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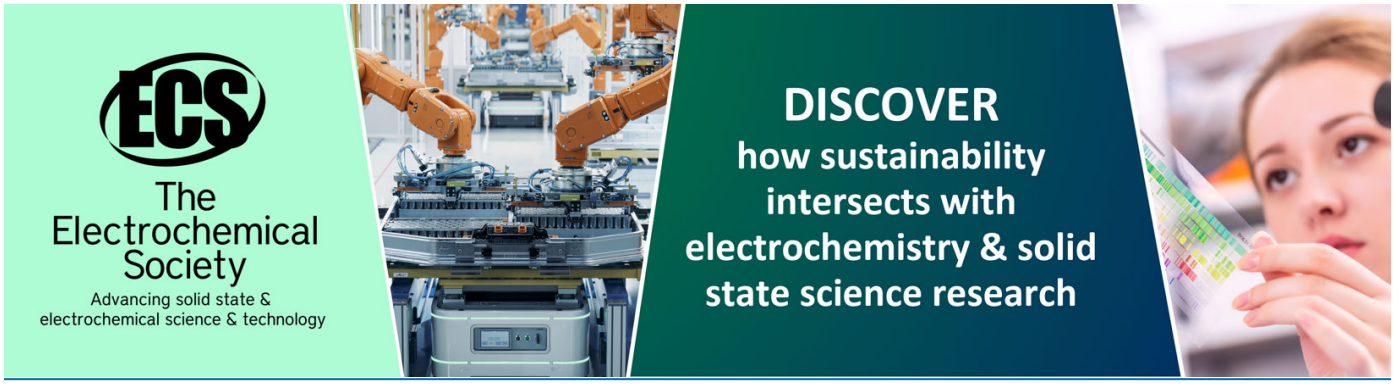

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Effect of nano Si addition on synthesized LTO for lithium battery anode

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Abstract. $Li_4Ti_5O_{12}$ or LTO is one of many compounds that could be used as anode component in lithium battery. The most interesting aspect of using LTO as an anode is its long cycle life which is affected by its zero strain property during insertion and extraction of lithium ions. Despite its advantages, LTO still has problem in its capacity value which is limited to 175 mAh/g. Researchers have tried many methods to increase the capacity of LTO, such as making a composite from LTO host. In this composite, nano sized Si is used as additional element because its high theoretical capacity could increase the overall capacity of the LTO composite. In this research, LTO was synthesized by hydrothermal-mechanochemical methods before we mix it with nano Si in slurry making process. The mass variation of nano Si was 1%, 5%, and 10% in wt. XRD and SEM were used for material characterization. For the battery performance testing we used EIS, CV, and CD. This research will explain the effect of Si on the LTO/Si composite performance. From the testing, it is known that the highest capacity was obtained from LTO/Si-10% sample with 216.15 mAh/g, and able to retain 42.76% of its capacity at higher C-rate (4C). The results show that LTO/Si-10% could be used as an alternative for anode component.

1. Introduction

Nowadays, automotive sector is one of the most advancing technologies. Several innovation has been done by automotive industry, such as developing hybrid car which called by hybrid electric vehicle (HEV). In order to take advantage from this electric motor, we need a source of energy which comes from conventional li-ion battery with carbon-based anode. But, carbon-based anode has its disadvantages which is dendritic structure could be formed on the carbon and eventually compromising the safety factor. This is caused by dendritic structure could make short circuit easily happen when the operation voltage is identical to Li/Li^+[1]. The other disadvantage is the formation of solid electrolyte interface (SEI) which leads to loss in performance.

Based on those problems, the research on better anode material is still on going. One of the material that could be used as anode material is $Li_4Ti_5O_{12}$ or simplified as LTO, is considered to overcome the disadvantages from carbon-based anode. This compound has several advantages such as fast charging because of its superior surface area which is contributed from its nanostructure, a long

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cycle life that is supported by its zero strain property, and better safety than carbon-based anode[2]. Despite all of that advantages, LTO still has its downsides. The concerning problems are its low conductivity with only 10^{-13}S/cm, low diffusion of Li^+ ion (10^{-9}-10^{-13} cm^2/s), and low capacity (175 mAh/g). To overcome the problems, LTO needs modification by mixing it with other element such as Si which has high capacity (4200 mAh/g)[3]. The performance of synthesized LTO anode is expected to improve by mixing with Si.

2. Experimental procedure

The particle size of nano Si according to the specification handed by the manufacturer is 100 nm. In order to discover how much Si is needed to make an optimal mixture of LTO/Si as anode material, we used three variation of %wt Si. The variables consist of 1%wt, 5%wt, and 10%wt Si. For the LTO component, we synthesize it by using hydrothermal-mechanochemical method.

Before the synthesis process of LTO started, we are required to synthesize its precursor which is TiO_2. The process used to synthesize this TiO_2 is sol-gel method, with titanium tetra-n butoxide and ethanol as its starting material. The result of this process is clear TiO_2 gel and we crushed the dried gel in order to make it into powder form. When TiO_2 powder is formed, we calcined it at 300^{o}C for 2 hours to reduce the water moisture, organic compounds, and improving crystallinity[4]. Calcination on the powder caused its color changed to light brown. The next step to make particle with broader surface area is using hydrothermal with temperature of 135^{o}C for 15 hours. This hydrothermal process is followed by drying on hot plate to release the trapped water after the hydrothermal process and the synthesis of TiO_2 is finished.

Beside TiO_2, we also require commercial LiOH as the precursor for LTO. The process used to synthesize LTO is mechanochemical or ball milling. We used TiO_2, LiOH, and zirconia ball in milling machine and run it for 10 minutes. The product of this process is fine light pink LTO particle. This process is followed by sintering in 750^{o}C for 3 hours in order to obtain the spinel phase of LTO and increasing the density of LTO powder[5,6]. After this sintering process, the LTO powder is ready to use.

The mixing process of LTO and Si is carried out in slurry making process in order to avoid the formation of silicon oxide. The slurry composition consists of active material, acetylene black as conductive agent, and PVDF as binder with ratio of 8:1:1. We also used 5 grams DMAC as solvent in this mixture. The active material composed by LTO and Si, with specific composition according to variable of %wt Si. Every sample's composition is in table 1. To make the slurry homogeneous, we made the slurry using magnetic bar to stir the mixture. After the slurry stirred, we used doctor blade to coat it on Cu foil and followed by drying for 2 hours. The anode material is ready to use.

Table 1. LTO/Si composite composition.

Material	Mass (gram)				
	LTO	Nano Si	Total Active Material	Acetylene Black	PVDF
LTO/Si 1%	1.98	0.02	2	0.25	0.25
LTO/Si 5%	1.9	0.1	2	0.25	0.25
LTO/Si 10%	1.8	0.2	2	0.25	0.25

After the synthesis process, then the composites are characterized. We used XRD to find out compounds contained in the synthesized LTO. Besides XRD, we also used SEM in order to understand the morphology of the powder. Meanwhile, to assess the performance of the battery we used cyclic voltammetry, electrochemical impedance spectroscopy, and charge-discharge testing. Specifically, cyclic voltammetry test to find out the working potential and the capacity. Electrochemical impedance spectroscopy or EIS test to compare the resistance of each variable. And charge-discharge test to get the information of retained capacity in particular C-rate.

3. Results and discussion

XRD pattern in figure 1 and figure 2 showed the pure Si sample and synthesized LTO respectively.It is found that there are few indications of SiO contained in the Si powder as showed in figure 1. After that, the first thing that must be checked is the compound contained in synthesized LTO. We used angle 10^o up to 80^o to find the existing compound. The obtained data is analyzed by X'pert High Score Plus application. From the application, it can be found that $Li_4Ti_5O_{12}$ compound is confirmed to be exist in the synthesized LTO powder. Beside the main compound, the trace of other compounds such as TiO_2 in rutile and anatase form are found as showed in figure 2. Those TiO_2 compounds are retained from the synthesis process. Actually, some previous research showed that rutile could give a negative effect on the battery performance because it can easily form Li_xTiO_2 when rutile exposed to lithiation. This Li_xTiO_2 will easily irreversibly transform to other form which lead to capacity loss[7].

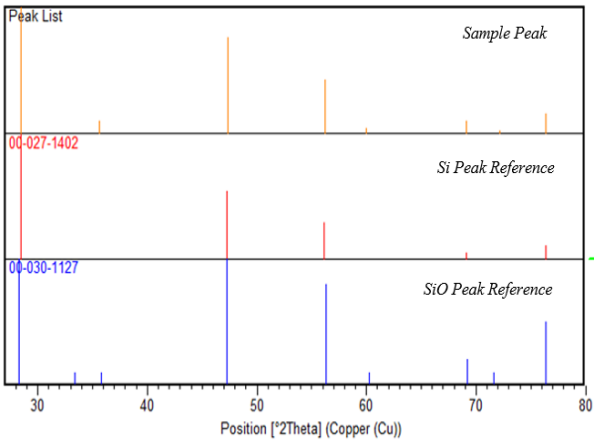

Figure 1. XRD Pattern for pure Si we used.

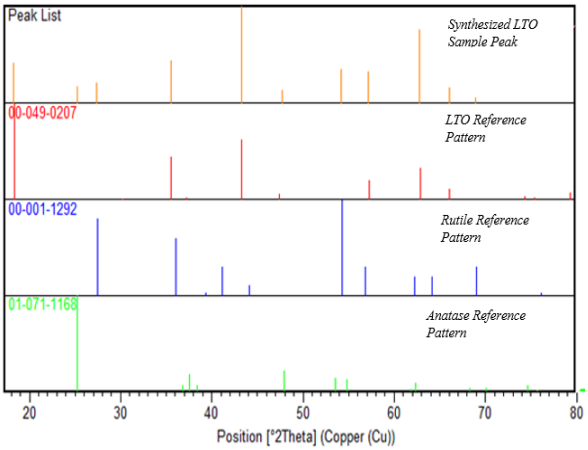

Figure 2. XRD pattern for synthesized LTO.

The observation of morphology of synthesized LTO was done by using SEM and compared to commercial LTO in figure 3 and figure 4 respectively. From the result, it is found that the morphology of the synthesized LTO and commercial LTO are generally different. The different aspect can be found in the homogeneity of the particle and also its particle size. In the synthesized LTO, the particles are less homogeneous and larger. Eventually from the previous study, larger particle could make the transfer range of lithium ion getting further and less surface area which could lead to slower charge-discharge time[8].

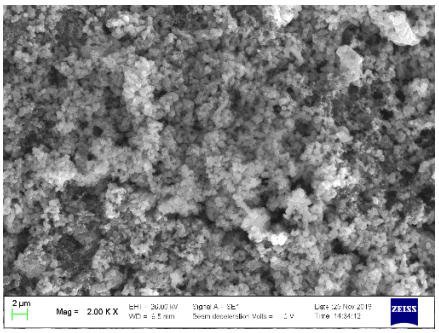

Figure 3. Commercial LTO SEM result.

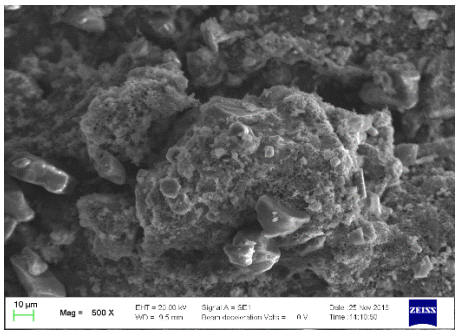

Figure 4. Synthesized LTO SEM result.

We also observed the morphology of LTO/Si composite after slurry making process at every composition. The results in figure 5 show the morphology of each composition are not too different and the particle sizes are observed in micro scale.

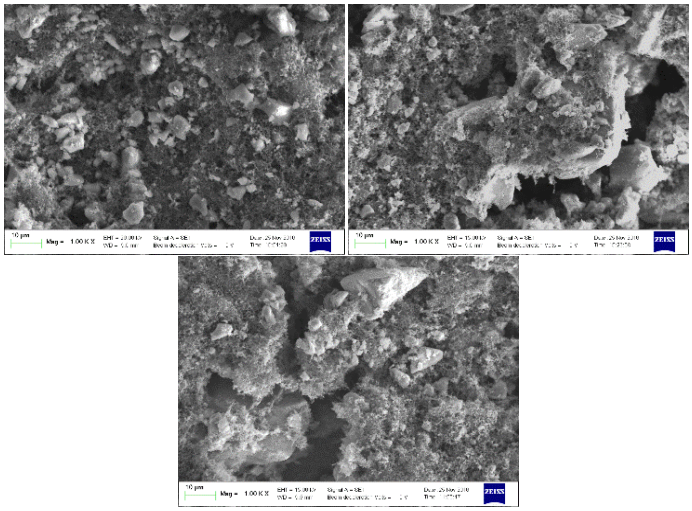

Figure 5. SEM result for LTO/Si-1% (top left), LTO/Si-5% (top right), and LTO/Si-10% (bottom).

From the EIS result in table 2, it is found that the lowest resistance to the highest resistance is in following order: LTO/Si-1%, LTO, LTO/Si-10%, and LTO/Si-5%. Generally, samples with higher Si content will have lower conductivity, which is supported by the fact that Si is one of the semiconductor or will have a good conductive property in high temperature. Beside that, the indication of SiO in the pure Si powder can affect the conductivity since SiO has the isolator property. The other reason of this result is the usage of PVDF binder, which is not the optimal binder for Si. This caused many gap exist on the surface and impedes the current [9].

Table 2. Rct values from all samples.

Sample	Rct (Ω)
LTO	10.6
LTO/Si-1%	4.165
LTO/Si-5%	120.61
LTO/Si-10%	88.425

We measured the working potential of every sample by using cyclic voltammetry test. From figure 6, there are two peaks which is consisted of cathodic and anodic peak at 1.703 V and 1.471 V respectively which means the average of those peak voltages or the working potential is 1.587 V. It also there is no significant difference from theoretical working potential.

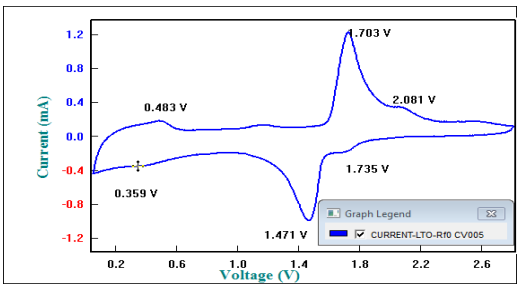

Figure 6. Cyclic voltammetry curve for synthesized LTO.

Meanwhile for the result of LTO/Si composite sampleson figure 7, it also shows that every sample also has two peaks around the same places. This means that LTO and Si do not disrupting each other's performance.

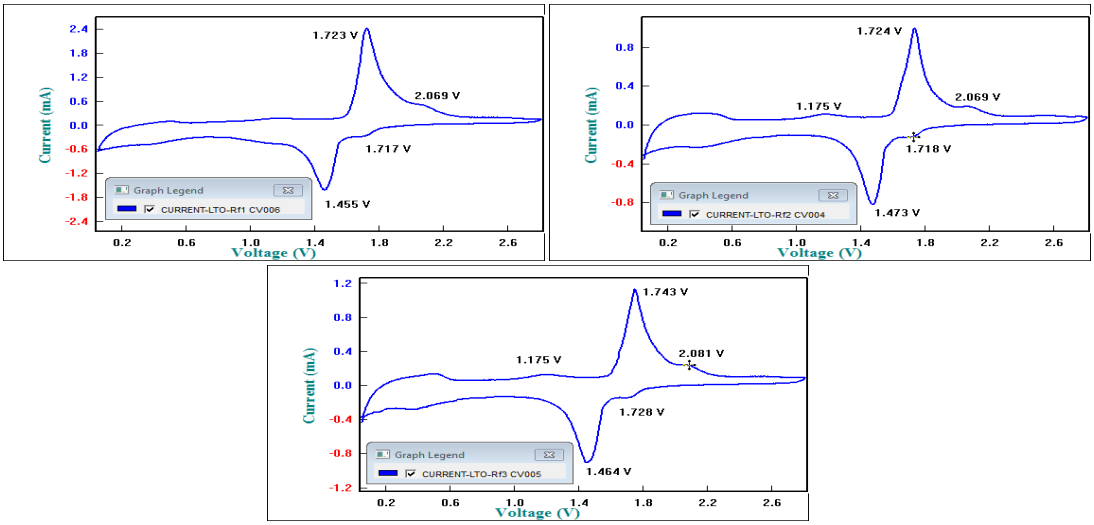

Figure 7. Cyclic voltammetry curve for LTO/Si-1% (top left), LTO/Si-5% (top right), and LTO/Si-10% (bottom).

Other aspect that we can study for the performance of battery is from its capacity, which is obtained from cyclic voltammetry testing and showed in figure 8. Our synthesized LTO without Si addition has capacity of 137.95 mAh/g, which is lower than the theoretical specific capacity of LTO (175 mAh/g) and the other commercial LTO sample which has 173.29 mAh/g. The effect of Si addition could be seen from the result, which generally has higher capacity with higher Si content. This is the result of the mixing process in composite, when the reinforce element has the better property then it could affect the mixture in good way. In this study, since Si has high theoretical capacity (4200 mAh/g), the mixture should be getting higher capacity than 137.95 mAh/g. The highest capacity that can be obtained from this study is the mixture of synthesized LTO and 10% wt Si with 216.15 mAh/g, which shows that Si can affect the overall capacity of the mixture.

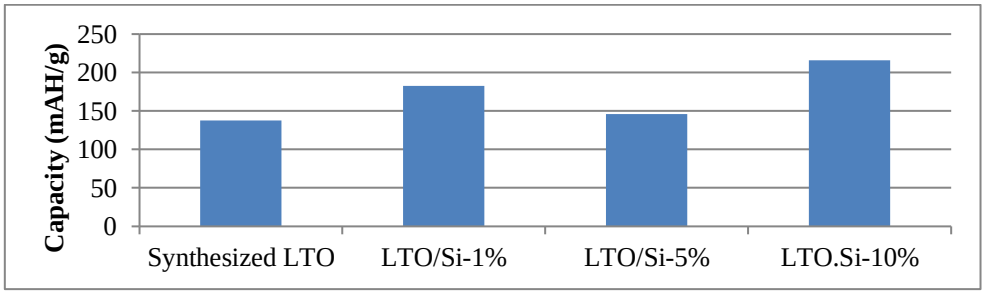

Figure 8. Capacity for every sample.

In charge-discharge test we will find out the capacity of the battery on certain C-rate and the results showed in figure 9. Generally the higher C-rate used, then the capacity on that C-rate is getting lower. From figure 9 it can be found that pure LTO and LTO/Si-1% has similar trend on the decreasing capacity with higher C-rate. But there's some exception for LTO/Si-5% and LTO/Si-10%. In higher C-rate, the LTO/Si-5% and LTO/Si-10% samples both has similar trend, which is they could still hold their capacity in higher value than LTO and LTO/Si-1%. Or in the other word, both LTO/Si-5% and LTO/Si-10% have better performance on higher C-rate. Previous study found that there are some complex effects from the lithiation process. We already know that some Si oxide have the isolator property. But from Chen, et al research, they found the complex effect of Si oxide [3]. The complex effects are the liberation of Si from lithiation process of SiO_x which will be the additional source of

Sifor higher capacity. Other product from lithiation of SiO_x is Li_ySiO_x which has the property to hold the volume expansion of Si[10]. The detail of Si addition will need further investigation to explain this complex effect. This complex effect can explain why the higher content of Si such as LTO/Si-5% and LTO/Si-10% have better performance in higher C-rate.

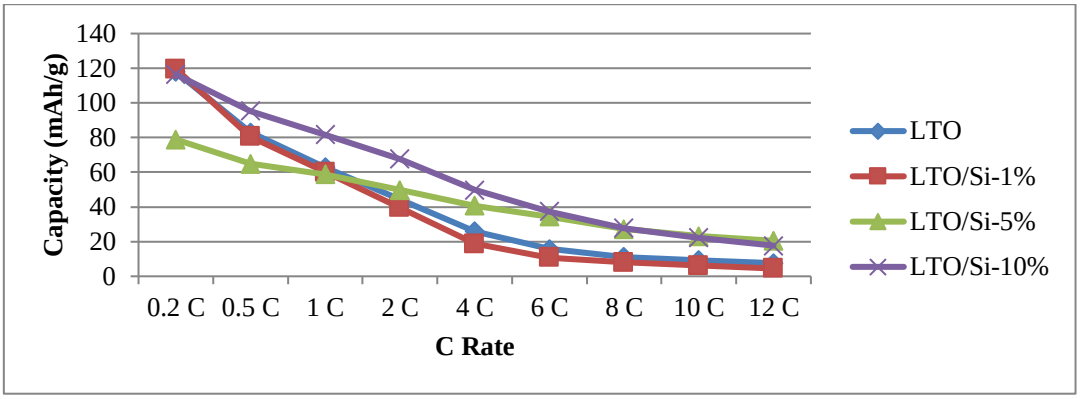

Figure 9. Specific capacity at particular C-rate.

Since HEV need C-rate around 4C, we also simplified the result from charge-discharge testing to see the retained capacity on table 3.

Table 3. Retained capacity at 4 C for every sample.

	LTO	**LTO/Si-1%**	**LTO/Si-5%**	**LTO/Si-10%**
Capacity Retained at 4 C	21.967 %	15.6354 %	51.584 %	42.7614 %

4. Conclusion

The addition of nano Si into synthesized LTO has been conducted by using slurry-making method. It's found that our synthesized LTO hasn't been made perfectly. But after we mixed it with nano Si, specifically LTO/Si-10%, our LTO/Si composite has been upgraded and has better performance in some aspect from its pure LTO counterpart. Although there are some complex effect from nanoSi addition into LTO host, this study indicates that nano Si additioncan be used to develop anode material further.

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