Effect of Activated Carbon Addition on Electrochemical Performance of Li$_4$Ti$_5$O$_{12}$/Nano Si Composite as Anode Material for LiB

N Annisa$^1$, I Orlando$^1$, Faizah$^1$, A Z Syahrial$^1$

$^1$Departement of Metallurgical and Materials Engineering, Universitas Indonesia, Depok, 16424, Indonesia

anne@metal.ui.ac.id

Abstract. Lithium titanate (Li$_4$Ti$_5$O$_{12}$/LTO) is one of the materials being developed as an anode in Li-ion battery. LTO has zero-strain properties that do not volume change during charge and discharge, does not cause SEI, and can be used for the high rate. However, LTO has a weakness such as low electrical conductivity of $10^{-13}$ S/cm and low capacity of 175 mAh/g. Therefore, it needs to be combined with high-capacity materials such as silicon and materials that have high electrical conductivity such as carbon. In this study, the LTO-C/nano-Si composite was made to obtain an anode with high capacity and electrical conductivity. Carbon is added with a variation of 1, 3, and 5 wt% during the sol-gel process, while nano-Si is added by 10 wt% of the total active material ingredient in the slurry making. The carbon added is activated carbon which has previously been activated by using NaOH. Activated carbon is characterized by BET and SEM, while LTO-C/nano-Si composite was characterized by XRD and SEM. For the battery electrochemical performance, EIS, CV, and CD tests are performed. Activated carbon has a surface area of 490,007 m$^2$/g. In this study, the optimum result achieved by the addition of 3% activated carbon (LTO-3%C/nano-Si) with 182.87 Ω resistivity and 17.14 mAh/g discharge capacity at 20C.

Keywords : Li$_4$Ti$_5$O$_{12}$, nano Si, LTO/nano Si composites, activated carbon, Li-ion battery

1. Introduction
In the industrial and economic development, people have been heavily dependent on fossil fuels such as oil, coal, and natural gas. The use of fossil fuels in the automotive world is still a major energy source to operate many vehicles. On the other hand, the use of fossil fuels can lead to serious problems such as global warming and environmental pollution [1]. One of the handlings to the effects of fossil fuels is by developing Electric Vehicle (EV) which in its operation using electrical energy and ultimately producing less harmful emissions [2]. In the storing that electrical energy needed a component in the form of batteries, such as lithium-ion batteries that are currently being developed for applications on electric vehicles. The simplest lithium-ion battery (LIB) uses graphite as the anode. Graphite has a good capacity which is 370 mAh/g [1], but graphite has a weakness because pulverization can happen in high rate application so that it can lose its capacity [3]. The other disadvantage is the formation of a solid electrolyte interface (SEI) which affects battery performance [4]. Lithium Titanate or Li$_4$Ti$_5$O$_{12}$ (LTO) anode is material that can be substituted on graphite anodes. LTO has several advantages such as zero strain characteristic that the battery does not go through volume change or very low volume change
(<1%) during charged-discharged and does not cause SEI [5]. Beside the advantages, LTO still has its downsides such as low conductivity (10^-8-10^-13 S/cm), poor lithium ion diffusion capability (10^-8-10^-13 cm^2/s), and low enough capacity (175 mAh/g) [1]. The disadvantages of lithium titanate can be overcome by combining it with other elements.

One element that has a huge capacity is silicon (Si). Silicon has a theoretical specific capacity of 4200 mAh/g [6] so that when combined with lithium titanate will increase the capacity of Li_4Ti_5O_12. However, silicon also has a limitation in which the process of charge and discharge on the battery will cause volume changes in silicon. However, the weakness can be overcome because lithium titanate has zero strain properties, so the addition of silicon to Li_4Ti_5O_12 matrix does not cause significant volume change. The addition of activated carbon to the LTO also can be an alternative to improve battery performance. Coating with carbon is considered to be a suitable surface treatment method because of its low cost and efficiency. The use of activated carbon to the LTO can increase the surface area that is formed due to the porous structure. Based on the electrochemical results of the tests performed by G.J.Wang et al. [7], the carbon-coated Li_4Ti_5O_12 will influence the diffusion of lithium ions to become larger and have excellent reversibility capability.

In this study, we discussed how to improve the capacity and conductivity properties of LTO anode by adding nano Si and activated carbon. With the volume stability of LTO, the large capacity of silicon, as well as the increase of LTO surface area due to the porous structure of activated carbon, is expected to produce a battery anode that has good volume stability and has a capacity higher than LTO theoretical capacity. To find out the best performance, the nano Si is added to LTO and some variations of active carbon addition to seeing the effect of its addition to lithium battery performance.

2. Experimental

2.1 Activated Carbon
Commercial carbon was activated in advance to obtain activated carbon. Commercial carbon sources have a form of granules with non-uniform sizes, so before doing the activation, carbon needs to be smoothed. Reducing the size of carbon can be done by using high energy ball milling tools involves the use of zircon balls. The fine coal of the milling result was heated in a furnace at the rate of 20°C min^{-1} from room temperature up to 500°C and maintained at this temperature for 2 h. The heated carbon was mixed with NaOH pellets under magnetic stirring for 2 h. The ratio of NaOH pellets and carbon is 3:1 accompanied by the addition of 10 mL of water [8]. The mixture of carbon and NaOH then heated at 130°C for 4 h and continued with heated into a furnace under N_2 flow to the final temperature of 700°C with maintained for 1.5 h. After cooling, the resulting mixture was washed with a 0.1 M solution of HCl followed by hot distilled water until pH ~6.5 and then filtered with filter paper. At the end of the process, the carbon obtained was dried at 110°C for 24 h. The activated carbon then subjected to BET testing by using NovaWin Quantachrome.

2.2 Synthesis of spinel Li_4Ti_5O_12-C powder
The synthesis of LTO-C can be done through several stages of the sol-gel process, calcination, hydrothermal, mixing with a lithium source, and sintering. The first stage is the sol-gel process performed to produce xerogel TiO_2-C. It takes 2 main solutions to get xerogel TiO_2-C that is a primary solution and secondary solution. The primary solution is a mixed solution of titanium tetra-n butoxide, pH 3 ethanol solution, and activated carbon with variations of 1, 3, 5 wt%. The secondary solution is a mixed solution of pH 3 ethanol with H_2O. The measurement for each variable is presented in Table 1. The sol-gel process can be done by slowly adding a secondary solution to a primary solution with a magnetic stirrer for 1.5 h. The result of this process is a clear blackish TiO_2-C gel. The precursor was then left in the beaker glass for 24 h. In the drying process, we crushed the precursor then subjected to an open-air drying for 120 h that there will be liquid solvent separation by an evaporation method. Xerogel TiO_2-C produced by drying process then crushed to make it into powder form. The powder calcined in a furnace at 300°C for 2 h to remove any solvents which may still be present in the powder.
and to promote the formation of TiO$_2$-C anatase phase. The O$_2$ gas that flows in the furnace aims to maximize the formation of TiO$_2$-C anatase. The next step to make a particle with a broader surface area is using the hydrothermal process which the powder heated at 135°C for 15 h. The hydrothermal process of TiO$_2$-C anatase can increase the surface area, reduce the particle, and increase the interaction between TiO$_2$ and LiOH to form Li$_4$Ti$_3$O$_12$ [9]. Commercial LiOH was used as lithium sources to LTO. TiO$_2$-C and LiOH were mixed by the mechanochemical process with high energy ball milling tools using zircon balls for 15 min. The LTO-C obtained was sintered at 750°C for 3 h to obtain the Li$_4$Ti$_3$O$_12$ spinel phase and increase the density of the powder.

### Table 1. Mass composition of each sample

| C (%) | pH 3 ethanol (mL) | Activated Carbon (gram) | Ti(OR)$_4$ (gram) | pH 3 ethanol (mL) | H$_2$O (gram) |
|-------|-------------------|-------------------------|------------------|------------------|---------------|
| 1     | 36                | 0.017                   | 6.119            | 9                | 1.133         |
| 3     | 36                | 0.051                   | 6.119            | 9                | 1.133         |
| 5     | 36                | 0.087                   | 6.119            | 9                | 1.133         |

#### 2.3 Li$_4$Ti$_3$O$_12$-C/nano-Si composite anode coin cell

In this study, the mixing process of LTO-C and nano-Si was carried out in a slurry making the process to avoid the formation of silicon oxide. LTO-C and nano-Si as the active material, acetylene black as the conductive material, and PVDF as the binder was measured with a ratio of 8:1:1. Every sample's composition is in Table 2. The slurry was made by using 6 grams of DMAC as the solvent. The material was added while the DMAC was stirred using a magnetic stirrer with a temperature of 80°C to make the slurry homogeneous. The slurry then coated on Cu foil by a doctor blade and crimped with LiPF$_6$ electrolyte. The samples then subjected to XRD, SEM, and electrochemical performance studies.

### Table 2. LTO-C/nano-Si composite composition

| Material        | LTO  | Nano-Si | Acetylene Black | PVDF |
|-----------------|------|---------|-----------------|------|
| LTO-1% C/nano-Si| 1.8  | 0.2     | 0.25            | 0.25 |
| LTO-3% C/nano-Si| 1.8  | 0.2     | 0.25            | 0.25 |
| LTO-5% C/nano-Si| 1.8  | 0.2     | 0.25            | 0.25 |

### 3. Results and discussion

The activated carbon from the activation process has been done by BET testing. The purpose of this test is to find out the large surface area of activated carbon. Addition of activated carbon in the LTO is to increase the surface area of the sample because the activated carbon is a material that has a high surface area and high adsorption capability [8]. With the increased surface area of activated carbon, the place for lithiation-delithiation reactions is increasing so that the addition of activated carbon is expected to increase the capacity and conductivity value of the LTO sample.

BET testing was performed with involving nitrogen gas adsorption at 77.3 K. Based on BET test results, the surface area owned by activated carbon was 490.007 m$^2$/g. X-Ray Diffraction (XRD) was performed to determine the phase formed and measure the crystallites in the Li$_4$Ti$_3$O$_12$-C/nano-Si samples. XRD result data is analyzed by X'pert HighScore Plus program. XRD pattern in figure 1 showed the result of synthesized LTO-C/nano-Si. Those phases are the Li$_4$Ti$_3$O$_12$ spheres (JCPDS No.49-0207), TiO$_2$ rutile (JCPDS No.01-1292), TiO$_2$ anatase (JCPDS No.21-1272), silicon (JCPDS No.27-1402), silicon oxide (JCPDS No.30-1127), Li$_2$TiO$_3$ (JCPDS No.33-0831). This indicates that the synthesis of Li$_4$Ti$_3$O$_12$-C/nano-Si is not entirely successful, because not only Li$_4$Ti$_3$O$_12$ and silicon
phases, but there are phases such as TiO$_2$ rutile, TiO$_2$ anatase, Li$_2$TiO$_3$, and silicon oxide. Those TiO$_2$ and Li$_2$TiO$_3$ compounds are retained from the synthesis process, while the silicon oxide is indicated by Si powder. The presence of undesirable compounds can negatively affect to the quality of battery performance, as when TiO$_2$ rutile undergoes high degree lithiation (x>0.5) to Li$_x$TiO$_2$, its crystal structure will change so that can lead to loss of capacity [10]. In this study, the carbon added to the LTO did not show the diffraction peak. The undetectability of carbon in XRD results can be due to the amount of carbon added being too low and influenced by the amorphous nature of the carbon itself.

The observation of morphology of synthesized LTO was done by using SEM with 1000X magnification of the sample LTO-1%C/nano-Si, LTO-3%C/nano-Si, and LTO-5%C/nano-Si are shown in Figures 2(a), (b), and (c), respectively. It can be seen that the morphology of each anode sheet showed crack. The cracks are supported by massive volume expansion of silicon. The volume expansion might have happened after the slurry that coated to the Cu foil was in a drying process, where the heat has been given to the sheet. Besides that, in Fig.2 can be seen the agglomerates of the sample. The agglomeration can negatively affect to the sample because it could reduce the surface area and the expansion volume that occurred was too large in one part only, so it can initiate the pulverization at that place which ends on the capacity loss [11]. The agglomeration may occur due to less slurry agitation time, so the slurry product becomes less homogeneous.

**Figure 1.** XRD pattern of synthesized Li$_4$Ti$_5$O$_{12}$-C/nano-Si
From the EIS result in table 3, it is shown that the addition of carbon increases the resistivity of the samples. The conductivity value is reverse to the resistivity value, which means that the lower resistivity is, the higher the conductivity. Therefore, LTO-1%C/nano-Si has the highest conductivity followed by LTO-3%C/nano-Si and LTO-5%C/nano-Si. The highest conductivity found in the sample with the lowest carbon content is supported by XRD results that indicates the LTO-1%C/nano-Si sample has the highest number of LTO intensities and high crystallinity. Also the number of impurities in LTO-1%C/nano-Si sample tends to be less compared to the other samples. Y.J.Gu et al. [12], investigated that the presence of TiO$_2$ and Li$_2$TiO$_3$ may negatively affect the electrochemical properties of Li$_4$Ti$_5$O$_{12}$.

| Sample             | Rct (Ω) |
|--------------------|---------|
| LTO-1%C/nano-Si    | 27.01   |
| LTO-3%C/nano-Si    | 182.87  |
| LTO-5%C/nano-Si    | 208.57  |

Cyclic voltammetry (CV) test was performed to determine the working voltage and capacity of the material. From Figure 3, it can be seen the result of the CV test on the LTO-C/nano-Si samples. By calculating the average of anodic and cathodic peaks, the working voltage can be obtained. The LTO-1%C/nano-Si sample has two peaks at 1.69 V and 1.46 V which the average is 1.575 V, that relatively close to the theoretical working voltage of LTO which is 1.55 V [1]. Also the LTO-3%C/nano-Si and LTO-5%C/nano-Si samples has the working voltage around 1.55 V that represents of synthesized LTO by sol-gel, hydrothermal, and mechanochemical methods succeed to be obtained the working voltage of ~1.55 V. The highest capacity that can be obtained from cyclic voltammetry test showed by LTO-3%C/nano-Si with 168 mAh/g followed by LTO-1%C/nano-Si with 150 mAh/g and LTO-5%C/nano-Si with 131 mAh/g. Besides the LTO peak in Fig.3, there are also other observable peaks such as at 2.092 V on anodic peak and 1.67 V on a cathodic peak in the LTO-1%C/nano-Si sample. It shows peak from TiO$_2$ that the presence on the CV test result can be reviewed from the XRD characterization results, which detected the TiO$_2$ rutile and TiO$_2$ anatase phases in the sample. Based on figure 3 can also be observed the existence of peak-like mound at the beginning of each CV curve. It indicates the presence of silicon in each sample, such as at 0.395 V in the LTO-5%C/nano-Si sample. The existence of Si on the CV curve result was supposed to be at around 0.34 V and 0.51 V that corresponds to the formation of intermediate Li$_x$Si and amorphous silicon [13].

Figure 2. SEM result of (a) LTO-1%C/nano-Si, (b) LTO-3%C/nano-Si, (c) LTO-5%C/nano-Si
Figure 3. Cyclic voltammetry curve of (a) LTO-1%C/nano-Si, (b) LTO-3%C/nano-Si, (c) LTO-5%C/nano-Si

Figure 4 shows the charge-discharge curve and voltage on a given C. The charge-discharge (CD) test was performed to know the capacity of the battery on certain C-rate. In this study, the CD test is done at several current rates, from 0.2 C until 20 C. The result showed that sample with 5 wt% activated carbon has the highest capacity of the battery, which is shown by the plateau that is longer than the other samples, followed by LTO-1%C/nano-Si and LTO-3%C/nano-Si. In this condition, Si and carbon have successfully contributed its capacity to the mixture of the sample even though it is operated in a high rate condition. The LTO-3%C/nano-Si sample has a lower capacity than LTO-1%C/nano-Si can be due to the number of impurities from synthesis process of LTO-3%C/nano-Si is more than the LTO-1%C/nano-Si and LTO-5%C/nano-Si samples that imparted to the battery performance.

Figure 4. Charge and discharge curve of (a) LTO-1%C/nano-Si, (b) LTO-3%C/nano-Si, (c) LTO-5%C/nano-Si
Table 4 illustrates the efficiency of the coulomb obtained from the ratio of charging and discharging capacity with the fullest potential at 0.2 C. In its use, EV need C rate around 4 C. The capacity at 4 C represents almost half of the battery capacity was a loss, then continue at high C rate.

| C Rate | C LTO-1%C/Nano | D LTO-1%C/Nano | C LTO-3%C/Nano | D LTO-3%C/Nano | C LTO-5%C/Nano | D LTO-5%C/Nano |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0.2    | -              | -              | -              | -              | -              | -              |
| 4      | 51.51          | 57.39          | 48.21          | 52.48          | 45.42          | 47.87          |
| 20     | 95.71          | 97.25          | 82.86          | 84.78          | 83.65          | 84.38          |

4. Conclusion
Li$_4$Ti$_5$O$_{12}$-C has been successfully synthesized by a sol-gel process in which the activated carbon was added and produces xerogel TiO$_2$-C, calcination process, hydrothermal process, mechanochemical process with LiOH as the lithium ion source, and sintering process. The addition of nano-Si into synthesized LTO was carried out in a slurry making process and obtained LTO-C/nano-Si. The optimum result achieved by the addition of 3% activated carbon (LTO-3%C/nano-Si) with 182.87 Ω resistivity and 17.14 mAh/g discharge capacity at 20C.

Acknowledgments
The authors would like to thank the Directorate Research and Public Services Universitas Indonesia for their financial support to do this research under HIBAH PITTA 2018 with contract No: 2377/UN2.R3.1/HKP.05.00/2018.

References
[1] B. Zhao, R. Ran, M. Liu, and Z. Shao, “A comprehensive review of Li$_4$Ti$_5$O$_{12}$-based electrodes for lithium-ion batteries: The latest advancements and future perspectives,” Mater. Sci. Eng. R, vol. 98, pp. 1–71, 2015. doi: 10.1016/j.mser.2015.10.001
[2] J. Jaguemont, L. Boulon, and Y. Dubé, “A comprehensive review of lithium-ion batteries used in hybrid and electric vehicles at cold temperatures,” Appl. Energy, vol. 164, pp. 99–114, 2016.
[3] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, “Li-ion battery materials: present and future,” Mater. Today, vol. 18, no. 5, pp. 252–264, 2015. doi: 10.1016/j.mattod.2015.11.034
[4] P. Verma, P. Maire, and P. Novák, “A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries,” Electrochim. Acta, vol. 55, no. 22, pp. 6332–6341, 2010.
[5] B. Scrosati and J. Garche, “Lithium batteries: Status, prospects and future,” J. Power Sources, vol. 195, no. 9, pp. 2419–2430, 2010. doi: 10.1016/j.jpowsour.2010.05.072
[6] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, “High-performance lithium battery anodes using silicon nanowires,” Nat. Nanotechnol., vol. 3, no. 1, pp. 31–35, 2008. doi: 10.1038/nnano.2007.411
[7] G. J. Wang, J. Gao, L. J. Fu, N. H. Zhao, Y. P. Wu, and T. Takamura, “Preparation and characteristic of carbon-coated Li$_4$Ti$_5$O$_{12}$ anode material,” J. Power Sources, vol. 174, no. 2, pp. 1109–1112, 2007. doi: 10.1016/j.jpowsour.2007.06.107
[8] A. L. Cazetta, A. M. M. Vargas, E. M. Nogami, M. H. Kunita, M. R. Guilherme, A. C. Martins, T. L. Silva, J. C. G. Moraes, and V. C. Almeida, “NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption,” Chem. Eng. J., vol. 174, pp. 117–125, 2011. doi: 10.1016/j.cej.2011.08.058
[9] K. Byrappa and M. Yoshimura “Handbook of Hydrothermal Technology - A technology for Crystal Growth and Materials Processing,” Byrappa, M. Yoshimura–Noyes Publ. Park Ridge, NJ, pp. 62–69, 2001.

[10] R. Wen, “Nanostructured Li$_4$Ti$_5$O$_{12}$ as Anode Material for Lithium Ion Batteries,” M.Sc Thesis, Faculty of Science, The University of New South Wales, 2012.

[11] S. A. Firmadya, A. Z. Syahrial, and A. Subhan, "Enhancing battery performance by nano-Si addition to Li$_4$Ti$_5$O$_{12}$ as anode material on the lithium-ion battery," Ionics, 2017. doi: 10.1007/s11581-017-2284-6

[12] Y.-J. Gu, Z. Guo, and H.-Q. Liu, “Structure and electrochemical properties of Li$_4$Ti$_5$O$_{12}$ with Li excess as an anode electrode material for Li-ion batteries,” Electrochim. Acta, vol. 123, pp. 576–581, 2014. doi: 10.1016/j.electacta.2013.12.159

[13] C. Chen, R. Agrawal, and C. Wang, “High-Performance Li$_4$Ti$_5$O$_{12}$/Si Composite Anodes for Li-Ion Batteries,” Nanomaterials, vol. 5, pp. 1469–1480, 2015.