Effect of Carbon Active Addition to Electrochemical Performance of Li$_4$Ti$_5$O$_{12}$/SnO$_2$ Composite Anode on Lithium-ion Battery

Ebsan Simamora$^1$. Jeffrey Riady$^1$. Bambang Priyono$^1$. *Anne Zulfia Syahrial$^1$

$^1$Metallurgical and Material Engineering, Universitas Indonesia, Depok

E-mail: *anne@metal.ui.ac.id

Abstract. As a potential material on lithium ion battery, the composite Li$_4$Ti$_5$O$_{12}$ (LTO) has a limitation due to its low theoretical capacity compared to graphite. To decrease the limitation, this research was conducted by adding activated carbon and SnO$_2$ to LTO. The addition of activated carbon was conducted in 1%, 3% and 5%. Meanwhile, the addition of SnO$_2$ was conducted in 10%. LTO was synthetized by using sol-gel method, hydrothermal method and mechano-chemical method. The sample was characterized with XRD and SEM-EDX. The XRD results showed that SnO$_2$ particle were formed with no residue from previous reaction. The results of SEM-EDS showed that SnO$_2$ particle had a small size and distribute evenly as the active carbon. Furthermore, to determine the addition effect of activated carbon and SnO$_2$ on electrochemical performance of the battery, we conducted EIS, CV and CD testing. The results of CV testing showed that the addition of activated carbon increased the specific capacity of LTO. Meanwhile, the results of CD testing showed that the addition of activated carbon reduced the capacity loss on high c-rate.

1. Introduction

In recent years, pollution produced by the usage of combustion engine-based vehicle has been a serious problem. Automotive industry has developed Electric Vehicles (EV), Plug-in hybrid electric vehicles (PHEV) and pure-electric vehicle (EV) to reduce the pollution problem caused by the usage of fossil fuel. Lithium Ion Batteries (LIBs) have been widely used in portable electronic devices and their potential for electric vehicle application due to their high voltage, high power density and long-life cycle [1]. Conventional Lithium Ion Battery uses graphite as its anode material [2] due to its low price, high electrical conductivity, and high gravimetric capacity at 372 mAh/g [3]. At a high discharge rate, graphite electrode forms reactive dendritic lithium on the electrode surface, which can cause an internal short circuit, thus causing safety concern [4]. Graphite anode form unstable Solid Electrolyte Interface (SEI), which decreases its coulombic efficiency and specific energy capacity [5].

Because of these reason, Lithium-ion battery with graphite anode is not suitable to be used for EVs application [6]. Lithium titanate or Li$_4$Ti$_5$O$_{12}$ (LTO) is a titanium-based anode that has zero strain property that restrain volume change when its charged and discharged [7]. Because of the zero-strain property, Li$_4$Ti$_5$O$_{12}$ has a longtime life cycle and excellent cycle stability [8]. Li$_4$Ti$_5$O$_{12}$ has high insertion voltage (1.55 V vs Li+/Li) [9], that avoid the formation of solid-electrolyte interphase film that occur
below 1.0 V vs Li+/Li [7]. But \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) has low theoretical capacity (175 mAh/g) [10] compared to graphite (372 mAh/g) and low electronic conductivity (10-13 S/cm) [11]. Several methods has been done to improve the property of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) such as mixing with another element that has higher specific capacity to improve the capacity with \( \text{SnO}_2 \) which has high specific capacity but suffer from high volume expansion leading to electrode pulverization [12] and coated the particle with carbon to increase electronic conductivity [13]. In this study, activated carbon will be added to \( \text{TiO}_2 \) in sol-gel process to improve the crystallinity of sol-gel product. \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) synthesized from \( \text{TiO}_2/\text{AC} \) and \( \text{LiOH} \) through mechano-chemical method and mixed with \( \text{SnO}_2 \) through in-situ deposition method to improve the capacity of the anode.

2. Experimental method

2.1. Preparation Of Activated Carbon

Activated carbon was prepared from charcoal. The charcoal was crushed and grind using ball mill with zircon ball to reduce the particle size and sieved using 80 mesh sieve. The sieved product was placed in a tube furnace and heated at the rate of 20\(^0\) C/min to 500\(^0\) C and maintained at this temperature for 2 hours to remove volatile matter and moisture. The later product was activated with NaOH pellet and mixed with weight ratio of 3:1 in water. During activation, the mixture was stirred with magnetic stirrer for 2 hours and then dried at 110\(^0\)C for 24 hours to remove the water. The dried product was placed in a tube furnace under \( \text{N}_2 \) gas and heated at the rate of 20\(^0\) C/min to 700\(^0\) C and maintained for 1.5 hours. After that, the resulting mixture was washed with a 0.1 M solution of HCl followed by hot distilled water until pH 6-7 to remove activating agent residues. The activated carbon was separated during washing step with membrane filters. The separated activated carbon was dried at 110\(^0\) C for 24 hours.

2.2. Synthesis of \( \text{TiO}_2/\text{AC} \)

\( \text{TiO}_2/\text{AC} \) was synthesized using a sol-gel method with titanium tetra butoxide (\( \text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti} \)) as titanium source. The primary solution were prepared by mixing titanium tetra butoxide and activated carbon (1%, 3% and 5%) into a solution of \( \text{pH} 3 \) ethanol. The secondary solution were prepared by mixing distilled water into a solution of \( \text{pH} 3 \) ethanol. After that, the secondary solution was slowly added drop by drop into primary solution with continuous stirring by magnetic stirring for 2 hours. During stirring, sol gel hydrolysis and alcohol condensation process take place from the solution, the precursor viscosity will increase and solidify into a clear gel. The xerogel was dried in air under room temperature for 5 days and mashed in mortar to reduce its size. The \( \text{TiO}_2/\text{AC} \) xerogel was calcined at 30\(^0\) C for 2 hours under oxygen flow to obtain \( \text{TiO}_2/\text{AC} \) anatase. The obtained \( \text{TiO}_2/\text{AC} \) anatase undergo hydrothermal process to increase surface area and reduce particle size for better interaction between \( \text{TiO}_2 \) and \( \text{LiOH} \). The hydrothermal process uses teflon-lined autoclave and filled with distilled water. A filter containing \( \text{TiO}_2/\text{CA} \) was inserted with in the autoclave and kept at 135 \(^0\)C for 15 hours.

2.3. Preparation of \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SnO}_2/\text{AC} \)

\( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC} \) was prepared by mechanical milling process. The \( \text{TiO}_2/\text{CA} \) and \( \text{LiOH} \) were mixed with molar ratio 4:5. Then the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) was sintered at 750\(^0\) C for 3 hours. \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SnO}_2/\text{AC} \) was prepared by mixing \( \text{SnO}_2 \) into \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC} \) with in-situ deposition method. \( \text{SnC}_{12}.\text{nH}_2\text{O} \) were dissolved in absolute alcohol under stirring condition. The LTO/AC powder were immersed in \( \text{SnC}_{12}.\text{nH}_2\text{O} \) solution and then \( \text{NH}_3.\text{H}_2\text{O} \) (25%) was dropped into the solution with stirring to deposited Sn-oxide precipitation on \( \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC} \). The Solid phase inside the solution was removed by filtration followed by washing with distilled water. The filtered product was dried at 85 C for 5 hours then followed by calcined at 500 C for 3 hours. The prepared composite powder then made into slurry by mixing the active material powder with PVDF as the binding material and acetylene black as the conducting additive with weight ratio of 8:1:1. These materials were measured according to mass stated in Table 1 and mixed into 5 gram of DMAC solvent with mixing condition in 300 rpm at 80\(^0\) C. The composition of the slurry for each sample can be seen in table 2. The prepared slurry was coated on the surface of Cu foil that acts as a
current collector for the anode. The coating is made by using a doctor blade and dried for 2 hours at 80°C. The prepared coated Cu foil was used to make battery coin by assembling the coin cell, spacer, spring, anode, cathode and electrolyte (LiPF$_6$). The assembly of battery cell is done inside a glove box with vacuum atmosphere.

Table 1: Mass Composition of each sample

| Sample          | Massa (gram) |
|-----------------|--------------|
|                 | LTO/AC | SnO$_2$ | Active Material | Acetylene Black | PVDF |
| LTO – 10% SnO$_2$ – 1%C | 1.8 | 0.2 | 2 | 0.25 | 0.25 |
| LTO – 10% SnO$_2$ – 3%C | 1.8 | 0.2 | 2 | 0.25 | 0.25 |
| LTO – 10% SnO$_2$ – 5%C | 1.8 | 0.2 | 2 | 0.25 | 0.25 |

3. Material Characterization
Activated carbon is tested using Brunauer–Emmett–Teller (BET) testing to know the increase of surface area produced by chemical activation. All composite powder sample was tested using X-ray diffraction. Cu-K$_\alpha$ radiation was used in XRD with 0.02° s$^{-1}$ scanning rate and the angle (2θ) range from 10° to 80°. The result of the XRD then analyzed using X’pert Highscore software. The composite powder was tested using scanning electron microscopy (SEM) to observe the powder morphology and energy dispersive X-ray Spectroscopy (EDX) to observe the distribution of the materials.

4. Electrochemical Measurements
The prepared coin cell then tested using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and charge-discharge (CD). The EIS test is done to obtain the resistivity of sample to determine its conductivity, while CV is done to know the insertion and extraction voltage. Then CD test is done to obtain the charge and discharge capacity of each sample and to understand the performance of the battery.

5. Result and discussion
5.1. Analyses of Activated Carbon by BET
The result of the BET is seen in Table 2; the surface area of carbon before activation is 224.847 m$^2$g$^{-1}$ and after activation with NaOH is 490.007 m$^2$g$^{-1}$. The result shows the surface area of carbon has increased by 117.93%. From these results, the activation of carbon using NaOH has been successfully done.

Table 2: BET test result of activated carbon.

| Sample | Specific surface area (m$^2$/g) |
|--------|---------------------------------|
| Before activation | After activation |
| Carbon | 224.847 | 490.007 |
5.2. Analyses of XRD

The result of the XRD is seen can be seen in Fig x and Fig y. On Fig. 1 beside Li$_4$Ti$_5$O$_{12}$ phase, the result found the peak of TiO$_2$ rutile, TiO$_2$ anatase and Li$_2$TiO$_3$ phase in all sample. The presence of these impurity show that the synthesis process is not done very well. TiO$_2$ rutile phase is undesirable because its give negative effect on battery performance. The presence of TiO$_2$ rutile cause irreversible reaction that lead to capacity loss in the first cycle [14]. Li$_2$TiO$_3$ is an impurity from Li$_4$Ti$_5$O$_{12}$ synthesis [15] that formed by reaction between TiO$_2$ and LiOH with molar ratio of 2:1 [16]. The presence of these impurity phase show that the sintering time for 3 hours is not enough and the distribution of lithium source to make the reaction with TiO$_2$ to occur is not evenly distributed. These impurities can be reduced by increase the sintering time especially the holding time. On Fig. 2 a couple of peak appear in the degree of 26.6, 34 and 51.9 except for sample LTO-SnO$_2$-AC(5). Those peak in sample LTO-SnO$_2$-AC(1) and LTO-SnO$_2$-AC(3) was identified as SnO$_2$ phase formed by in-situ deposition method in the mixing process. SnO$_2$ peak was not able to be identified at sample LTO-SnO$_2$-AC(5) despite its undergo the same process as the other 2 sample. Low amount of SnO$_2$ in sample will result in low SnO$_2$ peak [17]. Sample LTO-SnO$_2$-AC(5) may has less SnO$_2$ than LTO-SnO$_2$-AC(1) and LTO-SnO$_2$-AC(3) or none at all. The result of SEM-EDX testing will be used to identified the presence of SnO$_2$ on sample LTO-SnO$_2$-AC(5).

5.3. Analyses of LTO/SnO$_2$/AC Powder by SEM and EDX

Image of sample powder obtained by SEM with x50 and x250 magnifications are shown in Fig. 3. It can be seen from Fig. 3 that the particle size on all sample varies from large particle to fine particle. From these results, the synthesis process used produced particle with wide distribution of particle size.
size of large particle reaches up to 300-200 µm. Large particle size is undesirable because large particle tends to tear Cu foil in coating process. Further process must be done to produce fine particle with uniform particle size distribution that suitable for coating process into Cu foil. From Fig y, it can be seen that the morphology of the particle has hexagonal form both on large particle and fine particle.

5.4. EDX
EDX testing was done to observed the distribution of particle (Li, O, C and Sn) in each of the sample powder. The result of EDX mapping of LTO-SnO$_2$-AC(1), LTO-SnO$_2$-AC(3), LTO-SnO$_2$-AC(5) are shown in Fig.4 with x250 magnification. From fig 4a, it can be seen that SnO$_2$ and AC has a uniform distribution with little agglomeration visible on some point. From Fig.4b, the SnO$_2$ and AC particle form a little agglomeration on the surface of large particle that identified containing titanium element. Particle agglomeration of mixing element is undesirable that need to be avoided because it could lead to volume expansion in certain area that could result in pulverization and capacity loss. From Fig.4c, it can be seen that the SnO$_2$ phase exist, but in less amount than Fig.4a and Fig.4b. XRD test result on sample LTO-SnO$_2$-AC(5) was not able to identify SnO$_2$ phase peak, due to either small amount of SnO$_2$ phase or the
presence of SnO\textsubscript{2} phase is absent. On further magnification to x2000 was done to observe the SnO\textsubscript{2} phase more clearly. The particle size of SnO\textsubscript{2} measured by scalebar ranged around 8.5 µm. The largest particle sized to be found is 10 µm. From these observation, in-situ deposition method produced SnO\textsubscript{2} particle with relatively small particle size and good particle distribution.

5.5. EIS Analysis

Figure 5 show the result of EIS test in semi-circle graph form. The graph shows the charge transfer resistance (Rct) of the sample. The bigger radius of the semi-circle will result in higher value of Rct. From Fig. X and table 3, it is shown that the addition of activated carbon increase the resistivity of the sample except for sample LTO – SnO\textsubscript{2} – AC(5). Sample LTO – SnO\textsubscript{2} – AC(5) has lower SnO\textsubscript{2}, which has semiconductor property [12] that increase the resistivity, according to XRD test result. The high value of resistivity indicates the low value of conductivity. Therefore, LTO – SnO\textsubscript{2} – AC(5) has the highest conductivity followed by LTO – SnO\textsubscript{2} – AC(1) and LTO – SnO\textsubscript{2} – AC(3). However the differences of Rct value between sample LTO – SnO\textsubscript{2} – AC(1) and LTO – SnO\textsubscript{2} – AC(3) is too significant considering the difference in the amount of activated carbon is only 2%. Other factor such as the morphology of coated surface may affect the big difference in Rct value. Further studies need to be done to confirm this anomaly. Other way to improve conductivity is to coat the anode material with conductive layer [14, 15] or to dope the anode material with more conductive material [16, 17].

![Fig. 4 SEM-EDX image at 250x of (a) LTO-SnO\textsubscript{2}-AC(1), (b) LTO-SnO\textsubscript{2}-AC(3), (c) LTO-SnO\textsubscript{2}-AC(5)](image)

![Fig. 5 Graph of EIS results of LTO-SnO\textsubscript{2}-AC composites](image)
Table 3 Charge Transfer Resistivity of LTO-SnO$_2$-AC Composite

| Sample                | Rct (ohm) |
|-----------------------|-----------|
| LTO-SnO$_2$-AC(1)     | 142.22    |
| LTO-SnO$_2$-AC(3)     | 182.01    |
| LTO-SnO$_2$-AC(5)     | 117.75    |

5.6. CV Analysis
From Fig 6, it can be seen the result of CV test on LTO – SnO$_2$ – AC(1), LTO – SnO$_2$ – AC(3) and LTO – SnO$_2$ – AC(5) sample. The voltage of cathodic and anodic peak of pure LTO are 1.686 V and 1.461 V [5] which correspond to the insertion and extraction of Li$^+$ ion on LTO. Based on the result of CV test, the voltage of cathodic and anodic peak obtained on all sample is relatively close from pure LTO which is 1.703 V and 1.452 V on LTO – SnO$_2$ – AC(1), 1.68 V and 1.41 V on LTO – SnO$_2$ – AC(3), and 1.695 V and 1.44 V on LTO – SnO$_2$ – AC(5). The working voltage can be obtained by calculating the average of anodic and cathodic peak. The working voltage of LTO – SnO$_2$ – AC(1), LTO – SnO$_2$ – AC(3) and LTO – SnO$_2$ – AC(5) are 1.577 V, 1.545 V and 1.577 V respectively that is relatively close to the theoretical working voltage of LTO which is 1.55 V.

A cathodic and anodic peak with voltage value of ~2.098 V and ~1.71 V was observed in all sample. These peaks correspond to the insertion and extraction of Li$^+$ ion on TiO$_2$ [14]. An increase in peak intensity of TiO$_2$ reaction was observed on the addition of activated carbon. Similar pattern was found on XRD result on TiO$_2$ peak. The addition of carbon increase peak intensity and affect the conductivity of the material [18].

There are two peak that related with SnO$_2$ reaction based on CV test. The peak at ~0.85 V indicated SnO$_2$ reduction into Sn. This reaction appears to be irreversible because its not appear in 2nd cycle of the test. The Peak at ~0.56 V was related to dealloying process of LixSn [19]. It appear the SnO$_2$ reduce into Sn at the first cycle then Sn react at second cycle reversibly.

5.7. Charge And Discharge Analysis
The CD test is done to know the performance of each sample on several current rate, from 0.2C to 20C. Current rate of 1C means that charging and discharging process takes 1 hour; meanwhile at current rate of 2C the time takes half of 1C which is 30 min. The current rate used for electric car are above 4C which mean its important for battery to has good performance on high current rate.

In Fig 7, it can be seen the result of CD test from each sample of on LTO – SnO$_2$ – AC(1), LTO – SnO$_2$ – AC(3) and LTO – SnO$_2$ – AC(5). The result show that the battery capacity has increase in stability with addition of activated carbon, which is indicate by longer plateau at sample with larger amount of activated carbon. It is shown that sample LTO – SnO$_2$ – AC(1) suffer high capacity loss on high current rate from the plateau length. Sample LTO – SnO$_2$ – AC(3) suffer relatively stable capacity loss until current rate 4C meanwhile sample LTO – SnO$_2$ – AC(5) able to maintain stable capacity loss until current rate 8C.
Coulombic efficiency can be calculated from the result of CD test. Coulombic efficiency is the ratio of battery capacity when its discharged compared to battery capacity when its charged. If the value obtained close to 100%, it means there are no energy loss in the discharge and charge process. In fig xx, the coulombic efficiency of each sample is close to 100% for the exception on sample on LTO – SnO₂ – AC(1) with lowest efficiency of 51%. High coulombic efficiency value over 100% caused by usage of lithium metal electrode as cathode in coin cell. Lithium metal has higher specific capacity than LTO that affect charge-discharge process. Some of lithium ion left behind and transferred on next cycle caused coulombic efficiency reach over 100%.

Fig. 6 Graph of CV result of (a) LTO-SnO₂-AC(1), (b) LTO-SnO₂-AC(3), (c) LTO-SnO₂-AC(5)
6. Conclusion
1. LTO/AC composite is successfully synthesized with sol-gel method, calcination process, hydrothermal process, mixing with LiOH and sintering process.
2. The addition of SnO$_2$ with in-situ deposition method produced SnO$_2$ particle with small size (2-10 µm) and good particle distribution.
3. The result of XRD and SEM show the synthesize method is not optimal because it contains impurity that affect battery performance.
4. The EIS test showed a decrease in conductivity value with the addition of activated carbon with an exception of sample LTO – SnO$_2$ – AC(5) that has lower amount of SnO$_2$, which has semiconductor property.
5. The specific capacity of the battery appear to increase with addition of activated carbon with an exception of sample LTO – SnO$_2$ – AC(5). The highest capacity value owned by sample LTO – SnO$_2$ – AC(3) which is 231.4 mAh/g.
6. The CD test showed that the capacity loss at high current rate is decrease with addition of activated carbon.

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