Improved electrochemical performance of Ag-modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material in a broad voltage window

YAN-RONG ZHU^a, TING-FENG YI^{a,b,c,*}, HONG-TAO MA^c, YONG-QUAN MA^c,
LI-JUAN JIANG^a and RONG-SUN ZHU^a

^aSchool of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan, Anhui 243002, People's Republic of China

^bPostdoctoral Research Station of Chemical Engineering & Technology, Harbin Institute of Technology, 150001 Harbin, China

^cChilwee Power Co. Ltd., Changxing, Zhejiang 313100, People's Republic of China
e-mail: tfyihit@163.com

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Abstract. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites were synthesized by a solid-state method. The effect of Ag modification on the physical and electrochemical properties is discussed by the characterizations of X-ray diffraction, scanning electron microscopy, cyclic voltammetry, electrochemical impedance spectroscopy, cycling and rate tests. The lattice parameter of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with a low Ag content is almost not changed, but the lattice parameter becomes larger due to the high content of Ag. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ material has a uniform particle size which is about 1 μm . Modification of appropriate Ag is beneficial to the reversible intercalation and deintercalation of Li^+ . Modification of Ag not only decreases the charge transfer resistance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material, but also improves the diffusion coefficient of lithium ion. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) material has the lowest charge transfer resistance, the highest diffusion coefficient of lithium ion and the best rate cycling performance.

Keywords. Lithium-ion battery; anode material; $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$; electrochemical performance.

1. Introduction

Recently, lithium-ion batteries (LIBs) have become very important in electronic devices as well as in electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs) because of their high energy density and output voltage among the best in known rechargeable devices.¹ Among many anode materials for LIB, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been considered as one of most promising candidates due to its low raw material cost, long-term stability at high capacity, high inherent safety and fairly stable Li-insertion potential at around 1.55 V (vs. Li/Li^+).^{2–5} The higher Li-insertion voltage than that of commercial graphite anode (near 0 V vs. Li/Li^+) can avoid reduction of electrolyte on the surface of the electrode and the growth of lithium dendrites. However, its high working potential (1.55 V vs. Li/Li^+) is also a drawback for energy density because it requires the use of high potential positive electrodes. The discharge behaviour of LTO discharged to 0 V can increase the energy density and discharge capacity due to the lower

discharge potential. Despite the above mentioned advantages, the poor high-rate performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ seriously limits its wide application.⁶ The poor high current performances can be ascribed to several possible factors such as the poor electronic and lithium ionic conductivities.⁷ So far, extensive studies has been conducted to improve the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material by preparing nanoparticles,⁸ doping with Zn^{2+} ,⁹ Mg^{2+} ,¹⁰ Sr^{2+} ,¹¹ Al^{3+} ,¹² Cr^{3+} ,¹³ Co^{3+} ,¹⁴ Fe^{3+} ,¹⁵ La^{3+} ,^{16,17} Zr^{4+} ,¹⁸ Mo^{4+} ,¹⁹ V^{5+} ,²⁰ Ta^{5+} ,²¹ Nb^{5+} ,²² Mo^{6+} ,²³ F^- ²⁴ and Br^- ²⁵ in Li, Ti or O site and forming composites with carbon and metal powder.^{5,26–28} $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was synthesized by sol–gel synthesis,¹⁸ microwave method,²⁹ modified rheological phase method,³⁰ microwave-assisted hydrothermal synthesis,³¹ and so on. However, the synthetic methods mentioned here not only need high synthesis cost but also take a complicated synthesis route. Solid state method has several advantages over the above methods: simple synthesis route, low synthesis cost, and easy for commercial applications. Up to now, solid state method has been used successfully to synthesize electrode materials of $\text{Li}_4\text{Ti}_5\text{O}_{12}$,²³ $\text{Li}_3\text{V}_2(\text{PO}_4)_3$,³² LiMn_2O_4 ³³ and LiFePO_4 ,³⁴ and so on. It has been reported in previous studies^{6,35,36} that Ag

*For correspondence

additives increased electronic conductivity, decreased polarization of cathode, and improved its cycling stability obviously. Liu *et al.*⁸ and Huang *et al.*³⁶ reported $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composite prepared via a facile electroless deposition (ED) process, which showed good electrochemical performance. However, electroless deposition process is complicated and costly, which limits commercial applications. In the previous studies, the discharge performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ was evaluated in a voltage window of higher than 0.5 V. As in our previous report,²³ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can also offer a higher discharge capacity and a higher cell voltage at a lower voltage, thereby resulting in higher energy density of LIBs. Hence, it is necessary to study the LIB performance of LTO at a voltage lower than 1 V, in view of the aspects mentioned here. In this study, a solid state method was used to synthesize the uniformly distributed LTO/Ag composite. The physical and electrochemical performances (down to 0 V) of the LTO/Ag composites were investigated.

2. Experimental

2.1 Materials preparation and characterization

$\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites were prepared by a solid-state reaction from Li_2CO_3 (AR), TiO_2 (rutile) and AgNO_3 (AR). Homogeneous mixture of the ternary compounds were obtained by planet ball milling for 5 h with alcohol as solvent and then heated at 80°C for 10 h to evaporate the alcohol. Samples were heated in a muffle furnace at 850°C for 15 h in air, and then cooled down to room temperature naturally. The powders obtained were ground again. For comparison, the undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was also prepared by the same method. Excess Li was provided to compensate for the loss of Li during synthesis, and the molar ratio of Li:Ti was maintained as 4.3:5.

X-ray diffraction (XRD) was performed on Rigaku D/MAX-2400 X-ray diffractometer with $\text{Cu K}\alpha_1$ ($10^\circ < 2\theta < 80^\circ$) monochromated radiation in order to identify the crystalline phase. Particle morphologies were examined with scanning electron microscopy (SEM) (Hitachi, S-4000). Cyclic voltamograms (CV) of both electrodes were measured on an electrochemical workstation (CHI 852C) between 0 and 3 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) measurements were carried out in two-electrode cells by using Zahner Zennium IM6ex electrochemical workstation with a ± 5 mV AC signal and a frequency range from 10^4 to 0.01 Hz. Charge–discharge performance was characterized galvanostatically on Land 2000T (Wuhan, China) tester at 0.5 C (1 C =

175 mA g^{-1}) and 3 C charge–discharge rate between 0.0 and 2.5 V (vs. Li/Li^+), respectively.

2.2 Preparation of lithium-ion batteries

The composite electrodes were made of the titanate powders (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF) binder (10 wt%) homogeneously mixed in N-methyl pyrrolidinone (NMP) solvent and then coated uniformly on a copper foil with the doctor blade technology. Finally, the electrode was dried under vacuum at 100°C for 10 h before electrochemical evaluation. Two-electrode batteries (CR2025) for cycles were assembled in an Ar-filled glove box using a metal lithium foil as counter electrode, 1M LiPF_6 in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte and Celgard 2300 polypropylene as separator.

3. Results and discussion

Figure 1 shows the XRD patterns of LTO and the LTO/Ag composites. All diffraction peaks are sharp and well-defined, suggesting that all samples are highly crystallized. The pristine LTO can be completely indexed to the spinel structure. As we know, AgNO_3 can decompose into Ag, NO_2 and O_2 under the condition of heating in air. The reaction equations are as follows.

In addition, Ag_2O can decompose into Ag, O_2 under the condition of heating in air.

Hence, it can be concluded that the modified LTO should be $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites. Figure 1b shows the standard PDF card of Ag and Ag_2O . According to the references,^{26,35} it can also be concluded that the impurity is Ag additive as shown in figure 1a and b. It was noticed that several of the detected peaks can be ascribed to the detection of Ag, most noticeably the (1 1 1) plane at 2 theta near 38.2° and the (2 0 0) plane at 2 theta near 44.2° besides the main spinel structure. Moreover, with the increasing of Ag additive, the peak intensity of Ag is correspondingly enhanced. From the enlarged (111) peaks, there is almost no shift in the diffraction peaks for the sample LTO/Ag composites compared to LTO. This suggests that the Ag modification almost does not affect the lattice parameter of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The reason may be that the atom radius of Ag is much large, and it is difficult to enter the crystal

Figure 1. (a) XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents (mass %), (b) PDF cards of Ag and Ag_2O and (c) enlarged (111) peaks $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites.

inside of LTO, then coat the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle in the way of the elemental Ag. However, there is a slight shift in the diffraction peaks to the lower 2θ values for the sample LTO/Ag (10 mass%) compared to LTO as plotted in figure 1. The reason may be that a substitutional compound ($\text{Li}_4\text{Ti}_{5-x}\text{Ag}_x\text{O}_{12}$) may be formed treated at a very high temperature. The radius of Ag^+ (1.15 Å)³⁷ is larger than that of Ti^{3+} (0.67 Å)³⁷ ion and Ti^{4+} (0.605 Å)³⁷ ion.

Figure 2 shows SEM images of LTO and the LTO/Ag composites. All samples have a uniform, nearly cubic structural morphology with narrow size distribution of about 1 μm . The small and uniform particle was good for contact between active materials and electrolyte.

Figure 3 presents the typical steady-state CV of LTO and the LTO/Ag composites obtained at a slow scan rate of 0.2 mV s^{-1} , and values of the CV peaks are listed in table 1.

It can be seen that there are two pairs of redox peaks in the range of 1.5–2.0 V and below 0.6 V in all samples, indicating that Ag modification does not change the electrochemical reaction process of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the voltage range of 0–3 V. In addition, redox peaks of all electrodes are sharp and show well-defined splitting, which indicates the lithium insertion into and extraction from these electrodes are almost reversible. Potential differences between anodic and cathodic peaks for LTO/Ag composites (0, 1, 3, 5, 10 mass%) are 0.271, 0.240, 0.244, 0.240 and 0.288 V, respectively, suggesting a lower electrode polarization for the LTO/Ag composites.⁹ This observation suggests that the Ag modification enhances the reversibility of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This phenomenon confirms that the Ag modification is beneficial to the reversible intercalation and de-intercalation of Li^+ . However, LTO/Ag composite (10 mass%) has the largest potential difference among all samples, indicating the worst reversibility. Hence, it is important that a proper Ag modification level should be optimized to achieve a good cell performance.

Figure 4 shows the Nyquist plots of fresh LTO/Li cell and the LTO/Ag composites/Li cells.

All impedance spectra of the cells show a depressed semicircle in the high middle frequency region and an oblique straight line in the low frequency region. The semicircle (high frequency region) and a straight line (low frequency region) shapes are noted, which are related to the formation of SEI (solid electrolyte interface) film and diffusion of Li^+ ions.³⁸ Equivalent circuits to analyse the impedance spectra data are depicted in figure 5. In this fitted equivalent circuit, R_s was the ohmic resistance of electrolyte and electrode; R_{ct} was the charge-transfer resistance at the

Figure 2. SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents. (a) 0 mass%, (b) 1 mass%, (c) 3 mass%, (d) 5 mass% and (e) 10 mass%.

active material interface. Interfacial capacitance is represented by the constant phase elements (CPE). The low frequency region cannot be modelled properly by a finite Warburg element reflecting the solid-state diffusion of Li ions into the bulk of the anode material. We have chosen, therefore, to replace the finite diffusion by a CPE, i.e., Q . CPE involves double layer capacitance with a rough electrode surface, in the Nyquist plot, and it is shown with a characteristics of depressed semi-circle at high frequency region.³⁹ It is obvious that Ag-modified LTO materials exhibit much lower charge transfer resistance than the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ because Ag modification improves the conductivity of

LTO. With the increasing of Ag content, the charge transfer resistance of LTO/Ag composites decreases. As analysed here, it can be concluded that the minimum R_{ct} value of Ag-modified LTO means a lower electrochemical polarization, which leads to higher cycle performance at high charge–discharge rate.

Several techniques such as the capacity intermittent titration technique (CITT),⁴⁰ galvanostatic intermittent titration technique (GITT),⁴¹ potentiostatic intermittent titration technique (PITT),⁴² cyclic voltammetry (CV),⁴³ and electrochemical impedance spectroscopy (EIS),⁴⁴ have been extensively used to measure the chemical diffusion coefficient (D_{Li}). EIS is considered as a very powerful technology to determine the rate of individual electrode kinetic steps because it can also be obtained under more equilibrium conditions compared with other methods. Hence, the chemical diffusion coefficients of Ag-modified LTO are evaluated by EIS. Determination of diffusion characteristics is dependent on the solution of the Warburg impedance

Figure 3. Cyclic voltammery (CV) of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents at a voltage sweep of 0.2 mV s^{-1} .

Table 1. Values of CV peaks for $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents.

Ag contents/ mass %	$\varphi_{\text{pa}}(\text{V})$	$\varphi_{\text{pc}}(\text{V})$	$\Delta\varphi(\text{mV})$
0	1.746	1.475	271
1	1.731	1.491	240
3	1.732	1.488	244
5	1.717	1.477	240
10	1.754	1.466	288

* $\Delta\varphi = \varphi_{\text{pa}} - \varphi_{\text{pc}}$

Figure 4. Nyquist plots of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents. (a) 0 mass%, (b) 1 mass%, (c) 3 mass%, (d) 5 mass% and (e) 10 mass%.

response, and the chemical diffusion coefficient (D_{Li}) can be calculated from the plots in the low-frequency region according to the following equations:^{23,45}

$$Z_{\text{re}} = R_{\text{ct}} + R_s + \sigma \omega^{-\frac{1}{2}}, \quad (3)$$

$$D_{\text{Li}} = \frac{(RT)^2}{2(An^2F^2C_{\text{Li}}\sigma)^2}, \quad (4)$$

where T is the absolute temperature, R the gas constant, n the number of electrons per molecule during oxidation, A the geometric area of the electrode,^{23,46} F the Faraday's constant, C_{Li} the concentration of lithium ion in solid, and ω the angular frequency. The plot of the real axis Z_{re} vs. the reciprocal square root of the lower angular frequencies $\omega^{-0.5}$ is illustrated in figure 6. From figure 6, the value of Warburg impedance coefficient (σ) can be obtained.

The lithium diffusion coefficients of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (0, 1, 3, 5, 10 mass%) are calculated to be 4.05×10^{-16} , 2.17×10^{-15} , 3.30×10^{-15} , 2.23×10^{-15} and $3.04 \times 10^{-15} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively. It can be found that $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) has the highest lithium diffusion coefficient among three samples. Therefore, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ samples with uniform morphology, narrow size distribution, little agglomerations, high electronic conductivity and large lithium diffusion

Figure 5. Equivalent circuit of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ electrode.

Figure 6. Graph of Z_{re} plotted against $\omega^{-1/2}$ at low frequency region for $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents. (a) 0 mass%, (b) 1 mass%, (c) 3 mass%, (d) 5 mass% and (e) 10 mass%.

coefficient would exhibit much better electrochemical performance than the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Figure 7 shows the initial charge/discharge curves for LTO/Li cell and the LTO/Ag composites/Li cells. It can be seen that all samples exhibit flat plateaus, two flat plateaus near 1.55 and 0.7 V, and an inclined curve from 0.6 to 0.0 V. (vs. Li/Li^+). A plateau is present at around 1.55 V, which corresponds to the reversible two-phase transition between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$, and can be attributed to the redox of $\text{Ti}^{4+}/\text{Ti}^{3+}$. The inclined curve below 0.6 V could be proposed to another change of $\text{Ti}^{4+}/\text{Ti}^{3+}$. The cyclic stabilities of LTO/Li cell and

Figure 7. Initial charge-discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents at 0.5 C. (a) 0 mass%, (b) 1 mass%, (c) 3 mass%, (d) 5 mass% and (e) 10 mass%.

Figure 8. Cycling performance of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites with different Ag contents at different charge-discharge rates. (a) 0.5 C and (b) 3 C.

the LTO/Ag composites/Li cells are studied at a current density of 0.5 and 3 C, and the results are shown in figure 8.

It can be found that there is large irreversible capacity for all samples during the first cycle. A similar irreversible capacity during the first charge/discharge cycle has been reported.^{18,22} Irreversible capacity above 1.0 V can be attributed to the dissolution of surface impurities such as adsorbed trace water, from the electrodes into the liquid electrolyte.⁴⁷ Irreversible capacity below 1.0 V may be contributed from the intercalation and deintercalation of lithium-ion in this low voltage range and side reactions such as solid electrolyte interface layer formation on the surface of lithium titanate particles.²⁰ In figure 8a, specific capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) after 60 cycles at 0.5 C charge-discharge rate are 206.4, 211.6, 218.9, 206.2 and 197.2 mA h g^{-1} , respectively. It can be seen that the specific capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) remains stable after several cycles at both charge-discharge rates, and exhibits the best discharge performance among all samples. For $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the irreversible capacity rapidly decreases upon cycling at high discharge rate. As we know, the portability, safety and excellent cyclability contribute to the commercial success of lithium-ion batteries. Hence, the fast charge-discharge is very important during practical commercial applications. After 60 cycles, specific capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (0, 1, 3, 5, 10 mass%) discharged at 3 C are determined as 187.1, 193, 202.3, 196.2 and 186.2 mA h g^{-1} , respectively. When the discharge rate increases from 0.5 to 3 C, there is only a small capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) decrease of about 16.6 mA h g^{-1} (i.e., from 218.9 to 202.3 mA h g^{-1}). The excellent electrochemical performance could be due the high conductivity

of Ag at the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which reduced overall reaction resistance. $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (10 mass%) shows the worst discharge capacity among all samples. This may due to the formation of substitutional compound ($\text{Li}_4\text{Ti}_{5-x}\text{Ag}_x\text{O}_{12}$), and the spinel structure may be destroyed because of the large radius of Ag^+ (1.15 Å). These results confirm that the incorporation of Ag with proper content is an effective method to increase the conductivity of the LTO/Ag composite electrode, and can greatly enhance the electron transport during the electrochemical lithium insertion/extraction reaction compared to the pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode.

4. Conclusion

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ composites were synthesized by a simple solid-state method. Results demonstrate that the Ag modification can greatly enhance the rate capability and cycling stability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without degrading the spinel structure, even discharge to 0 V. The sample $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Ag}$ (3 mass%) displays the best performance among all samples. A large capacity of 218.9 mA h g^{-1} at 0.5 C charge-discharge rate and a stable 202.3 mA h g^{-1} at 3 C charge-discharge rate can be delivered after 60 cycles. The remarkably improved rate properties of the Ag-modified samples are due to the high conductivity of Ag at the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and faster kinetics of both the Li^+ diffusion and the charge transfer reaction. This novel LTO/Ag composite (3 mass%) with high reversible capacity, high-rate capability and excellent cyclic stability is an excellent candidate as anode material for lithium-ion battery.

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