Synthesis of Li$_4$Ti$_5$O$_{12}$-Sn by ultrasonic method as anode materials for lithium ion battery

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Abstract. Research on synthesis of Li$_4$Ti$_5$O$_{12}$ has been carried out using ultrasonic method with the objective to study the influence of the Sn addition to the materials conductivity and structure of lithium titanate. The starting materials used were LiOH and TiO$_2$, while Sn was used as an additive with percentages of 0, 5%, 10%, 15% and 20%. Lithium hydroxide, titanium dioxide, and Sn were mixed into an aquabidest media and stirred for two hours at a rate of 300 rpm. Then it was reacted with the help of ultrasound for two hours, filtered and washed with distilled water and then rinsed with acetone. After drying overnight at room temperature, the resulting powder material is compacted using a hydraulic press at a pressure of 4000 psi and the obtained pellets were sintered in the furnace at 800 °C for two hours. Characterization was performed using LCR meter and X-ray diffraction (XRD) to measure the conductivity and the crystal structure, respectively. The SEM-EDS are used to observe the morphology and the composition of the material. The results of the Rietveld analysis showed that the un-doped sample correspond to cubic crystal structure with space group of Fd-3m that belong to Li$_4$Ti$_5$O$_{12}$ and monoclinic crystal structure with space group of C12/c1 that belong to Li$_2$TiO$_3$. It turned out that the increase of Sn; did not change in the ratio between Li$_4$Ti$_5$O$_{12}$ and Li$_2$TiO$_3$, as well as in the lattices constant for all three phases. The optimum conductivity of 6.57 x 10$^{-6}$ S/cm was obtained for 5 % Sn addition to Li$_4$Ti$_5$O$_{12}$. A more homogeneous particle distribution was observed by SEM, due to ultrasonic method. It is concluded that the Sn addition to Li$_4$Ti$_5$O$_{12}$ has improved structural and electrical performance of the anode materials for lithium ion battery.

1. Introduction

The battery research is one of fast growing researches in developing country such as in Indonesia [1]. A battery is a device that can convert the chemical energy in an active material into electrical energy, a process known by the electrochemical process present in oxidation and reduction reactions. A battery consists of three parts, namely the anode, cathode and electrolyte. The anode is defined as the negative electrode where oxidation takes place and the cathode is the positive electrode where reduction process takes place.

Battery anodes used in lithium batteries are generally composed of graphite material. The advantages of graphite is its high capacity, nevertheless it also has limitations which are not suitable
for high discharge rates due to formation of lithium dendrites, and is susceptible to the occurrence of short circuits in the battery which could cause an explosion, so it is less safe to use. There are other materials that have a high enough voltage difference against Li/Li that therefore ensures the formation of the lithiation phenomenon on the electrode surface [2]. One that has been useful is the lithium titanate (Li$_4$Ti$_3$O$_{12}$) ceramic material.

Li$_4$Ti$_3$O$_{12}$ is a ceramic lithium-titanium oxide (LTO), better known as lithium titanate, which has a spinel structure. The main properties of the ceramic material is the ability of the crystalline structure or the crystalline symmetry to undergo a transformation during a Li$^+$ ion insertion. Ariyoshi et al. [3], reported 0002 A and 0006 A discharge lattice shrinkage in subsequent discharge processes observed using a high precision synchrotron XRD to measure the minute changes in the crystal lattice.

Lithium titanate is one of the most promising anode material for lithium batteries despite having a lower specific capacity of 175 mAh g$^{-1}$. In comparison graphite has a capacity of 372 mAh g$^{-1}$ [4]. Lithium titanate is a good anode material for applications that have battery power capability and long life cycle. LTO superiority lies in its power density and chemical stability, and LTO-based batteries has a higher voltage: 2.5 V compared to LiCoO [5] and LFP-based 1.9 V batteries [6]. Lower operating voltage brings significant advantages in terms of security. These batteries can also be recharged quickly. Data show that LTO-based batteries can be safely charged at a higher rate at 10 $°$C, and can be charged in less than 10 minutes. LTO-based batteries also have a wider operating temperature range and their coulombic efficiency is exceeding 98%. The energy density is lower compared to other lithium ion batteries, but still higher than the lead-acid (accu) and NiCd batteries [7].

In various studies, researchers add additives to lithium titanate. Some additives have been added to the original material synthesized with only LiOH and TiO starting materials. Various additives such as chromium (Cr) [8], silicon (Si) [9], magnesium (Mg) [10], graphene [11], aluminum (Al) [12], and carbon (C) [13] were added to LTO. Synthesis of lithium titanate (Li$_4$Ti$_3$O$_{12}$) by addition of excess lithium carbonate (Li$_2$CO$_3$) in titanium dioxide (TiO$_2$) xerogel was done by Syahrial et al. [14].

The aim of this research is to synthesis Li$_4$Ti$_3$O$_{12}$ with addition of tin (Sn) to increase conductivity. The use of ultrasonic process is expected to produce a homogeneous composite LTO-Sn particles and to further increase the conductivity. It is necessary to optimize the concentration of Sn during the formation of LTO-Sn composite.

2. Experimental method
Lithium hydroxide (Li$_2$O) was mixed with 60 mL aquabidest and stirred for 30 minutes by a magnetic stirrer, followed by the addition of titanium dioxide (TiO$_2$). The batches were stirred for 15 minutes and then SnO was added with various concentrations of 0%, 5%, 10%, 15% and 20%. The mixture was stirred for another 15 minutes.

The mixture in the form of suspension was treated by ultrasonic method for 2 hours at a frequency of 50 Hz. Then it was filtered using a vacuum filter, washed with acetone and finally the powder products were dried for 15 hours at room temperature. The powder samples was compacted under pressure of 4000 psi for 1 minute with hydraulic presser to form pellets. The five samples in the form of pellets were then sintered in a furnace at a temperature of 800 °C for two hours. Detailed experiment has been described elsewhere [15].

Characterizations were done by XRD (X-ray diffractometer), LCR meter, and SEM-EDS (Scanning Electron Microscope Energy Dispersive Spectroscopy) to determine the crystal structure, the conductivity, and the morphological observation.

3. Results and discussion
The X-ray diffraction results is shown in Figure 1. The data was analyzed by Rietveld method using Profex-BGMN that employed Fundamental Parameter Approach (FPA) to determine the instrument profile [16]. The results of the Rietveld analysis was shown in Table 1 where the un-doped sample correspond to cubic crystal structure with space group of Fd-3m that belong to Li$_4$Ti$_3$O$_{12}$
[5] and monoclinic crystal structure with space group of C12/c1 that belong to Li₃TiO₃. It turned out that the addition of Sn; oxidized and became SnO₂ (P42/mmm), because there is no diffraction peaks of pure Sn (Fm-3m). The expected R-factor ($R_{wp}$) and weighted profile R-factor ($R_{wp}$) for all patterns is less than 10% indicated a good data quality and a good agreement between simulated pattern and experimental data, as shown in Figure 1 [17]. The goodness of fit ($\chi^2$) has an average value of 1.5, indicated the successful performed of the Rietveld refinements.

There is no change in the ratio between Li₃Ti₅O₁₂ and Li₃TiO₃ as the addition of Sn. There is also no significant change in the lattices constant for all three phases as the Sn concentration increase. The use of ultrasonic is intended to produce a homogeneous particle distribution with a small grain size data before ultrasonic. It has been very helpful in optimizing the calcination process. Figure 1 shows that the addition of 5% SnO causes diffraction peaks to appear at $2\theta = 17.36^\circ$ which is a characteristic of Sn peak. This peak also appears at other concentration as shown in Figure 1 (c-e). Other peaks at $2\theta = 35^\circ$ and $43^\circ$, also appear for addition of SnO into LTO. The rest of the peaks are similar to the diffraction of LTO sample with no Sn addition.

This means that the LTO-Sn composite can be obtained upon the addition of 5% to 20% SnO. Addition of 20% SnO give another peak at 33.9°. The addition of Sn exceed 10% could result in a new phase at the $2\theta$ angular positions of 18.37°; 35.60°; 43.27°; 62.85°; 82.33° and denoted as the SnO phase. This shows that there is an excess of SnO which can no longer usefully interact with Li₃Ti₅O₁₂. The refinement results of the x-ray diffraction data are shown in Table 1.

![X-ray diffraction pattern of the sample with additives Li₃Ti₅O₁₂ - Sn: 0% Sn, 5% Sn, 10% Sn, 15% Sn, and 20% Sn.](image)

Figure 1. X-ray diffraction pattern of the sample with additives Li₃Ti₅O₁₂ - Sn: 0% Sn, 5% Sn, 10% Sn, 15% Sn, and 20% Sn.

It shows that as the Sn concentrations increase, the crystallite size of Li₃Ti₅O₁₂ and SnO₂ decrease up to Sn=15% and then increase at Sn=20%. The opposite effect happened to strain where the %strain of Li₃Ti₅O₁₂ and SnO₂ decrease as the Sn concentration increase up to Sn=15% and then decrease at
Sn=20%. The crystallite size of Li$_2$TiO$_3$ not significantly change as the addition of Sn, but the %strain pattern follow the Li$_4$Ti$_5$O$_{12}$.

### Table 1. X-ray Refinement results of Li$_4$Ti$_5$O$_{12}$-Sn with various concentrations.

| Sn  | Chemical Formula | Space group | Crystallite Size (nm) | Strain (%) | Lattice Parameters : | QPA | R$_{wp}$ (%) | R$_{exp}$ (%) | X$^2$ |
|-----|-----------------|-------------|-----------------------|-------------|-----------------------|-----|--------------|--------------|------|
| 0 % | Li$_4$Ti$_5$O$_{12}$ | F d -3 m | 79.3 ± 6.2 | 0.000143 | 8.3545 (4) | 62.32 (68) | 7.48 | 5.08 | 1.47 |
|     | Li$_2$TiO$_3$ | C 1 2/c 1 | 69.5 ± 3.1 | 0.000403 | 5.0713 (1) | 9.7421 (1) | 37.68 (68) | 7.48 | 5.08 | 1.47 |
|     | SnO$_2$ | P 42/m n m | - | - | - | - | - | - |
| 5 % | Li$_4$Ti$_5$O$_{12}$ | F d -3 m | 139.9 ± 8.0 | 0.000206 | 8.3586 (2) | 59.64 (57) | 7.46 | 5.07 | 1.47 |
|     | Li$_2$TiO$_3$ | C 1 2/c 1 | 66.6 ± 3.1 | 0.000015 | 5.0709 (6) | 8.7788 (1) | 9.7550 (1) | 35.49 (57) | 7.46 | 5.07 | 1.47 |
|     | SnO$_2$ | P 42/m n m | 97.4 ± 3.4 | 0.0000436 | 4.7380 (2) | 3.1865 (2) | 5.81 (10) | 7.46 | 5.07 | 1.47 |
| 10 % | Li$_4$Ti$_5$O$_{12}$ | F d -3 m | 128.8 ± 7.5 | 0.000084 | 8.3578 (2) | 57.32 (57) | 6.94 | 4.84 | 1.43 |
|     | Li$_2$TiO$_3$ | C 1 2/c 1 | 63.7 ± 3.0 | 0.000065 | 5.0718 (1) | 8.7768 (1) | 9.7540 (1) | 34.11 (57) | 6.94 | 4.84 | 1.43 |
|     | SnO$_2$ | P 42/m n m | 90.3 ±4.5 | 0.000047 | 4.7377 (0) | 3.1854 (0) | 9.47 (12) | 6.94 | 4.84 | 1.43 |
| 15 % | Li$_4$Ti$_5$O$_{12}$ | F d -3 m | 109.1 ± 6.6 | 0.000094 | 8.3586 (0) | 53.95 (64) | 6.86 | 4.81 | 1.43 |
|     | Li$_2$TiO$_3$ | C 1 2/c 1 | 61.8 ± 3.2 | 0.000076 | 5.0736 (1) | 8.7751 (1) | 9.7562 (1) | 32.10 (65) | 6.86 | 4.81 | 1.43 |
|     | SnO$_2$ | P 42/m n m | 83.2 ± 3.9 | 0.000071 | 4.7380 (0) | - | 3.1857 (0) | 14.79 (14) | 6.86 | 4.81 | 1.43 |
| 20 % | Li$_4$Ti$_5$O$_{12}$ | F d -3 m | 135.7 ± 7.5 | 0.0000314 | 8.3590 (0) | 50.57 (62) | 6.74 | 4.66 | 1.45 |
|     | Li$_2$TiO$_3$ | C 1 2/c 1 | 66.3 ± 3.5 | 0.000031 | 5.0705 (1) | 8.7805 (2) | 9.7536 (2) | 30.10 (66) | 6.74 | 4.66 | 1.45 |
|     | SnO$_2$ | P 42/m n m | 110.2 ± 4.4 | 0.0000126 | 4.7383 (0) | - | 3.1863 (0) | 20.13 (17) | 6.74 | 4.66 | 1.45 |

**Figure 2.** Mean crystallite size and strain of Li$_4$Ti$_5$O$_{12}$-Sn compound as a function of 0 Sn addition.
Observations using optical microscopy showed the morphology of Sn distribution in the sample. The SEM observation results in Figure 3(b-e) show that the addition of SnO into Li$_4$Ti$_2$O$_{12}$ are well distributed and homogenous. In comparison to LTO with 0% Sn addition in Figure 3(a), they all show similarity to each other, meaning that the use of ultrasonic does not change the microstructure of LTO. Sn particles with a concentration of 5% Sn seemed to be more homogeneously spread than in samples with higher Sn concentrations. This shows that the use of Sn as an additive with a concentration up to 5% is effective. This is confirmed by the EDS (energy dispersive spectrometer) measurement results in the range of 0-20 keV and counting rate of 2449 cps, as shown in Figure 3, which shows the appearance of the Sn peak in the EDS spectrogram. The atomic% of Ti, O and Sn for various Sn concentration is shown in Table 2.

![SEM Observation of morphology of samples Li$_4$Ti$_2$O$_{12}$-Sn](image)

**Figure 3.** SEM Observation of morphology of samples Li$_4$Ti$_2$O$_{12}$-Sn (a) 0% Sn (b) 5% Sn; (c) 10% Sn; (d) 15% Sn; (e) Sn 20%.

![EDS measurements of samples Li$_4$Ti$_5$O$_{12}$-Sn (5% Sn)](image)

**Figure 4.** Results of EDS measurements of samples Li$_4$Ti$_5$O$_{12}$-Sn (5% Sn).
Table 2. Atom% of the components containing in Li$_4$Ti$_5$O$_{12}$-Sn with variation of % Sn.

| No | %Sn | C     | O     | Ti    | Sn    | Al     | Fe     |
|----|-----|-------|-------|-------|-------|--------|--------|
|    |     | 0.277 keV | 0.277 keV | 0.277 keV | 0.277 keV | 1.486 keV | 6.398 keV |
| 1  | 0   |       | 68.98 | 31.02 |      |        |        |
| 2  | 5   |       | 51.72 | 44.78 | 3.50 |        |        |
| 3  | 10  |       | 66.38 | 17.42 | 0.94 | 0.09   | 14.40  | 0.76   |
| 4  | 15  |       | 70.84 | 28.47 | 0.69 |        |        |
| 5  | 20  |       | 18.58 | 53.19 | 19.22| 2.22   | 6.89   |

The distribution of Sn in the Li$_4$Ti$_5$O$_{12}$ sample will affect the value of ionic conductivity. A smoother distribution of Sn in a material would increase the conductivity. Ions will flow evenly throughout the surface of the material. Inversely, an uneven or coarse distribution of Sn in the material would cause the value of the conductivity of the material to decrease, the ions will only flow through dots or lines formed in some parts of the sample. The obtained conductivity values sample of LCR meter measurement are shown in Table 3.

Table 3. Conductivities of Li$_4$Ti$_5$O$_{12}$-Sn with variation of % Sn.

| No. | Sn (%) | Conductivity (S/cm) |
|-----|--------|---------------------|
| 1.  | 0      | 2.61 x 10$^{-5}$    |
| 2.  | 5      | 6.57 x 10$^{-6}$    |
| 3.  | 10     | 3.31 x 10$^{-5}$    |
| 4.  | 15     | 3.03 x 10$^{-6}$    |
| 5.  | 20     | 8.41 x 10$^{-7}$    |

Conductivity values of Li$_4$Ti$_5$O$_{12}$ changes with addition of Sn in not linear trend. The maximum conductivity of 6.57 x 10$^{-6}$ is found in the sample with 5% Sn, while the lowest conductivity of 8.41 x 10$^{-7}$ is found in the sample with 20% Sn. The Li$_4$Ti$_5$O$_{12}$ conductivity is influenced by the distribution of Sn in the sample. In this case the optimum addition is less than 15% Sn, further increasing will reduce the conductivity.

4. Conclusion
Synthesis of Li$_4$Ti$_5$O$_{12}$-Sn using LiOH, TiO$_2$ and Sn as additive using ultrasonic method has been successfully performed. The composite materials consisted of three phases, a cubic crystal structure with space group of Fd-3m that belong to Li$_4$Ti$_5$O$_{12}$ and monoclinic crystal structure with space group of C12/c1 that belong to Li$_2$TiO$_3$ and SnO. The best Li$_4$Ti$_5$O$_{12}$-5% Sn is a good candidate for anode material in lithium ion battery. The ultrasonic method is found to be good method to synthesis the LTO with various additives.

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