Synthesized of Li$_4$Ti$_5$O$_{12}$ Materials via Sol-Gel Method to Lithium Ion Battery Anodes

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Abstract. Li$_4$Ti$_5$O$_{12}$ (LTO) anode is one of ion lithium battery important components. LTO anode has been synthesized using solid state reaction method that was calcined at 900°C and produced relatively large particle sizes and low electrochemical performance. The Low electrochemical performance can be improved by replacing the anode synthesis method using sol-gel method. This research used the sol-gel method to synthesize LTO anodes with calcination temperature at 900°C and holding time at 2hr with the aim of obtaining homogenous particle size distribution with small particle size average and high discharging capacity. X-ray diffraction (XRD) characterization was carried out to find the crystalline phase formed while field emission-scanning electron microscopy (FE-SEM) was carried out to find the morphology and particle sizes distribution. Electrochemical performance of LTO anodes was measured from cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge-discharge (CD). The LTO-spinel phase was identified as the primary phase and TiO$_2$-rutile phase as the impurity phase. The particle size distribution is 0.24μm and the sample consisted of particles that agglomerate without any pores. This anode has high electrochemical performance especially discharging capacity of 302 mAhr/gr at 1C.

1. Introduction
Portable electronic devices such as hand-phone, digital camera, laptop, electric vehicle and others are increasingly being produced [1, 2]. Portable electronic devices require high energy storage devices specifically lithium ion battery. Lithium ion battery are secondary batteries that are rechargeable, so that it can be used many times because the electrochemical reaction in the battery is reversible [3]. Components used in lithium ion batteries are cathode, anode, electrolyte and separator. Anode material of lithium ion battery which is currently used is graphite material because graphite has high electrical conductivity [4]. Graphite anode has low working voltage (~0.5 Volt) which creates a thin layer (solid electrolyte interphase/SEI) on the surface of graphite anode. SEI will inhibit the transfer of lithium ions during the intercalation and de-intercalation processes [5, 6]. Furthermore, there was a lattice volume expansion (~30%) in the graphite crystal structure during charging and discharging processes which will hinder the process of lithium ion diffusion [7].

The weakness of graphite anodes causing limited application of graphite as a lithium ion battery anode, so replacement materials are needed as alternative storage Lithium titanate (Li$_4$Ti$_5$O$_{12}$ / LTO) is
one of the replacement anodes which has a working voltage ~1.5 – 1.75 Volt [8, 9]. The working voltage of LTO is higher than the voltage of SEI formation (~0.8 Volt) so that low possibility of SEI formation on the surface of the LTO anode. LTO is known as “zero strain” material, which undergoes less than ~0.4% of volume expansion during charging and discharging process [10]. LTO have low electric conductivity in the range ~10^{-8} – 10^{-13} S/cm. The theoretical capacity of the LTO anode is 175 mAh/gr while graphite anode is 375 mAh/gr. Previously, Mahmoud et al, 2015, Sandhya et al, 2016 and Kuo et al, 2014 have synthesized LTO using sol-gel method and reported that LTO powder produced have small and homogenous particle size distribution [9, 10, 11]. The used of sol-gel method was expected to improve electrochemical performance especially charging-discharging capacity, Li ion diffusion coefficient and electronic conductivity.

Based on that background, the synthesis and characterization of Li_{4}Ti_{5}O_{12} (LTO) anode using sol-gel method have been done to find out the morphology and particle size distribution of LTO and its electrochemical performance as anode of Li ion battery. In general, the synthesis of LTO via sol-gel method using LiOH with water solvent and TTIP with ethanol solvent obtained non-homogenous mixture. In this research, CH_{3}COOLi and TBT as raw material were dissolved in ethanol solvent and HCl as a catalyst. CH_{3}COOLi has a high solubility in ethanol so that it’s possible to produce homogenous mixture.

2. Materials and Method
In this study, the raw material used is Lithium acetate (CH_{3}COOLi) powder 99.95%, Sigma Aldrich; Titanium (IV) Butoxide ((C_{4}H_{9}O)_{4}Ti) 97%,Sigma Aldrich; Hydrochloric acid (HCl) 37%,Sigma Aldrich and ethanol (C_{2}H_{5}OH) 98.6%,Sigma Aldrich.

2.1. Sample Preparation
LTO anode synthesis process was carried out by the sol-gel method. First of all, the preparation of solution A (CH_{3}COOLi+ HCl+ C_{2}H_{5}OH) and solution B ((C_{4}H_{9}O)_{4}Ti+ HCl+ C_{2}H_{5}OH) was carried out in a fume hood used magnetic stirrer with rotating speed 250 rpm. Solution A was poured into solution B and allowed to form a gel. The obtained gel was dried and calcined at 900°C with a holding time of 2 hours. Then, to make anode sheets, additional materials that used was LTO powder, PVdF, Super P by comparison 80%;10%;10% and DMAc as a solvent. The anode sheets assembled into a coin cell in the glove box.

2.2. Sample Characterization
X-ray diffraction (XRD) was carried out using Rigaku SmartLab 3 kW type with angular ranges 10-90°, XRD characterization used to find the phase formed in LTO powder. The morphology and particle size distribution of LTO powder was observed using a Hitachi SU3500 field emission-scanning electron microscope (FE-SEM) type at magnification 1k and 10k. The electrochemical performance of LTO anode were examined using cyclic voltammetry (CV), charging-discharging (CD) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry testing used to find out the diffusion coefficient of lithium ion at the scan rate variation 50, 100, 150 and 200 μV/s. Charge-discharge testing used to find out charging and discharging capacity at 0.1 C-rate. CV and CD testing was carried out using WonAtech WBCS3000 while electrochemical impedance spectroscopy (EIS) was carried out using LCR meter Hioki 353250 at the frequency 0.1-20k Hz. EIS testing used to find out the electric conductivity.
3. Results and Discussion

Figure 1. XRD curve of LTO powder with LTO and rutile TiO\textsubscript{2} JCPDS Card (a= LTO phase and b= TiO\textsubscript{2} rutile phase).

At the Fig.1, black curve shows the database of LTO (JCPDS Card No. 49-0207, red curve shows the database of rutile TiO\textsubscript{2} (JCPDS Card No. 21-1276) and blue curve shows the x-ray diffraction of LTO powder that synthesized with sol-gel method. LTO powder still contains impurity phase, namely rutile TiO\textsubscript{2} phase. This is because when the LTO synthesized process wasn’t perfect because of the lack of H\textsubscript{2}O elements during the hydrolysis process. Based on research by Zhou et al, the H\textsubscript{2}O ratio is very important on the use of the sol-gel method although it will produce a white gel. Even though, the highest peak of the x-ray diffraction results belongs to the LTO phase. The x-ray diffraction curves of LTO was matched with the database and shows that LTO have the same peak position of diffraction angle and hkl with database. The x-ray diffraction results from LTO powders were analysed using Match! software to identify the crystalline phase formed.

The morphology of the LTO powders were investigated using field emission-scanning electron microscopy (FE-SEM) with magnification 1k and 10k. Fig. 2(a) shows that LTO powders was composed of particles that are spherical in shape. In addition, LTO particles do not have pores. The FE-SEM micrographs at 10k magnification also show that LTO particles are still agglomerating. This is indicated by many different particle sizes. Fig. 2(b) shows the particle size distribution at 1k magnification. Particle size distribution was known from the analysis using image J software and displayed in the form of a histogram graph at Fig 3. Fig 3 show that the LTO powders consists of submicron particles assembled into dense aggregate with smaller size distribution (~0.24 μm).
Figure 2.a. FE-SEM micrographs of LTO powder at 10k magnification.

Figure 2.b. FE-SEM micrographs of LTO powders at 1k magnification.

Figure 3. Particle size histograms of LTO powders.
In the half cell testing was conducted with a sample in the form of a coin cell. LTO acting as a cathode and lithium metal as anode as the voltage was lower than LTO. Data from the CV testing in the form of a curve that shows the relationship between voltage (V) as input and output in the form of current (I). Fig. 4 shown the results of CV testing with scan rate variation 50, 100, 150 and 200 μV/s. The characteristic voltages are determined from the peak values of oxidation and reduction. On cyclic voltammogram of LTO at fig 4 shown by different colour for each scan rate variation. However, the peak oxidation and reduction values for each scan rate did not change at 1.5 – 1.75 Volt which is the characteristic voltage of LTO. The value of the peak voltage that doesn’t change with increasing scan rate shows that lithium ion batteries with LTO anode are reversible. In the CV testing results also can’t be known peak oxidation and reduction of the rutile TiO$_2$ phase. This is because rutile TiO$_2$ doesn’t show any significant amount of Li storage and this is due to the characteristic tetragonal structure, which doesn’t allow facile Li ion transport [4].

![Cyclic voltammetry curves of LTO at different scan rate 50, 100, 150 and 200 μV/s.](image)

In addition, from the CV testing can be known the diffusion value of lithium ion battery through the equation by Randless-Sevcik [12]

$$D_{Li} = \frac{i_p^2}{(2.659 \times 10^5)^2(n^{1.5})^2A^2C^2v}$$

Where $D_{Li}$ is the diffusion coefficient of Li ion (cm$^2$/s), $i_p$ is the peak current (A), $n$ is number of electron per-molecule, $A$ is the surface area (cm$^2$), $C$ is concentration of Li ion (mol/cm$^3$) and $v$ is the voltage scan rate (V/s). The peak current value increases with increasing scan rate variation. LTO anode peak currents for each scan rate variation are 0.0018 A, 0.0021 A, 0.0029 A and 0.003 A. This happened because a high scan rate means that the faster the voltage was applied every second so that the resulting current also increases. The results of diffusion coefficient LTO anode is $3.48 \times 10^{-4}$ cm$^2$/s. This shows that the intercalation and de-intercalation process of lithium ions happened rapidly. Where as for the result of charging-discharging capacity shown in the figure 5.
Figure 5. Charge-discharge curves of LTO.

In the charge-discharge curves shown that the blue lines are cycle 1 of charge-discharge testing, the red lines are cycle 2 and the black lines are cycle 3 of charge-discharge testing. In the Fig. 5, when the applied voltage is 1.5 Volt the result of charging and discharging capacity forms a straight line called the plateou voltage. The plateou voltage shows the value of the working voltage of the LTO anode which is 1.5 Volt. Fig 5 also shows the highest capacity in the first cycle of charging and discharging is 302 mAh/Gr. The results of this capacity confirmed the results of FESEM and CV tests which mean that the smaller of particle size distribution made the higher of diffusion coefficient of lithium ion and charging-discharging capacity. Fig. 6 shows the nyquist plots and straight lines of LTO anodes. The straight lines called impedances of wargburg which determines the ionic conductivity of LTO anodes. Furthermore, the semicircle plot / nyquist plot determines the electric conductivity of LTO anodes. The smaller of semicircle area means the higher electrical conductivity of LTO anode. Data from the EIS testing shows the relationship between the x-axis as the real impedance ($Z'$) and the y-axis as the imaginary impedance ($Z''$). From the value of charge-transfer resistance ($R_{ct}$) and electronic resistance ($R_{e}$) can obtained electric conductivity value of LTO anode. The value of $R_{e}$ and $R_{ct}$ entered into the equation [13, 14]:

$$\sigma = \rho \frac{l}{A}$$

Where $\sigma$ is electric conductivity (S/cm), $\rho$ is resistivity (Ω.cm), $l$ is sample thickness (cm) and $A$ is a surface area (cm$^2$). So that the electric conductivity value of LTO anode is $6.87 \times 10^{-3}$ S/cm. The low particle size distribution also made high electric conductivity, this is because more electrons and lithium ions move from anode to cathode and vice versa.
4. Conclusion

LTO anode synthesized using sol-gel method at 900°C and holding time of 2 hours was successfully carried out. LTO powder composed of LTO phase as the main phase and rutile TiO$_2$ phase as the impurity phase. LTO powder also consisted of poreless and agglomerated particles. The value of particle size distribution powder is 0.24 μm measured using Image-J software. The small particle size distribution value made lithium ion moved easily during the charging-discharging process so that the electrochemical performance of LTO anode in lithium ion battery was increased. The diffusion coefficient of the LTO anode is 3.48 x 10$^{-4}$ cm$^2$/s, the electrical conductivity value is 6.87 x10$^{-3}$ S/cm while the charging-discharging capacity is 302 mAhr/gr at 1C.

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