

Letter to the Editor

Electrical conductivity and rate-capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a function of heat-treatment atmosphere

Keywords: Anode; Li-ion batteries; $\text{Li}_4\text{Ti}_5\text{O}_{12}$; Rate; Conductivity

Recently there has considerable interest in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a potential anode for use in Li-ion batteries [1–8]. It has many advantages compared to the currently used graphite. For example, it is a zero-strain lithium insertion host suggesting virtually unlimited cycle life. It features a flat, operating voltage of about 1.5 V versus lithium, above the reduction potential of common electrolyte solvents thus, it does not form a solid electrolyte interface based on solvent reduction which should be a favorable property for high rate and low temperature operation. This voltage also is sufficiently high such that the dangers of lithium plating that can occur at high rate and/or low temperature are removed. However, several disadvantages exist compared to graphite. These include low rate-capability as a result of its low electronic conductivity [6]. Consequently, there have been several studies which have focused on improving electronic conductivity with the intent of improving its rate-capability [4,6,8]. For example, recently Huang et al. [8] have shown that the formation of a $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite anode that was formed by heat-treatment under a 3 vol.% H_2 in N_2 atmosphere at high rates ($>2\text{C}$) had a higher capacity over a similar powders heat-treated under air. For example, at 10C the capacity of the powders heated under the 3 vol.% H_2 in N_2 atmosphere was about 1.8 X that for the powders heated under air and was attributed to the higher electrical conductivity of the composite heated under the reducing atmosphere compared to under air. The electrical conductivity of the composite formed under the reducing atmosphere was about an order magnitude higher than that for the composite heated under air. Huang et al. [8] suggested that the improved electrical conductivity was a result of the reduction of some Ti^{4+} to Ti^{3+} in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and/or reduction of $\text{Cu}^{2+}/\text{Cu}^+$ in Cu_xO to Cu metal under the reducing atmosphere. However, they did not separate these effects. For example, they did not compare the results of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ matrix material heated under the reducing atmosphere to that for heat-treatment under air. It is the purpose of this letter to investigate and compare the electronic conductivity and rate-capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere to that for heat-treatment under air and to determine the contribution of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ matrix to the excellent

rate-capability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite heated under a reducing atmosphere.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared using a solid-state method from TiO_2 (rutile structure) and Li_2CO_3 . Three weight percent excess Li_2CO_3 was used to compensate for lithia volatilization during the high temperature heating [9]. The starting materials were ground with an alumina mortar and pestle with enough methanol to form a slurry. The dried and mixed reactant mixture was pelletized and then heated at 800°C for 12 h in air or 3 vol.% H_2/Ar (H_2/Ar). The sample was reground, pelletized and heated for another 24 h at 800°C in air or H_2/Ar . The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were first characterized by X-ray diffraction. Lattice constants were determined by fitting the data using Rietveld refinement [10]. To get a qualitative indication if the oxidation state of the Ti-ion varied as a function of heat-treatment atmosphere, X-ray photoelectron spectroscopy (XPS) was conducted. XPS was conducted using a Mg $\text{K}\alpha$ excitation source. TiO_2 and Ti_2O_3 powders were used as reference samples. The electronic conductivity was measured on sintered and polished disk samples (~ 12 mm diameter and ~ 1 mm thickness) using the two-point dc method [11–13]. Silver paste electrodes were applied to the top and bottom surfaces of the disk. A high impedance multimeter was used to measure the resistance at room temperature. Conductivity was calculated from the resistance and specimen dimensions. The rate-capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as function of heat-treatment atmosphere was determined using coin cells with metallic lithium as the anode. A typical cathode was prepared by mixing 78-wt.% active powders, 10-wt.% carbon and 12-wt.% polyvinylidene fluoride dissolved in *N*-methylpyrrolidinone. The mixture was coated onto an Al substrate. The cathodes were dried under vacuum at 100°C for 20 h. The electrolyte solution was 1 M LiPF_6 in a 1:1 (wt.%) mixture of propylene carbonate and 1,2-dimethoxyethane. The cells were cycled between 3.0 and 1.0 V at C-rates between 0.5 and 4.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples that were heated under air were white colored, whereas the samples heated under H_2/Ar were grey. The X-ray diffraction pattern(s) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are shown in Fig. 1. From Fig. 1 it can be observed

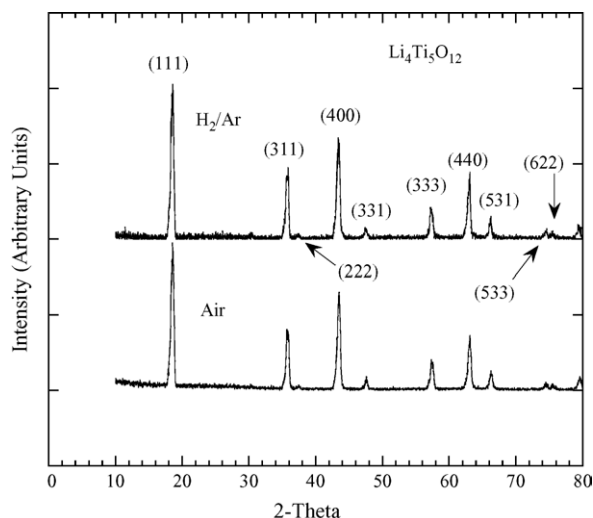


Fig. 1. X-ray diffraction pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized under air or 3 vol.% H_2/Ar (H_2/Ar).

that the patterns for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are similar. They both represent a single-phase cubic material with a $Fd\bar{3}m$ space group. The only difference is a slight shift in the diffraction peaks to the lower 2θ values for the sample heated under H_2/Ar compared to under air. The lattice parameter of the air sample determined from Rietveld analysis of the XRD pattern is $a \sim 8.356 \text{ \AA}$. This value is in good agreement with values for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared under an air atmosphere [7,9,14]. The lattice parameter of the H_2/Ar sample ($a \sim 8.372 \text{ \AA}$) is slightly larger than for the air sample. A larger lattice parameter for the H_2/Ar sample compared to the air sample is expected if some of the Ti^{4+} transformed to Ti^{3+} , because of the larger size of the Ti^{3+} ion (0.81 \AA [15]) compared to the Ti^{4+} ion (0.75 \AA [15]). XPS of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under air revealed that all the Ti was in the 4+ oxidation state. XPS of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under H_2/Ar revealed that some of the Ti^{4+} ions had been reduced to Ti^{3+} ions. A quantitative determination of the relative proportion of Ti^{4+} to Ti^{3+} was not determined for the present paper. In any case, it is important to note that the air sample had only Ti^{4+} present whereas the H_2/Ar sample revealed the presence of both Ti^{4+} and Ti^{3+} . The presence of the mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valence in the H_2/Ar sample can explain the darker color and increased lattice parameter of this sample compared to the air sample, where only Ti^{4+} is present.

It would be expected that the H_2/Ar sample would exhibit higher electronic conductivity than the air sample as a result of the mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valence, which would lead to increased number of electrons and hence, higher electronic conductivity. It should be noted that with our experimental set-up and sample size that the lower limit of electronic conductivity which can be accurately measured is $\sim 10^{-9} \text{ S cm}^{-1}$. The electronic conductivity of the sample heated under air was below the lower limit of the experimentally measurable value. Thus, it can be concluded that the electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under air was $< 10^{-9} \text{ S cm}^{-1}$. Chen et al. [6] using the four-point dc method suggested that the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is $< 10^{-13} \text{ S cm}^{-1}$. The electronic

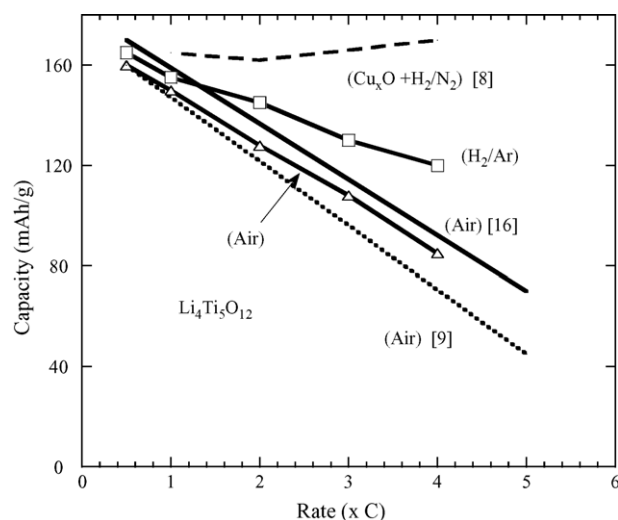


Fig. 2. Discharge capacity as a function of rate for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air [9,16] or 3 vol.% H_2/Ar and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ heated under 3 vol.% H_2/N_2 [8].

conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar atmosphere was $\sim 1 \times 10^{-5} \text{ S cm}^{-1}$. This is an increase in electronic conductivity of at least four orders of magnitude compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air and can be attributed to the presence of the mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valence. Hence, it would be expected that as result of the higher electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar compared to under air that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar would exhibit better rate-capability.

The discharge capacity as function of rate for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar or air is shown in Fig. 2. Also shown in Fig. 2 is data for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air from the literature [9,16] and the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite heated under a 3 vol.% H_2 in N_2 atmosphere [8]. From Fig. 2 several important points are noted. Firstly, all data for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air shows an almost linear decrease in capacity as a function of rate. Secondly, the capacity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under H_2/Ar at rates greater than 1C is higher than for the air samples. This difference increases with increasing rate. This result is expected because of the higher electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar compared to under air as a result of the mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valence. This result confirms that heat-treatment atmosphere (i.e., oxygen partial pressure) can affect the rate-capability of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Thirdly, it can be seen as previously reported by Huang et al. [8] that the rate-capability of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite is excellent. More importantly from Fig. 2, it can be seen at 4C that the difference in capacity between the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, heated under air used in this study, is $\sim 80 \text{ mAh g}^{-1}$. The difference between the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under H_2/Ar and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under air is $\sim 40 \text{ mAh g}^{-1}$. This suggests that a significant portion ($\sim 50\%$) of the higher capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Cu}_x\text{O}$ composite is a result of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ matrix, which has a mixed $\text{Ti}^{4+}/\text{Ti}^{3+}$ valence as a result of heat-treatment under a reducing atmosphere [6,8].

The results of this study reveal that there is an increase in electronic conductivity and rate-capability for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated

under a reducing atmosphere compared to heat-treatment under air. This increase is a result that during heat-treatment under the reducing atmosphere that some Ti^{4+} transformed into Ti^{3+} , leading to mixed valence Ti-ion material. For the case of a $Li_4Ti_5O_{12}/Cu_xO$ composite heated under a reducing atmosphere a significant part of its excellent rate-capability is a result of the mixed Ti^{4+}/Ti^{3+} valence in the $Li_4Ti_5O_{12}$ matrix.

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