



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



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HIGHLIGHTS

- Ta doping in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ would enlarge the lattice parameter of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
- The ionic conductivity and electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are improved by Ta doping.
- The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with only 0.1 at% Ta doping exhibits superior electrochemical performance.

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ABSTRACT

A series of Tantalum-doped lithium titanate (Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$) samples have been successfully synthesized by one step solid-state method using TiO_2 , Li_2CO_3 , and Ta_2O_5 as raw materials. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with only 0.1 at% Ta doping ($\text{Li}_4\text{Ti}_{4.995}\text{Ta}_{0.005}\text{O}_{12}$) exhibits higher rate capability and better cyclic stability than the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. $\text{Li}_4\text{Ti}_{4.995}\text{Ta}_{0.005}\text{O}_{12}$ could deliver 95.1 mAh g^{-1} at 10C with much lower overpotential (216.1 mV) while the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ would enlarge the lattice parameter of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The improved ionic conductivity and electronic conductivity are beneficial to the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As a result, Ta doping is a new strategy for enhancing the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

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1. Introduction

Lithium ion batteries (LIBs) are widely used in consumer electronics, transportation and large-scale renewable energy storage [1,2]. Recently, the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) stimulates seeking new materials with high energy density, excellent power capability and long cycle life. Meanwhile, the conventional used graphite anode is not suitable due to two reasons: its lithiation potential below 0.2 V versus Li/Li^+ may cause the formation of dendritic lithium

on anode surface at high charging current and lead to safety issues [3–5]; graphite anode also has its limit on high rate performance which is unable to meet the requirements of the high power devices [6,7]. It is necessary to explore an alternative candidate with higher safety, higher power density and longer battery life.

Lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is regarded as a promising candidate anode material for commercial lithium-ion batteries and hybrid electrochemical storage devices, because of its outstanding ability to tolerate abuse and excellent cycle life. Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a flat and relatively high lithiation voltage plateau at about 1.54 V versus Li/Li^+ , which is very important property of the electrode material for long term high voltage in practical use. Particularly, it is a zero-strain insertion material, which has excellent reversibility toward lithium insertion/extraction [8,9]. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has an insulating character by empty Ti 3d-states with a band gap energy of ~2 eV which hinders

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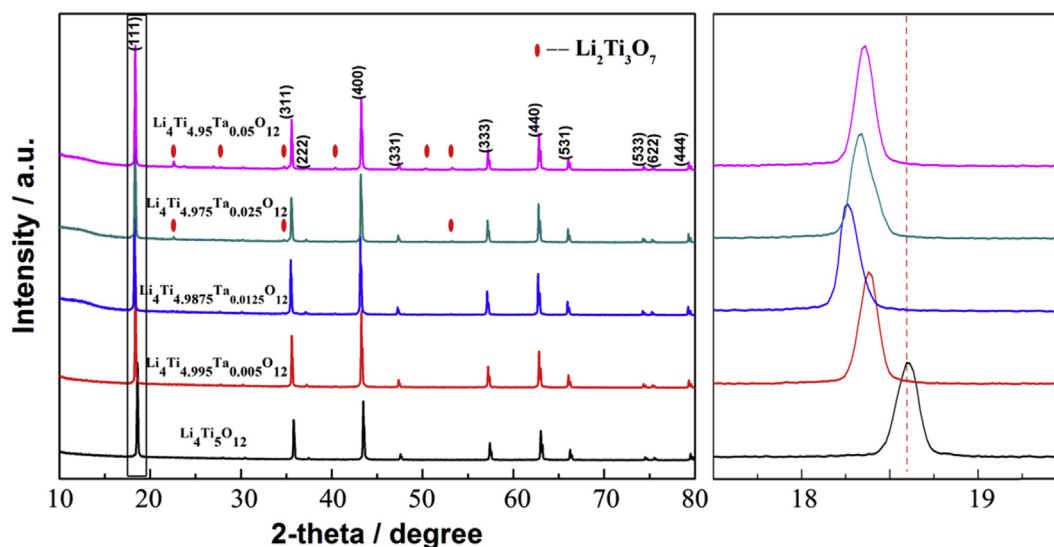


Fig. 1. Powder X-ray diffraction patterns of $\text{Li}_4\text{Ti}_{5-x}\text{Ta}_x\text{O}_{12}$ ($x = 0, 0.005, 0.0125, 0.025, 0.05$).

the practical applications on high power devices. So far, numerous strategies have been reported for enhancing the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ including nanostructure design, surface coating and ion doping on the Li site, the Ti site or the O site of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can enhance the electronic conductivity and then have a significant enhancement in the rate capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [13–15]. Another way to improve electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is ion doping. Doping with ions as Al^{3+} [16], La^{3+} [17], W^{5+} [18], Sc^{3+} [19], Br^- [20] etc to replace partially lithium, titanium or oxygen are proved to be effective to improve the rate capacity and cycling stability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Considering the industrial applications for the requirements of simplicity, economy and efficiency, doping method combined with solid-state method would not complex the synthesize process, is most easily to industrialization. Among various doping ions, Nb^{5+} and Ta^{5+} with a valence 5+ and similar ionic radii as Ti^{4+} , are considering to be reasonable solubility in Ti sites. From previous literatures, M^{5+} -doped ($\text{M} = \text{Nb}, \text{Ta}$) had been widely proved for improving physical and chemical properties of TiO_2 owing to the significant effects of the metal ion dopants on their inner electronic and crystalline structure. Yang et al. fabricated mono-disperse rutile TiO_2 with cross-medal morphologies via a simple Ta-doping method. The modified sample exhibits improved electron conduction in photocatalytic systems [21]. Marco used a facile method to grow ordered Ta-doped TiNTs. When Ta content is 0.1 at %, improved water splitting ability is achieved due to the enhanced electrical conductivity of crystalline Ta-doped TiNT arrays [22]. For M^{5+} doped TiO_2 , charge compensation of M^{5+} ($\text{M} = \text{Nb}, \text{Ta}$), which replaces Ti^{4+} , can be achieved in two ways: (1) electron concentration increased due to Ta doping; (2) the stoichiometric reduction of Ti^{4+} to Ti^{3+} for each M^{5+} introduced. Hence, substitute a M^{5+} on a Ti^{4+} site of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ might also lead to an increase in electron concentration and then an increase in electronic conductivity. Our group previously has proved that niobium (Nb^{5+}) doped into $\text{Li}_4\text{Ti}_5\text{O}_{12}$ might make the lattice parameter become larger and cause a transition of a certain amount of Ti^{4+} to Ti^{3+} as charge compensation, thus improving

the rate capability [23]. Furthermore, Ta doping in Ti site of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was found to benefit the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Wolfenstine [24] tested the conductivities of LTO and Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$, but did not give the electrochemical performance results. Hu [25] and Zhang [26] reported the synthesis $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ in reducing atmosphere (H_2/Ar) and tested the electrochemical performance. However, the electrochemical performance of Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized in oxidizing atmosphere which deducts the effect of reducing atmosphere on the reducing of Ti^{4+} to Ti^{3+} have not been reported.

Herein, we synthesized a series of Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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 $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{4.995}\text{Ta}_{0.005}\text{O}_{12}$) could enlarge the lattice parameter of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which would improve the lithium ion diffusivity during the charge/discharge process. In addition, the higher charge compensation of the stoichiometric reduction of Ti^{4+} to Ti^{3+} by the introduction of Ta also increases the electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As a result, the Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows improved electrochemical performance, especially the high rate capability.

2. Experimental

2.1. Synthesis and characterization

The pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{5-x}\text{Ta}_x\text{O}_{12}$, $x = 0.005, 0.0125, 0.025, 0.05$) were prepared by a solid state reaction. The mixture of TiO_2 (A.R., 4.000 g) and Li_2CO_3 (A.R., 1.545 g) with a Li:Ti molar ratio of 4.175:5 were blended with ethyl alcohol

Table 1
Lattice parameters of the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples.

| Sample | Lattice parameter (Å) | V (Å ³) |
|--|-----------------------|-----------------------|
| $\text{Li}_4\text{Ti}_5\text{O}_{12}$ | 8.3590 | 584.07 |
| $\text{Li}_4\text{Ti}_{4.995}\text{Ta}_{0.005}\text{O}_{12}$ | 8.3614 | 584.57 |
| $\text{Li}_4\text{Ti}_{4.9875}\text{Ta}_{0.0125}\text{O}_{12}$ | 8.3641 | 585.15 |
| $\text{Li}_4\text{Ti}_{4.975}\text{Ta}_{0.025}\text{O}_{12}$ | 8.3619 | 584.68 |
| $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ | 8.3607 | 584.42 |

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