Int. J. Electrochem. Sci., 8 **(2013)** 6449 - 6456

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Review

Recent Developments in the Doped-$Li_4Ti_5O_{12}$ Anode Materials of Lithium-Ion Batteries for Improving the Rate Capability

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Received: 27 March 2013 / *Accepted:* 12 April 2013 / *Published:* 1 May 2013

Lithium-ion batteries have become attractive for portable electric devices due to their higher energy density and long cycling life compared to other system. With a growing interest to develop rechargeable batteries for electric vehicles and large stationary power supplies, lithium titanate ($Li_4Ti_5O_{12}$) is considered to replace the currently used carbon anodes in lithium-ion batteries. $Li_4Ti_5O_{12}$ is a technically important anode material for new-generation power lithium-ion battery applications because of its abundant titanium dioxide raw materials, excellent cycle reversibility and stability, relatively high capacity (175 $mAh \cdot g^{-1}$), and safety characteristics due to its zero-strain volume during charge-discharge processes and high lithiation voltage plateau at 1.55 V *vs.* Li/Li^+, which sufficiently avoid the formation of metallic lithium and thus improve the safety of lithium-ion batteries. However, the commercial use of $Li_4Ti_5O_{12}$ anode material has been hindered to date by their poor electronic conductivity. This review highlights the recent progress in improving the rate ability of $Li_4Ti_5O_{12}$ anode by doping, which is considered to be an effective way to increase electronic conductivity of $Li_4Ti_5O_{12}$.

Keywords: Lithium-ion batteries; Anode materials; $Li_4Ti_5O_{12}$; Doping; High-rate capability

1. INTRODUCTION

In order to reduce the global warming effect coming from the production of carbon dioxide and to abate the energy crisis of fossil fuels, development of more efficient and viable sources of energy and their storage devices such as lithium-ion batteries have proven its own importance [1]. Lithium-ion batteries have been widely used for portable electric devices, such as mobile phones and notebooks. However, the performance of today's commercial lithium-ion batteries still cannot meet the requirements of some applications in electric vehicles, hybrid electric vehicles and energy storage system, in terms of high power density, long cycle life and high safety [2, 3].

The spinel-type $Li_4Ti_5O_{12}$ has attracted great interest as new anode material since the traditional carbon/graphite materials suffered from numerous problems [4-6]. $Li_4Ti_5O_{12}$ anode material with a theoretical capacity of 175 mAh·g^{-1} has excellent Li^+ insertion and extraction reversibility within the voltage of 1.0-2.5 V and displays a good structural stability with almost zero volume change during charge and discharge processes [7]. It also has a very flat voltage plateau close to 1.55 V (vs. Li/Li$^+$), which is higher than the reduction potential of most organic electrolytes [8]. All of these merits make $Li_4Ti_5O_{12}$ more competitive as a good candidate material for negative electrodes used in long life type power lithium-ion batteries. However, electrodes made from unmodified $Li_4Ti_5O_{12}$ usually exhibit poor rate performance [9], which mainly results from its inherent low electronic conductivity (ca. 10^{-13} S·cm^{-1}) and moderate Li^+ diffusion coefficient (10^{-8} cm^2·s^{-1}) [10]. Numerous ways involving compositional and morphological modification have been exploited to overcome this problem, such as reducing particle size [1, 11-14], coating carbon on the surface [2,7, 15-23], mixing with a conductive second phase [24-28] and doping with metal ions (such as K^+ [29], Ag^+ [44], Sn^{2+} [20], Mg^{2+} [10, 30], Ca^{2+} [31], Zn^{2+} [32-34], Al^{3+} [35-39], Ni^{2+} [40, 42], Ga^{3+} [37], Cr^{3+} [41, 42], Co^{3+} [42], La^{3+} [21, 43-47], Y^{3+} [48], Zr^{4+} [49], Ru^{4+} [50-52], Mo^{4+} [53], Mn^{4+} [40, 54], V^{5+} [29, 55-57], Ta^{5+} [58, 59], Nb^{5+} [60-62], Sr^{2+} [63]) or non-metal ions (such as F^- [36], Br^- [64]). Doping in the $Li_4Ti_5O_{12}$ has been proved to be an effective way to improve the electronic conductivity. This review sums up all the related research works in the doping of $Li_4Ti_5O_{12}$ as anode material for lithium-ion batteries. The latest research progresses of co-doping which highly enhances the rate capability of $Li_4Ti_5O_{12}$ are also presented.

2. $Li_4Ti_5O_{12}$ DOPED BY IONS

The structure of $Li_4Ti_5O_{12}$ belongs to a cubic system with space group Fd3m, in which 75% of lithium ions are located on tetrahedral 8a sites, and 25% of lithium ions and Ti^{4+} are randomly distributed at octahedral 16d sites. All the oxygen ions occupy the 32e sites [65]. When a trivalent metal cation is substituted into $Li_4Ti_5O_{12}$, it is known that the doping metal ions together with the Ti^{4+} occupy the 16d octahedral sites [66].

Among the critical requirements of lithium insertion electrode is that the electrode should have both excellent electronic conductivity and good lithium ion diffusion in order to achieve fast reaction rates (high power) for lithium-ion batteries [67]. A main obstacle of $Li_4Ti_5O_{12}$ is a poor rate capability due to its low electronic conductivity. To overcome this drawback, much effort has been carried out. Although coating with carbon or a metallic conducting layer is an efficient way to improve its conductance, the method helps nothing in the lattice electronic conductivity or lithium ion diffusion coefficient within the crystal. Ion doping is another effective way to improve the electronic conductivity of $Li_4Ti_5O_{12}$ materials, which forces transformation of partial Ti^{4+} into Ti^{3+} to generate mixing Ti^{3+}/Ti^{4+} as charge compensation and thus increase the concentration of electrons [68]. Substitution of a small quantity of Li^+, Ti^{4+}, or O^{2-} by other metallic ions can greatly improve the kinetics of materials in terms of capacity delivery, cycle stability and especially rate capability.

2.1 Doping in the Li site

A variety of cations including K^+, Mg^{2+}, Al^{3+}, Ca^{2+} , Zn^{2+} and Sn^{2+} are doped in Li^+ site and related investigations in structural properties, ion valence and conductive characteristics are also performed [29-39].

The first-principles calculations show that doping at Li site with alkali metal ions facilitates the Li^+ diffusion, which can increase the electronic and ionic conductivity [69]. Li et al. [29] reported K-doped $Li_4Ti_5O_{12}$ anode materials synthesized by a solid state reaction. The results show that K-doping do not affect the structure and change the electrochemical reaction process of cubic spinel $Li_4Ti_5O_{12}$. The research suggests that the sample $Li_{3.96}K_{0.04}Ti_5O_{12}$ exhibits a relatively good cycling stability and rate capability. Its discharge specific capacity remains at 137 $mAh \cdot g^{-1}$ even after 200 cycles at 3 C rate. Very recently, our research group reported the Ca-doped anode synthesized by a simple solid-state reaction in an air atmosphere. The results indicate that Ca^{2+}-doping do not affect the structure, and the particle size distribution is in the range of 1-2 μm. The $Li_{3.9}Ca_{0.1}Ti_5O_{12}$ electrode exhibited the highest electronic conductivity and fastest lithium-ion diffusivity [31].

Zhang et al. [20] reported the carbon coated $Li_{3.9}Sn_{0.1}Ti_5O_{12}$ porous powders synthesized by a new sol-gel method to improve rate capability. The doping of Sn^{2+} results in the lattice distortion without changing the phase composition. A thin layer of amorphous carbon is coated on the doped particles that contain numerous nanopores. The specific capacities of the doped $Li_{3.9}Sn_{0.1}Ti_5O_{12}$ are much higher than the corresponding values of neat $Li_4Ti_5O_{12}$ when discharged at both low and high current densities. Almost 100% capacity retention was obtained after 100 cycles of charge/discharge at 5 C. The improvements can be ascribed to the enhanced electric conductivity and electrode kinetics due to the Sn^{2+} modification. Zhang et al. [32] first reported the zinc-doped $Li_4Ti_5O_{12}$ synthesized by the solid-state route. Zn doping is favorable to improve the conductivity and rate performance of $Li_4Ti_5O_{12}$. Zhu et al. [70] reported spinel-type electrode material $Li_{4-x}Mg_xTi_5O_{12}$ ($x = 0.05, 0.1, 0.15, 0.2$) synthesized by solid state reaction to improve the electrochemistry and cycle performances. The results show that the electrochemistry properties and cycle performance of Mg^{2+}-doped $Li_4Ti_5O_{12}$ materials are improved. Among the series investigated samples, the $Li_{3.9}Mg_{0.1}Ti_5O_{12}$ sample has a good electrochemistry performance, and its first discharge special capacity was 123.6 $mAh \cdot g^{-1}$ even at 10 C rate. In addition, Cai et al. [71] reported that the controlled Al^{3+} doping into tetrahedral 8a Li^+ sites will promote the reduction of Ti^{4+} to Ti^{3+} to increase the electronic conductivity of $Li_4Ti_5O_{12}$ and then showed a higher electrochemical performance than that of pure $Li_4Ti_5O_{12}$.

2.2 Doping in the Ti site

According to the report mentioned above, many researchers proposed that the dopant occupy the Li site due to their similar ionic radius. Similarly, Ti site doping by small amounts of Cr^{3+}, Co^{3+}, Ni^{2+}, La^{3+}, Y^{3+}, Zr^{4+}, Ru^{4+}, Mo^{4+}, Mn^{4+}, V^{5+}, Ta^{5+}, Nb^{5+}, or Sr^{2+} also resulted in improved rate capability mainly by enhancing the electronic conductivity [40-63].

Hao et al. [42] reported the systematically investigated effects of dopant on the electrochemical properties spinel-type $Li_{3.97}M_{0.1}Ti_{4.94}O_{12}$ (M=Ni, Co) and $Li_{(4-x/3)}Ti_{(5-2x/3)}O_{12}$ ($x=0.1, 0.3, 0.6, 0.9, 1.5$).

The results showed that Cr^{3+} dopant improved the reversible capacity and cycling stability over the pristine $Li_4Ti_5O_{12}$. The substitution of the Co^{3+} ion to extent worsened the electrochemical performance of the $Li_4Ti_5O_{12}$, and the Ni^{3+} doped sample showed slight capacity fade. With respect to the conductivity behavior, only Cr^{3+} doping lead to an increase of electronic conductivity compared with the pure $Li_4Ti_5O_{12}$ sample, while Ni^{3+} and Co^{3+} doping did not, which was attributed to the localized Ni or Co 3d bands causing electrons to be not easily excited [72]. Gao et al. [43] first reported the spherical La^{3+}-doped $Li_4Ti_5O_{12}$ powders with high tap density synthesized by an outer gel method. The results indicate that the electrochemical performance has been obviously improved by doping La^{3+} in $Li_4Ti_5O_{12}$. The initial discharge capacity is 161.5 mAh·g^{-1} at 0.1 C rate, and the capacity still reaches 135.4 mAh·g^{-1} after 50 cycles. Yi et al. [44] reported a micro-size particle $Li_4Ti_{5-x}La_xO_{12}$ ($0 \leq x \leq 0.2$) material synthesized by a simple solid-state method at air. The obtained $Li_4Ti_{5-x}La_xO_{12}$ materials are $Li_{3x}La_{2/3-x}TiO_3$ -$Li_4Ti_5O_{12}$ solid solution, and well crystallized with a particle size in the range of 1-2 mm. The electronic conductivity and lithium diffusion coefficient of La-modified $Li_4Ti_5O_{12}$ are improved. Especially, in rate performance, the $Li_4Ti_{5-x}La_xO_{12}$ (x =0.1, 0.2) samples maintain capacity of about 181 mAh·g^{-1} until 5 C rates even after 200 cycles. Bai et al. [48] first reported Yttrium-modified $Li_4Ti_5O_{12}$ fabricated by a coprecipitation method followed by simply sintering at 600 ℃. The results show that Y-modified $Li_4Ti_5O_{12}$ exhibits excellent long-term cycling stability (over 1000 cycles) at a high current rate of 10 C and outstanding rate capabilities, which is ascribed to the increased lattice constant, improved electronic and ionic conductivities, refined grains with large surface area and uniform nanopores resulting from the Y-doping.

Li et al. [49] reported Zr-doped $Li_4Ti_5O_{12}$ prepared by solid-state reaction in an air atmosphere. Zr^{4+} doping was found to reduce the particle size to less than 100 nm and effectively alleviate particle agglomeration, contributing to the improvement in rate capability. The optimal composition of $Li_4Ti_{4.9}Zr_{0.1}O_{12}$ obtained a desirable rate capability by maintaining a discharge capacity of 118 mAh·g^{-1} at 20 C. It still remained at 141 mAh·g^{-1} after 100 cycles at 5 C. Several authors [50-52] reported that Ru^{4+}-doping could significantly improve the rate capability of $Li_4Ti_5O_{12}$. All research works proved that $Li_4Ti_{4.99}Ru_{0.01}O_{12}$ exhibited an excellent rate capability due to the improved electronic conductivity and higher lithium-ion diffusivity than that of other samples. It can be concluded that $Li_4Ti_{4.99}Ru_{0.01}O_{12}$ material may be a promising anode material for high-rate lithium-ion battery. Zhong [53] reported Mo^{4+} partially substituted spinel $Li_4Ti_{5-x}Mo_xO_{12}$ (x=0.5-1.5) synthesized by the Pechini method. Mo^{4+} substitution of Ti^{4+} can increase electronic conductivity of the spinel, which improves the high rate performance of the material in lithium-ion batteries. Nithya et al. [54] reported sub-micrometer sized $Li_4Ti_{5-x}Mn_xO_{12}$ (x= 0.0, 0.05 and 0.1) particles synthesized by a single step molten salt method. The doping of Mn^{4+} ion on the Ti site do not alter the crystal structure, but it causes a reduction in the particle size, which significantly improved the electrochemical performance. $Li_4Ti_{4.9}Mn_{0.1}O_4$ possesses a better discharge capacity (305 mAh·g^{-1}), cycling stability, and charge carrier conductivity than both $Li_4Ti_{4.95}Mn_{0.05}O_{12}$ (265 mAh·g^{-1}) and $Li_4Ti_5O_{12}$ (240 mAh·g^{-1}).

Kubiak et al. [74] had reported $Li_4Ti_{4.75}V_{0.25}O_{12}$ material and its discharge capacity is only 74 mAh·g^{-1} at less than 0.1 C rate. However, this V-doped material will not be sufficient for high current application in commercial productions. To investigate the effects of V^{5+} doping on the high-rate and cycle stability of $Li_4Ti_5O_{12}$, Yu et al. [55] Synthesized another late-model V-doped $Li_4Ti_5O_{12}$ by a simple solid-state reaction method under nitrogen atmosphere. Electrochemical impedance spectra (EIS) indicates that $Li_4Ti_{4.9}V_{0.1}O_{12}$ has a faster lithium-ion diffusivity than pristine $Li_4Ti_5O_{12}$. The $Li_4Ti_{4.9}V_{0.1}O_{12}$ exhibits excellent electrochemical performance especially at high rates, and the discharge capacity is 117.3 $mAh\cdot g^{-1}$ at 5 C rate. It still retains over 97.9% of its initial discharge capacity beyond 1713 cycles at 2 C rate. Hu et al. [58] reported Ta-doped $Li_4Ti_5O_{12}$ in the form of $Li_4Ti_{4.95}Ta_{0.05}O_{12}$ synthesized by a solid-state method. Ta doping dose not affect the lattice structure and particle morphology. The substitution of Ta for Ti site can enhance the electronic conductivity of $Li_4Ti_5O_{12}$ via the generation of mixing Ti^{4+}/Ti^{3+}, and then remarkably its cycling stability at high charge-discharge rate. $Li_4Ti_{4.95}Ta_{0.05}O_{12}$ exhibits excellent discharge capacities of 116.1 $mAh\cdot g^{-1}$ at 10 C and even 91.0 $mAh\cdot g^{-1}$ at 30 C. Tian et al. [60] reported Niobium doped lithium titanate with the composition of $Li_4Ti_{4.95}Nb_{0.05}O_{12}$ prepared by a sol-gel method. The $Li_4Ti_{4.95}Nb_{0.05}O_{12}$ exhibits an excellent rate capacity with a reversible capacity of 135 $mAh\cdot g^{-1}$ at 10 C, 127 $mAh\cdot g^{-1}$ at 20 C and even 80 $mAh\cdot g^{-1}$ at 40 C. It can be ascribed to the higher electronic conductivity and faster lithium-ion diffusivity by Nb^{5+}-doping. Wu et al. [63] reported Sr-doped $Li_4Ti_5O_{12}$ composites prepared by a solid-state reaction method. The results show that Sr^{2+} doping increases the lattice parameter, reduces the particle size, decreases the charge transfer resistance, and significantly enhances the rate capability of $Li_4Ti_5O_{12}$.

Some special ion doping could alter electrochemical behaviors of $Li_4Ti_5O_{12}$ by discharging the anode down to 0 V, and such deep discharge is favorable to widen the voltage window and increase the specific capacity of lithium-ion batteries [73]. A typical example is the Nb-doped sample $Li_4Ti_{4.95}Nb_{0.05}O_{12}$. It exhibits a capacity as high as 231.2 $mAh\cdot g^{-1}$ after 100 cycles at the potential window of 0-2 V, which can be ascribed to the improved electronic conductivity [62].

2.3 Doping in the O site

Besides cation doping, there are some researches relative to the substitution of the small amount of F^- and Br^- for O^{2-} anion. Huang et al. [36] reported $Li_4Al_xTi_{5-x}F_yO_{12-y}$ compounds were prepared by a solid-state reaction method. Charge–discharge cycling results at a constant current density of 0.15 $mA\cdot cm^{-2}$ between the cut-off voltages of 2.5 and 0.5 V showed that the Al^{3+} and F^- substitutions improved the first total discharge capacity of $Li_4Ti_5O_{12}$. Qi et al. [75] reported the Br-doped $Li_4Ti_5O_{12}$ in the form of $Li_4Ti_5O_{12-x}Br_x$ ($0 \leq x \leq 0.3$) compounds synthesized via solid state reaction. The $Li_4Ti_5O_{12-x}Br_x$ (x=0.2) presents the best discharge capacity among all the samples, and shows better reversibility and higher cyclic stability compared with pristine $Li_4Ti_5O_{12}$, especially at high current rates. When the discharge rate was 0.5 C, the $Li_4Ti_5O_{12-x}Br_x$ (x=0.2) sample presented the excellent discharge capacity of 172 $mAh\cdot g^{-1}$, which was very close to its theoretical capacity (175 $mAh\cdot g^{-1}$), while that of the pristine $Li_4Ti_5O_{12}$ was 123.2 $mAh\cdot g^{-1}$ only.

According to the reports mentioned above, although ion doping in the O site has been studied, findings related with the high-rate performances are far from reaching common ground and further research works are needed.

2.4 co-doping ions

Although many investigations have been done in order to enhance electronic conductivity of $Li_4Ti_5O_{12}$, not too much work has been reported using co-doping ions. Shenouda et al. [30] reported anode materials $Li_{4-x}Mg_xTi_{5-x}V_xO_{12}$ ($0\leq x \leq1$) for lithium-ion batteries synthesized by solid-state reaction. The addition of Mg^{2+} and V^{5+} ions improve the conductivity of the material as observed in $Li_{3.25}Mg_{0.75}Ti_{4.25}V_{0.25}O_{12}$, which shows higher electrical conductivity, specific discharge capacity and cycle life than the other samples. Wang et al. [40] reported Ni^{2+} and Mn^{4+} co-doped spinel $Li_4Ti_5O_{12}$ materials in the form of $Li_4Ti_{5-2x}Ni_xMn_xO_{12}$ (x = 0.000, 0.050, 0.075, 0.100, 0.125) prepared by sol–gel route and following calcination in an air atmosphere. The results show that the $Li_4Ti_5O_{12}$ samples co-doped with different molar fractions of Ni and Mn exhibit an enhanced electrochemical performance even at high current rate, especially the $Li_4Ti_{4.8}Ni_{0.1}Mn_{0.1}O_{12}$ sample exhibits a relatively good rate capability with an initial discharge capacity of 172.41 $mAh\cdot g^{-1}$.

With respect to the co-doping method, further insights into structural alternations, interface characteristics, interactions between the co-doping ions and matrix as well as the resulting ions distributions are necessary to evaluate the complicated effects of co-doping on the electrochemical properties of $Li_4Ti_5O_{12}$.

3. CONCLUSION

$Li_4Ti_5O_{12}$ has been considered as a promising anode material for lithium-ion battery due to attributes of environmental friendliness, high safety and excellent rate capability. The improvement of $Li_4Ti_5O_{12}$ anode materials is a big challenge in order to fulfill the requirements of future energy storage. Substantial efforts have been focused on the enhancement of the rate capability resulting from the intrinsic low electronic conductivity and slow lithium diffusion. One of the best methods to improve the electronic conductivity of $Li_4Ti_5O_{12}$ is doping with cations and anions. Since doped $Li_4Ti_5O_{12}$ exhibits excellent high rate capability, it is sure that doping will play an important role in improving the electrochemical performance of $Li_4Ti_5O_{12}$. It can be concluded that the doped $Li_4Ti_5O_{12}$ may be the trend of development of power lithium-ion battery anode material in the long term.

ACKNOWLEDGMENTS
This work was supported by National Natural Science Foundation of China (No. 61171008, 21103024), Shanghai Pujiang Rencai Project (No. 09PJ1401400), China Postdoctoral Science Foundation Special Funded Project (No. 201104236), and the funds from Dalian Mingjia Jinshu Products Limited Company and Suzhou Baotan New Energy Limited Company.

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