Optimizing the performance of Li$_4$Ti$_5$O$_{12}$/LTO by addition of silicon microparticle in half cell lithium-ion battery anode

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Abstract. The demand of lithium-ion battery (LIB) has been increased for high power application in transportation system. Thus, the current use of graphite as anode material needs to be replaced, due to formation of unwanted solid-electrolyte interphase (SEI) layer consuming intercalated Li$^+$ that reduces the LIB performance and may cause ignition of the battery in high load usage. One of the candidates for anode material to replace graphite is lithium titanate (LTO), since the LTO does not form SEI and exhibits high-power with outstanding safety properties. This LTO compound was synthesized by mixing the TiO$_2$ xerogel of anatase phase and lithium carbonate (Li$_2$CO$_3$) as a source of lithium-ion followed by sintering at temperatures of 750°C to obtain the LTO with spinel crystalline phase. However, the LTO has the low theoretical capacity, i.e: 175 mAh/g, with real specific capacity obtained is at 114 mAh/g. To increase the LTO specific capacity, the addition of 10, 20 and 30 wt.% silicon microparticle which has theoretical capacity of 4200 mAh/g was conducted during preparation of the slurry anode mixture to minimize the formation of SiO$_2$. Anode sheet was made with Si/LTO and assembled into half-cell coin battery with lithium metal sheet as the counter electrode. Electro-impedance spectroscopy (EIS), Cyclic voltammetry (CV), and charge discharge (CD) testing were conducted to examine the battery performance. From EIS testing, the lowest impedance was obtained for the sample of 20 wt.% Si, while the highest impedance value obtained in 30 wt.% Si. The CV testing shows that the highest capacity at 141.1 mAh/g is achieved at the composition of 10 wt.% Si. Finally, from the CD testing, this Si/LTO anode could withstand the charge-discharge until 12 C and shows good stability until 100 cycles. From EIS and CV testing known that the optimum composition having the best performance is ranging from 10 wt.% to 20 wt.% Si. It is predicted that at higher composition, the pulverization of Si particle is occurred declining the performance of Si/LTO anode.

1. Introduction
Currently, the energy conservation and reducing harmful gas emission are the most crucial challenges in the transportation industries. The usage of Electric Vehicles (EVs) is one of the most promising solutions to this matter. However, the main obstacle to increase the application of Electric Vehicles (EVs) is in the battery for electrical energy storage system. The most notable advantage of using lithium ion battery is the high energy density and not to mention the operation temperature which can be said to have wide temperature range and long shelf life.
This advantage has made lithium-ion battery (LIB) replacing the conventional battery systems [1]. The lithium batteries exhibit promising capabilities for energy storage used in hybrid or electric vehicle (EVs). However, for EVs application the current use of graphite as anode material needs to be replaced, due to formation of unwanted solid-electrolyte interphase (SEI) layer consuming intercalated Li+ that reduces the LIB performance and may cause ignition of the battery in high load usage. One of the candidates for anode material to replace graphite is lithium titanate (LTO), since the LTO does not form SEI and exhibits high-power with outstanding safety properties [2]. However Li4Ti5O12 also has a low both in the intrinsic conductivity (10^{-9} S.cm^{-1}) and in its theoretical capacity (175 mAh/g) [3].

Recent researches regarding increasing the capacity, conductivity and rate capability have been conducted to find the types of optimization to overcome the issues. Nano-structuring, morphological optimization, addition or even the combination of them can boost the capacity and rate capability [4]. The addition of silicon (Si) which is a semiconductor element and has the highest specific capacity of ~4200 mAh g^{-1} is one of the promising strategies to increase the conductivity and capacity. Obviously, silicon gain an extensive attention towards other benefits such as the element relatively abundant and easier to obtain, arguably inexpensive, and slightly has the lithiation and de-lithiation potential that is higher than found in lithium, which can contribute to safe feature for the electrode [5].

In this research, the experiment was focused to synthesize of Li4Ti5O12 (LTO) with the addition of silicon microparticle. The mixing of both active substances was carried out during slurry preparation to minimize the oxidation of Si element. Then, the slurry is coated to make an anode sheet and assembled into a Li-ion battery (LIB) half-cell with Li-metal sheet as the counter electrode. The influence of Si microparticle content (in weight %) in the LTO slurry mixture was observed using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Charge-Discharge (CD) testing. The EIS is conducted to measure the conductivity and CV is performed to measure the specific capacity and working voltage. Then, the CD test is carried out to know the rate capability and columbic efficiency. To prove the stability of the present LTO/Si anode, the CD test is conducted until 100 cycles.

2. Materials and Methods

2.1. Li4Ti5O12 Powder Preparation and Characterization

Methodology In the synthesis process of Li4Ti5O12/Si (LTO/Si) was prepared through a sol-gel method, calcination, ball-milling, sintering and mixing. The first stage is the sol-gel method, where a primary solution consisting of ethanol pH 3 and titanium butoxide is mixed with secondary solution that contains ethanol and distilled water to form a clear gel using a magnetic stirrer. The obtained gel was dried in the ambient temperature for about 12 h to form TiO2 xerogel. Calcination carried out at temperature of 300 °C for 2 h to obtain anatase TiO2. Then, the high energy ball mill was used to mix anatase TiO2 with Li2CO3. Finally, the sintering process was then performed at 750 °C in 3 hour to form LTO spinel phase and ready to be used for the active electrode material. Then, to form the LTO/Si, the addition of silicon microparticle is done by mixing of the LTO and silicon microparticle during slurry preparation to minimize the oxidation of Si element.

The active materials were characterized using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) mappings to analyse the topography, microstructure and elements distributions. Further, Brunauer-Emmet-Teller (BET) Quantachrome is used to measure the surface area of the samples.

2.2. Cell Assembly and Testing

In this research, the half-cell coins battery were assembled and tested to observe the electrochemical properties and performance of LTO/Si compounds and use a lithium foil as counter electrode, and LiPF6 1M as an electrolyte. Further, DMAC, Acetylene Black (AB) and PVDF were used as solvent, conductive additive and binder, respectively. The compositions were prepared with fixed binder content of 10% wt.%, while the LTO and Si-microparticle contents were 10 wt.% for LTO/Si10-sr...
sample, 20 wt.% for LTO/Si20-sr sample, and 30 wt.% for LTO/Si30-sr sample. All of these materials were then mixed by magnetic stirrer at 300 rpm at 70°C for 2 h to obtain slurry.

The slurry was coated at copper foil current collector by electrode coater (doctor-blade) with 200 µm of wet thickness to form 100 µm of dry thickness. Coated Cu foil was then dried at doctor blade at 80 °C and cut to form coin shape. The assembly process was carried out in a glove box filled with high purity argon gas. Electrochemical performances were measured using a CR2032-type coin cell with the following devices: Wonatech instrument for Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) and MTI Battery Testing instrument for Charge-Discharge (CD).

3. Results and Discussion

3.1. Structure and Morphology of LTO

The examination of SEM is intended to observe the morphology of a material. The Figure 1 shown representative SEM image of LTO powder with different percentage silicon microparticle. The main problem is that the samples were agglomerated occurring which influence cycles efficiency and rapidly capacity decreased [6]. Distribution silicon and oxygen elements described in figure 2 and figure 3 via elements mapping of the following.

![Figure 1](image1.png)

**Figure 1.** SEM image of LTO powder with different variables (a) LTO/Si10-sr, (b) LTO/Si20-sr, (c) LTO/Si30-sr

![Figure 2](image2.png)

**Figure 2.** Silicon mapping in different samples (a) LTO/Si10-sr, (b) LTO/Si20-sr, (c) LTO/Si30-sr

Based on silicon element mapping in each samples as shown in Figure 2, it can be seen that silicon content increased in mapping can be investigated. With increased silicon content for each samples, it seems the increased agglomeration has occurred as shown from in Figure 2 (a) to (c). This may affect electrochemical performance of the present LTO/Si anode.
In Figure 3, it is shown that oxygen distribution is relatively not the same as Si element mapping. It is proved that oxygen distribution is not related to the formation SiO$_2$. Thus, the effort to minimize the formation of SiO$_2$ conducted during mixing preparation of the slurry anode between LTO and Si element was successful.

Further, the surface area of the LTO/Si samples were measured and the result is listed in Table 1.

**Table 1. Surface area values LTO/Si microparticle powders.**

| Samples      | Surface area (m$^2$/g) |
|--------------|------------------------|
| LTO/Si10-sr  | 77.62                  |
| LTO/Si20-sr  | 95.30                  |
| LTO/Si30-sr  | 105.40                 |

Table 1 shown result of the surface area for every sample has shown relatively large surface area. The highest surface area is LTO/Si30-sr. Surface area increased with added silicon microparticle. The influence of surface area of samples to the performance will be discussed later.

3.2. *EIS Characterization of LTO Electrodes*

In the application of battery, conductivity is important for battery performance. The conductivity of battery could be measure by testing the resistance of the battery by using Electrochemical Impedance Spectroscopy) can show the charge transfer resistance (Rct) electrode as seen in Figure 4 as follows.

**Figure 4.** EIS semicircle curve of LTO electrode (a) pre-CV and (b) post-CV
As depicted in figure 4, the EIS test was conducted twice as shown on the above result. The first EIS was performed prior to cyclic voltammetry test (pre-CV) and the second EIS test was done after cyclic voltammetry (post-CV). The test result is presented in table 2.

| Sample          | Pre-CV | Post-CV | Decreasing resistivity value |
|-----------------|--------|---------|------------------------------|
|                 | Re (Ω) | Rct (Ω) | Rtotal (Ω)                  | Re (Ω) | Rct (Ω) | Rtotal (Ω) |
| LTO1/Si10-sr    | 4      | 107     | 111                         | 4      | 41      | 45          |
| LTO1/Si20-sr    | 4      | 68      | 72                          | 4      | 41      | 45          |
| LTO1/Si30-sr    | 4      | 84      | 88                          | 4      | 76      | 80          | 8           |

Based on the result of EIS after cyclic voltammetry, it could be seen in Table 2 that the resistivity of all samples shifting to the left which mean that the conductivity is better than before the CV. It could be seen that the sample of LTO/Si20-sr has the lowest resistivity. But, the sample LTO1/Si10-sr has better decreasing resistivity value from pre-CV into post-CV resistivity value. It could mean that this composition has the best increased conductivity value during CV or lithiation-delithiation process. Further, for the sample of LTO/Si30-sr, the resistivity of pre-CV and post-CV values did not change significantly. It means that this composition has not good response to the lithiation-delithiation process compared to the other samples. This could be predicted as the result of pulverization of the Si particle that reducing the performance of this LTO/Si [7]. Addition of more Si contents in the mixture of LTO/Si, the reactivity of this compounds to lithiation-delithiation process decreases.

The influence of surface area of the samples has not played dominant role in this matter. Although the LTO/Si30-sr has the largest surface area, but reactivity to the lithiation-delithiation process is not the best amongst the samples.

3.3 Cyclic Voltammetry (CV) Characterization of LTO Electrodes

The use of cyclic voltammetry for battery performance is intended to measure energy density of a lithium-ion battery. Based on previous research, theoretically lithium titanate has working current of about 1.55 V with the lithium electrode having the capacity of 175 mAh/g [8]. As in this research the use of silicon microparticle in addition to the LTO, it is predictable that the curve of cyclic voltammetry would have two peaks of LTO and also the added element of silicon.

![Figure 5](image-url)  
(a) CV curve of half-cell, sweep rate 100 mVs⁻¹: (a) LTO and (b) LTO/Si
In Figure 5, the highest peak is noted as the sample of LTO/Si20-sr and followed by LTO/Si10-sr. The sample of LTO/Si30-sr, which could be seen on the curve, having the lowest peak. It could be observed that there are anodic peak and cathodic peak in which indicating that the reaction is reversible. For silicon peak, the difference could be seen by comparing the LTO peak with the silicon peak. Silicon peak is not as high as the LTO peak and rather having a flat peak compared to LTO. However, it could be observe that in addition of silicon to the LTO has an impact to the LTO peak, in which the optimum is the silicon addition of 20 % wt, in which the addition of silicon of 30% would lower the peak of LTO.

Table 3. Specific capacities of LTO/Si half-cell batteries

| Samples      | Specific capacity [mAh/g] |
|--------------|---------------------------|
| LTO          | 113.74                    |
| LTO/Si10-sr  | 141.08                    |
| LTO/Si20-sr  | 134.24                    |
| LTO/Si30-sr  | 102.66                    |

Specific capacity in Table 3 shows the sample of LTO/Si10-sr has the capacity of 141.08 mAh/g. For LTO/Si20-sr has 134.24 mAh/g and LTO/Si30-sr for 102.66 mAh/g. As seen in Figure 3, the trend of the specific capacity of every samples decrease with the addition of silicon concentration to the LTO. From Table 3, it shows that the addition of silicon does not always raise the specific capacity of the anode material as expected. One reason is the limited ability of the binder polyvinylidene fluoride (PVDF) used for the manufacture of a slurry containing the active ingredient of silicon. Binder type polyacrylic acid (PAA) may yield better performance [9].

3.4. Charge-Discharge (CD) characterization of LTO electrodes

In the test of Charge-Discharge, the examination is intended to investigate the capacity and performance of a battery. In this examination the battery will be given different current rate, in the case of this study, the current rates which used from C/5 up to 12C. Figure 6 shows the result of the charge-discharge capacity from C/5 to 12 C with the different variables of LTO/Si.

![Figure 6. The discharge capacity of half-cell with current rate 0.2V to 12C](image)

The discharge capacity of the battery showing an increase by the addition of silicon concentration. However, the LTO/Si30-sr which having the higher concentration of silicon, showing the decrement of the discharge capacity. The presents of silicon oxide which can be confirmed in the previous examination of SEM result has been a major drawback to the performance of the battery. In this case,
the increase of the silicon concentration could increase the charge and discharge capacity which after reaching certain optimum point, the pulverization of Si microparticle would be inevitable and thus interfere with the properties and performance of the battery.

Figure 7. Coulombic efficiency of half-cell during charge and discharge cycling

The coulombic efficiency which has been plotted into a graph in Figure 7 with the current rates, it can be observed that the efficiency of the battery samples reaching 90-100%. This would mean that the properties of LTO active material in spinel phase in which having zero-strain, where there is no change in structure during charge and discharge, has been proven to be confirmed.

Figure 7 shown that the value of the specific capacity of the sample composition LTO/Si20-sr generate the highest value for each current sample rate and followed for LTO/Si10-sr and the lowest value is for a sample LTO/Si30-sr. This supports the above suggestion that the PVDF binder in this study has its limitations compared to the binder PAA (poly acrylic acid [9].

Furthermore, to determine the stability of the sample in the certain number of Charge-Discharge (CD) cycles, the CD testing then performed for one hundred (100) cycles with C-rate to charge is 0.5C while for discharge is at 1C. In Figure 8 is shown the value of specific capacity curve for 100 cycles of samples (a) LTO/Si10-sr, (b) LTO Si20-sr, and (c) LTO/Si30-sr.

The value of the CD test results for 100 cycle are presented in table 4 below.

| No. cycles | LTO1 / Si10-sr | LTO1 / Si20-sr | LTO1 / Si30-sr |
|------------|----------------|----------------|----------------|
| chg cap    | Disch cap      | chg cap        | Disch cap      |
| (mAh)      | (mAh g)        | (mAh/g)        | (mAh/g)        |
| chg cap    | Disch cap      | chg cap        | Disch cap      |
| (mAh/g)    | (mAh/g)        | (mAh/g)        | (mAh/g)        |
| 1 number   | 109            | 103            | 106            |
| 1          | 96             | 88             | 80             |
| 2 100th    | 75             | 74             | 67             |
| 2          | 67             | 65             | 64             |

The decline in capacity: 31% 28% 36% 30% 26% 20%
Figure 8 shows that all three samples have good stability and can last for 100 cycles. The decrease in the specific capacity of the battery cells occurred during charge-discharge process is due to the volume expansion of the silicon particles. The tension will cause cracking and collapse of silicon that causes loss of electrical contacts that will eventually eliminate its capacity [7].

The sample of LTO/Si20-sr is having a significant decrease compared with the sample of LTO/Si20-sr. This could indicate that pulverization as explained in previous section decreases the specific capacity of the battery. Nevertheless, if it is compared to the real capacity of LTO with specific capacity of 113.74 mAh/g, the addition of Si microparticle has increased the specific capacity of the LTO/Si compound.

4. Conclusion

Li₄Ti₅O₁₂/Si (LTO/Si) was successfully synthesized by a solid state reaction between xerogel TiO₂ and Li₂CO₃ for application in lithium ion batteries and mixing silicon microparticle during slurry preparation. Influence of surface area is not play major role in this LTO/Si compound. Influence of addition of silicon microparticle that has highest conductivity is at the silicon addition of 20 wt.%. The specific capacity of every samples decrease with the addition of silicon concentration to the LTO. The CV testing shows that the highest capacity at 141.1 mAh/g is achieved at the composition of 10 wt.% Si. The LTO/Si30-sr which having the higher concentration of silicon, showing the decrement of the discharge capacity. From EIS and CV testing known that the optimum composition having the best performance is ranging from 10 wt.% to 20 wt.% Si. Besides the limitation of PVDF binder capability,
it is suggested that at higher composition, the pulverization of Si particle is occurred declining the performance of Si/LTO anode. Finally, all samples of LTO/Si shows a good stability which could withstand at 100 cycles charge and discharge test.

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