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Enhanced electrochemical performances of Li$_4$Ti$_5$O$_{12}$/Sn composites anode via sol-hydrothermal method for lithium ion batteries

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Abstract. Li$_4$Ti$_5$O$_{12}$ (lithium titanate) were synthesized by sol-gel and hydrothermal method with LiOH as lithium ion source. Li$_4$Ti$_5$O$_{12}$/Sn composites anode were prepared by ball mill method with three of Sn variation. X-ray diffraction shows spinel, TiO$_2$, and Sn phases with anatase and rutile residue. The lowest electrolyte resistance obtained at the highest Sn value. The specific capacity of battery can be increased from addition of Sn by up to 258.6 mAh/g. Alloying and dealloying reaction of Li$_x$Sn accommodate the increased specific capacity from charge/discharge. However, the volume expansion from Li$_x$Sn leads to loss of capacity when the C rate increases. The efficient capacity at low and high charge-discharge rate obtained at the highest value of added Sn.

1. Introduction
The automotive industry is beginning to make progress towards renewable energy storage. Lithium-ion battery using graphite anode as its component is a conventional battery which often used in electric car. The lithium-ion battery is also considered one of the most promising candidates for the next generation as a large-scale power source in electric and hybrid cars with their high energy density and good cycle capabilities$^1$. Spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$, LTO) demonstrates a great potential as an alternative anode material that has great safety performance and stable face-centered cubic (fcc) with highly reversible crystalline structures (zero-strain material)$^2$. LTO has high lithiation voltage around 1.55 V vs. Li/Li$^+$, where this is higher than the reduction of the electrolyte solution, which may lead to the formation of a solid electrolyte intermediate (SEI) and lithium dendrite deposition on the surface of the anode material. However, the deficiencies in the LTO have, for example, almost half of the graphite theory capacity of 175 mAh/g, low Li ion diffusion capability, and low electrical conductivity$^3$. Several ways have been developed to overcome the weaknesses of LTO. One in particular is by giving addition of metal Sn$^4$. Sn has been found as an alternative anode material candidate with its

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theoretical capacity of 994 mAh/g. The advantages of mixing Li4Ti5O12/Sn using a solid-state method give a capacity of 480 mAh/g with an addition of 10 wt% Sn. Synthesized LTO using solid-state methods based on TiO2 and Li2CO3. For example, Sn nano is obtained from chemical reduction process, so that Sn is more economical because Sn price of nanoscale is relatively high[5].

This paper will discuss on how to improve the quality of Li4Ti5O12 by giving addition of Sn metal. Li4Ti5O12 were synthesized by using sol-gel and hydrothermal methods. LTO then mixed with Sn in variable wt% Sn using ball mill. From this variable, the author will discuss about the characteristic of LTO/Sn and the variation of added wt% Sn on its elemental, chemical, and electrochemical properties.

2. Experimental procedure

2.1. Synthesis of spinel Li4Ti5O12 powder

Synthesis of Li4Ti5O12 was prepared using 5 different main stages of sol-gel process, calcination, hydrothermal, mixing, and sintering. The first stage is a sol-gel process to produce xerogel TiO2. It takes 2 main solution to get xerogel TiO2 that is primary solution and secondary solution. The primary solution is a mixed solution of titanium tetrahydroxide (Ti(OH)4) with a pH 3 ethanol solution. The secondary solution is a mixed solution of pH 3 ethanol with aqueous water of H2O. The sol-gel process is carried out for 2 hours over a magnetic stirrer by slowly adding a secondary solution into a primary solution. After the sol-gel hydrolysis and alcohol condensation process occurs from the solution, the precursor will further thicken and eventually solidify to form a clear gel (aging). The precursor is then subjected to an open air drying in the beaker glass for 24 hours, which is called the drying process[6]. The precursor then calcined at a temperature of 300°C for 2 hours in the furnace with pure O2 gas. The heat treatment in this phase causes the TiO2 structure to change to anatase than to rutile or brookite due to lower anatase surface energy[7]. The hydrothermal process of TiO2 anatase is to increase the surface area, reduce the particle, and increase the interaction between solids, expected that the re’s and increase interaction between TiO2 and LiOH to form Li4Ti5O12[8]. The hydrothermal process is carried out in the furnace at a temperature of 120°C for 15 hours. The precursor the ball-milled with zircon ball for 15 minutes. The precursor was sintered at 750°C for 3 hours.

2.2. Li4Ti5O12/Sn composites anode coin cell

Li4Ti5O12/Sn composites were prepared using ball mill machine for 10 minutes with zirconia ball 1:10 ratio against the powder. The variation content of micro sized Sn particles on Li4Ti5O12 were ball milled composed with 5%, 10%, and 15% Sn in table 1. Composites anode powder then mixed with DMAC solvent by slurry method using active material, acetylene black, and PVDF in 8:1:1 ratio, respectively. The samples then leveled by doctor blade on Cu foil and crimped with LiPF6 electrolyte. The samples then subjected to EDS, XRD, and electrochemical performance studies.

| Table 1. Comparison of Sn content of each variation on Li4Ti5O12 powder. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Active Material Sample Li4Ti5O12/Sn (gr) | LTO+5%Sn | LTO+10%Sn | LTO+15%Sn |
| Li4Ti5O12 | 2.85 | 2.7 | 2.55 |
| Sn | 0.15 | 0.3 | 0.45 |

3. Results

3.1. Synthesis

Tests using X-Ray Diffraction (XRD) were performed to determine the phase formed and measure the crystallites in the Li4Ti5O12/Sn sample. XRD result data is processed using X’pert High Score Plus program with Semi Quant percentage. In figure 1, the data generated from the X’pert High Score program display 3 phases formed from the Li4Ti5O12 synthesis results. Those phases are the Li4Ti5O12 spheres (JCPDS NO.49-0207), TiO2 anatase (JCPDS NO. 21-1272), and TiO2 rutile (JCPDS NO. 01-
This indicates that the synthesis of Li$_4$Ti$_5$O$_{12}$ is not fully successful and there are phases such as TiO$_2$ anatase and rutile. The scores of the X’pert High Score program showed a fairly high fit of 71 (Li$_4$Ti$_5$O$_{12}$), 68 (rutile), and 53 (anatase). The presence of rutile and anatase indicates that when synthesis of Li$_4$Ti$_5$O$_{12}$ on sintering process with 750°C temperature for 3 hours was not sufficient.

Figure 1. XRD sample test Li$_4$Ti$_5$O$_{12}$/Sn graphic.

There are five detected series in the sample which is Sn, Ti, C, O, and F. From the EDS test in figure 2, the purple color indicates that Sn is present in Li$_4$Ti$_5$O$_{12}$. The Ti element also indicates the presence of Li$_4$Ti$_5$O$_{12}$, means that the presence of spinel phases is dispersed in the sample. Li element cannot be detected by EDS testing due to low radiation energy characteristics. However, the authors can conclude that the Li element is adjacent to the Ti element. The element C as a yellow color is also spread evenly indicating that acetylene black as a conductive material where the path of the electron path is scattered close to the elements Ti, O, and Sn.

3.2. Electrochemical Performances

The profile form of the EIS shows a semi-circle on its Nyquist plot. In the anode material of lithium ion batteries, the better pattern is the smaller semicircle. In figure 3, the entire half-circle line can be seen with Re and Rct. LTO+5%Sn and LTO+10%Sn has more Re value than LTO Synthesis and LTO+15%Sn. This indicates that when the coin cell is crimped, the emphasis is not the same on both samples. In table 2, the largest Rct is owned by LTO Synthesis among the samples with the addition of Sn. This shows that Sn influences the conductivity of the LTO/Sn sample, where Sn has good conductivity values. Conductivity is always inversely proportional to its resistance value. Sn metal has high conductivity value.

Figure 2. EDS mapping sample LTO + 10% Sn with 250x magnification.

Figure 3. Semi-circle plot Nyquist.
From table 2, LTO+5%Sn has the lowest Rct value and makes the greatest conductivity value. Re as an electrolyte constraint, reflects the electrical conductivity of electrolytes, separators, and electrodes\(^{[13]}\), indicate the diffusion velocity of lithium ions from the LTO/Sn sample. Therefore, among the Li\(_4\)Ti\(_5\)O\(_12\) samples with the addition of Sn, the LTO + 15% Sn sample with Re value of 9.55 Ω is estimated to have better lithium ion diffusion. There are different impedance values in LTO/Sn, LTO+5%Sn has a larger Rct value than other LTO/Sn. This may be due to the presence of rutile and anatase phases in Li\(_4\)Ti\(_5\)O\(_12\) may increase its conductivity to Rct in the range of 45 Ω and have an increase in current density at low charge/discharge rates.

### Table 2. Parameter impedance of sample LTO/Sn.

|                | Re (Ω) | Rct (Ω) |
|----------------|--------|---------|
| LTO Synthesis  | 5.87   | 35.13   |
| LTO+5%Sn       | 35.7   | 27.40   |
| LTO+10%Sn      | 32.9   | 27.90   |
| LTO+15%Sn      | 9.55   | 34.35   |

![Figure 4. Cyclic voltammetry curve of sample (a) LTO Synthesis, (b) LTO + 5% Sn, (c) LTO + 10% Sn, and (d) LTO + 15% Sn.](image)

Seen from figure 4, the peak at 1,703 V figure 5a is the working voltage of Li\(_4\)Ti\(_5\)O\(_12\). Li\(_4\)Ti\(_5\)O\(_12\) has a working voltage of ~ 1.5 volts\(^{[14]}\), this means that synthesis of sol-gel and hydrothermal method has obtained a working voltage of ~1.5 volts. The cathodic peak at 2,081 V can be defined as the working voltage by anatase or rutile\(^{[10,15]}\). Figure 4b-d shows that there is a working stress on Sn metal at a peak of about 0.6 volts. The cathodic and anodic peaks of pure Sn metal have a voltage position of 0.58 and 0.43 V which is quite reversible\(^{[8]}\). These two main peaks constitute the alloying and dealloying abilities of Sn metal\(^{[14]}\). The process of alloying and dealloying can be written as follows.

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3e^- \rightleftharpoons \text{Li}_{6-7}\text{Ti}_5\text{O}_{12} \quad \text{(reversible)}
\]

\[
x\text{Li}^+ + xe^- + \text{Sn} \rightleftharpoons \text{Li}_x\text{Sn}(0 \leq x \leq 4.4) \quad \text{(reversible)}
\]

It is similar to LTO that has Li value of 4 to 7, while for Sn interacts with lithium ions can reach Li\(_x\)Sn alloys up to 4.4. It is clearly seen that with the increase of Sn metal content on the Li\(_4\)Ti\(_5\)O\(_12\) anode into a composite material, it will raise the current value from the peak of Sn. We can obtained the specific capacity by dividing the results with mass active materials which is 137.95, 152.6, 162.27, 258.6 mAh/g, with the increasing value of Sn on LTO/Sn. LTO Synthesis has a specific capacity value of 137.95 mAh/g. Theoretically, Li\(_4\)Ti\(_5\)O\(_12\) has a capacity value of 150-160 mAhg\(^{[14]}\). Of the three
samples, the LTO+15% Sn sample has the highest capacity of 258.6 mAh/g. This high capacity is the contribution of the theoretical nature of the Sn metal capacity of 994 mAh/g[16].

Figure 5 shows the relationship between charging-discharging and voltage on a given C. The LTO Synthesis sample in figure 5a has the characteristic of a straight line or plateau at a voltage of ~1.6 volts. The plateau voltage 1.5 and 0.6 V are the charge and discharge plateau characteristics of Li4Ti5O12 spinel and are attributable to Ti4+/Ti3+ transitions[5]. This plateau is the scene of the transition from the Li4Ti5O12 spinel to the Li7Ti5O12 rock salt. Looking from figure 6b, this is the charge-discharge graph of pure Sn. There is a characteristic charge-discharge curve for Sn that is in the range below 1.0 V, this is due to Li-Sn’s multi-step alloying reaction when charging and responding to Li-Sn alloy to LiSn, Li7Sn3, and Li2Sn5[5]. From this comparison, seen in figure 6a, it has a plateau at voltage of about 0.5 V indicating the reversible properties of Li,Sn. Figure 5b-d also shows that with the addition of Sn level, the resulting plateau will be more elongated so as to increase its capacity.

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Figure 7 shows the specific capacity relationships in the charging process of the LTO/Sn sample. This data shows that the highest charging capacity at 0.2C and 12C LTO+15%Sn. While the lowest is owned by LTO+10%Sn. This maybe due to an overload of anatase and rutile. In the graph of discharge capacity to C rate. Discharging graph is almost identical as charging. Only the process of charging makes the resulting capacity slightly larger than the discharging process. At 0.2C, the resulting capacity of LTO Synt, LTO+5%Sn, LTO+10%Sn, and LTO+15% Sn respectively are 117.9, 142.1, 134.9, and 185.5 mAh/g. LTO+10%Sn has the lowest capacity. Sivashanmugam et al. (2011)[5],
reported that with increasing levels of Sn on Li$_4$Ti$_5$O$_12$ will increase its capacity. This can be due to the unpredictable spread of anatase and rutile. Table 3 also illustrates the efficiency of the coulomb obtained from the ratio of charging to discharging capacity. Fullest potential can be obtained at 0.2 C. However, for the use of EV-HEV at 0.4 C, the capacity loss is considered to be extreme due to the Sn pulverization which has an expansion volume of up to 360% and increases the internal stresses\textsuperscript{[17]} then continue into exhaustion at high C rate.

Table 3. Capacity loss from charge-discharge.

| C Rate | CLTO Syn | D LTO Syn | CLTO+ 5%Sn | DLTO+ 5%Sn | CLTO+ 10%Sn | DLTO+ 10%Sn | CLTO+ 15%Sn | DLTO+ 15%Sn |
|--------|----------|-----------|-------------|-------------|-------------|-------------|-------------|-------------|
| 0.2    | 0        | 0         | 0           | 0           | 0           | 0           | 0           | 0           |
| 4      | 78.1     | 78.0      | 78.4        | 78.4        | 88.9        | 89.0        | 77.9        | 78.1        |
| 12     | 93.4     | 93.6      | 95.7        | 95.5        | 97.2        | 97.3        | 93.0        | 93.5        |

4. Discussion
Li$_4$Ti$_5$O$_12$ has been successfully prepared by sol-gel process which produces xerogel TiO$_2$, calcination process, hydrothermal process, mechanochemical ball mill process with lithium ion source using LiOH powder, and sintering process produces brownish white sample. LTO + 15% Sn has the lowest resistance value for Re compared to LTO+10% Sn and LTO+5% Sn. There is a decrease in the value of Rct in all samples with the addition of Sn. Specific capacity increase with the increase of Sn value on cyclic voltammetry test up to capacity of 258.6 mAh/g on LTO+15% Sn. There is a reversible LTO and Li$_x$Sn reaction in charge-discharge process with LTO+15% Sn resulting on having a better CD among other samples. Volume expansion due to Li$_x$Sn phase changes. In conclusion, the addition of 15% Sn has better performance than 5% and 10% Sn.

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6. Reference
[1] Scrosati B and Garche J 2010 J. Pow. Sources 195(9) 2419-30
[2] Etacheri V, Marom R, Elazari R, Salitra G and Aurbach D 2011 Energy Environ. Sci. 4(9) 3243-62
[3] Mosa J, Vélez J F, Lorite I, Arconada N and Aparicio M 2012 J. Pow. Sources 205 491-4
[4] Kuo Y C and Lin J Y 2014 Electrochim. Acta 142 43-50.
[5] Sivashanmugam A, Gopukumar S, Thirunakaran R, Nithya C and Prema S 2014 Mat. Research Bull. 46(4) 492-500
[6] Guglielmi M and Kickelbick G 2014 Sol-Gel Nanocomposites vol 1, ed A Martucci (New York: Springer) pp 2-4
[7] Hanaor D A and Sorrell C C 2011 J. Mat. Sci. 46(4) 855-74
[8] Yoshimura M and Byrappa K 2008 J. Mat. Sci. 43(7)2085-103
[9] Zhang Z, Cao L, Huang J, Wang D, Meng Y and Cai Y 2013 Electrochim. Acta 88443-6
[10] Yang L, Li H, Liu J, Lu Y, Li S, Min J, Yan N, Men Z and Lei M 2016 J. All. Comp. 689 812-9
[11] Gu Y J, Guo Z and Liu H Q, 2014 Electrochim. Acta 123 576-81
[12] Subhan A, Prihandoko B and Syahrial A Z 2011 J. Ilmu Penge. Tehno. Telahah 29 27-35
[13] Yi T F, Yang S Y, Zhu Y R, Ye M F, Xie Y and Zhu R S 2014 Ceramic. Internat. 40(7)9853-8
[14] Nitta N, Wu F, Lee J T and Yushin G 2015 Mat. Today 18(5)252-264
[15] Liu S, Zhu K, Tian J, Zhang W, Bai S and Shan Z 2015 J. Alloy. Comp. 639 60-7
[16] Wen C J and Huggins R A 1981 *J. Electrochem. Soc.* **128(6)** 1181-7
[17] Tamura N, Ohshita R, Fujimoto M, Kamino M and Fujitani S 2003 *J. Electrochem. Soc.* A **150(6)** 679-83