Both the pristine Li4Ti5O12 and the Li4Ti5-xTaxO12 are gradually activated in the first few cycles. Both samples display good cyclic performances and high coulombic efficiencies near 100%, which is due to the near zero volume variation of Li4Ti5O12-based spinel structure during the charge–discharge process, and the Ta doping does not change its structure characteristics. After 100 cycles, the discharge capacity of the Li4Ti4.995Ta0.005O12 is 132.2 mAh g⁻¹, which is much higher than that of the pristine Li4Ti5O12 (92.4 mAh g⁻¹). The specific capacity retentions of the pristine Li4Ti5O12 and the Li4Ti4.995Ta0.005O12 after 100 cycles at 5C are 85.1% and 99.2%, respectively. The improvement in capacity retention of the Li4Ti4.995Ta0.005O12 is ascribed to the enlarged lattice parameter after Ta doping, which is beneficial to lithium ion diffusion and is helpful for the insertion and extraction of Li ion.

The first discharge/charge cycles at 0.2C rate for Li4Ti5O12 and Li4Ti4.995Ta0.005O12 were shown in Fig. 7a. The first discharge capacities of Li4Ti5O12 and Li4Ti4.995Ta0.005O12 reach 196.5 mAh g⁻¹ and 193.0 mAh g⁻¹, respectively. The first cycle coulombic efficiency of the Li4Ti4.995Ta0.005O12 electrode is 95.5% which is higher than that of the Li4Ti5O12 electrode (90.5%). Both curves show a flat voltage plateau at around 1.55 V (vs. Li⁺/Li), which is characteristic of two phase reaction. Aside from the two-phase insertion reaction, the sloping voltage curves appear at the beginning (or end) of the discharge curve indicate a single-phase insertion reaction of Li4Ti4.995Ta0.005O12 [36]. Fig. 7b–c displays the voltage profiles of the pristine Li4Ti5O12 and the Li4Ti4.995Ta0.005O12 at the current rates from 0.5C to 20C. At lower rate of 0.5C, the Li4Ti4.995Ta0.005O12 exhibits a higher discharge capacity of 184.8 mAh g⁻¹ than that of the pristine Li4Ti5O12 (164.2 mAh g⁻¹). As the current rate increases from 2C to 20C, the discharge capacity of the Li4Ti4.995Ta0.005O12 decreases gradually from 165.3 to
of $\text{Ti}^{4+}$/$\text{Ti}^{4+}$ in the cubic structure during lithium insertion and extraction processes. The oxidation peaks are about 1.69 V corresponding to the process of lithium insertion in the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Ti}_4\text{O}_{12}$, and the reduction peaks occurred at around 1.46 V which is related to the lithium extraction from the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is found that the CV curves are well overlapped for the three cycles, indicating the good electrochemical reversibility and stable structure of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Fig. 8b-c exhibit CV curves of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different scans rates from 0.2 to 2.0 mV s$^{-1}$. It is observed that both samples exhibit the similar oxidation and reduction peaks, indicating the dopant (Ta) does not change the electrochemical reaction process of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in this voltage range. Fig. 8d shows the correlation between the anodic peak currents and the square roots of the scan rate for both electrodes, which matches the linear relationship very well. It is the typical behavior of diffusion-controlled electrode reaction process. The diffusion coefficient can be estimated based on the slope of the oblique line [37]. Hence, it can be easily deduced that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows larger diffusion coefficient than the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Since both materials have almost the same particle size distribution, the increased diffusion coefficient of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ should be attributed to the Ta doping. The transition of a certain amount of $\text{Ti}^{4+}$ (0.61 Å) to $\text{Ti}^{4+}$ (0.67 Å) by Ta doping leads to the larger lattice constant than the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The enlargement lattice parameter makes the diffusion of Li ions become more easy, and then increases the ionic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

In order to further verify the effects of Ta doping on the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, EIS measurements of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were carried out after 100 cycles (Fig. 9). Both EIS diagrams are composed of a depressed semicircle in high frequency range and an oblique linear Warburg part in low frequency range. It is usually considered that the semicircle in the high frequency range is related to the charge transfer resistance [38]. The Nyquist plots show that the diameter of the semicircle for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the high-medium frequency region is smaller than that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ composite (Fig. 9a). Therefore, the result indicates that the charge transfer resistance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is much lower than that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The EIS method has been considered as a useful method to identify the chemical diffusion coefficient [39]. The low frequency Warburg impedance corresponding to the diffusion of Li ions in the bulk of the electrode, has been used to determine the Li diffusion coefficient in the compound [36,40]. The Warburg coefficient $\sigma_w$ can be obtained from the slope by Eq. (1):

$$Z_{re} = R_s + R_{ct} + \sigma_w \omega^{-1/2}$$

(1)

Where $Z_{re}$ is the real part of the impedance; $R_s$ is the resistance of electrolyte; $R_{ct}$ is the charge transfer resistance and $\omega$ is the angular frequency in the low frequency region.

The plot of $Z_{re}$ vs. the reciprocal square of the lower angular frequencies ($\omega^{-1/2}$) for both samples is shown in Fig. 9b. It is observed that the Warburg impedance coefficient ($\sigma_w$) is 51.27 $\Omega$ cm$^2$ s$^{-1/2}$ for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is lower than that of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (74.09 $\Omega$ cm$^2$ s$^{-1/2}$).

The lithium ion diffusion coefficient can be calculated from the formula as following equation [39]:

$$D_{li} = \frac{1}{2} \left( \frac{V_m}{AFm} \right) \frac{dE}{dx}^2$$

(2)

Where $V_m$ is the molar volume of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (45.73 cm$^3$ mol$^{-1}$), $F$ is the Faraday constant (96486 C mol$^{-1}$), $A$ is the total contact area between the electrolyte and the electrode, $dE/dx$ is the slope of the
open-circuit voltage versus mobile Li$^+$ concentration $x$.

The calculated lithium diffusion coefficient $D_{Li^+}$ of the Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$ material is $3.01 \times 10^{-10}$ cm$^2$ s$^{-1}$, while that of the pristine Li$_4$Ti$_5$O$_{12}$ is only $7.55 \times 10^{-12}$ cm$^2$ s$^{-1}$. Obviously, the Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$ has larger lithium diffusion coefficient, which indicates that the lithium ion mobility of the Li$_4$Ti$_5$O$_{12}$ can be effectively improved by Ta doping. Consequently, the electrochemical performance of the Li$_4$Ti$_5$O$_{12}$ can be improved substantially by Ta doping.

4. Conclusions

The Ta-doped Li$_4$Ti$_5$O$_{12}$ (Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$) with different Ta contents have been successfully synthesized via a facile one step solid-state reaction. The Li$_4$Ti$_5$O$_{12}$ with only 0.1 at% Ta doping (Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$) exhibits higher specific capacity and better cyclic stability than the pristine Li$_4$Ti$_5$O$_{12}$. The Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$ shows much lower polarization at high rates than the pristine Li$_4$Ti$_5$O$_{12}$. The Li$_4$Ti$_{4.995}$Ta$_{0.005}$O$_{12}$ also exhibits good cycling stability, could deliver 132.2 mAh g$^{-1}$ at 5C even after 100 cycles. The excellent electrochemical performance can be attributed to the improved electronic conductivity and lithium ions diffusivity by the enlarged lattice parameter and introduction of the mixed valence of Ti$^{4+}$/Ti$^{3+}$ by Ta doping. Because the solid-state reaction method is a facile, low cost and repeatable synthetic method, it has a great potential to extend the production of the Ta-doped Li$_4$Ti$_5$O$_{12}$ to meet practical need in battery industry. Ta doping is a new strategy for enhancing the electrochemical performance of the Li$_4$Ti$_5$O$_{12}$.

Acknowledgments

The authors greatly acknowledge the financial support by National Science Fund for Distinguished Young Scholars of China (No. 21225262), Natural Science Foundation of China (No. 21306057), the Australian Research Council (ARC) through the Future Fellow Program (FT140100757), the Specialized Research Fund for the Doctoral Program of Higher Education (2012012120011), the Pearl River Scholar Program of Guangdong Province and Fundamental Research Funds for the Central Universities, SCUT.

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