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Effect of Acetylene Black Content to Half Cells Li-ion Battery Performance Based on Li₄Ti₅O₁₂ using Li₂CO₃ as Lithium Ion **Source with Hydrothermal Mechanochemical Process**

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Abstract. Lithium titanate $(Li_4Ti_5O_{12})/LTO$ is a promising candidate to be used as anode electrode in Li-ion battery, to replace graphite in Li-ion battery application. Crystal structure of lithium titanate/LTO is more stable or undergoes less strain than graphite during intercalation and de-intercalation process Li^+ ions. However, although lithium titanate has good stability, the material has low electrical conductivity and lithium ion diffusion. The purpose of this research is to synthesis the spinel LTO using combinated hydrothermal and mechanochemical processes from xerogel TiO₂. Then, to increase the conductivity, in the half-cell battery assembly process it was added acetylene black conductive (AB) additive with various from 10%, to 15% in wt. The LTO obtained were characterized using scanning electron microscope (SEM), X-Ray Diffraction (XRD) and Brunauer-Emmett-Teller (BET). The XRD showed a rutile as minor phase, while SEM showed homogeneous distribution of particle with an average particle size of 0.35 μ m. The BET showed that the surface area of LTO formed is 2.26 m²/g. The assembled coin half cells used this Li₄Ti₅O₁₂ as a cathode and lithium metal foil as the anode were tested using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and charge discharge (CD). The conductivity value obtained from EIS corresponds to the contents of AB. Meanwhile, the CV and CD testing showed that higher percentage of AB causing the decrease of battery specific capacity. The highest specific capacity at the rate of 10C is obtained at the mixture of 10wt% AB with the value of 40.91 mAh/g.

1. Introduction

To the world concern on the environmental pollution and global warming, usage of renewable energy is considered as the most promising solution. This kind of energy needs the storage ultimately. One of useful storages is lithium ion batteries (LIBs), which could be applied for the hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and storage systems for others renewable energy resources [1]. Most LiBs were made with graphite anodes since it is relatively cheap, discharge capacity 375 mAh/g [2] and the intercalation and de-intercalation of lithium ion is very stable [3]. However, it has limitation of formation SEI layer during the first charge or discharge cycle and lower rate capability [4].

The use of Li₄Ti₅O₁₂ (LTO) to replace graphite has been developed for optimal results. During intercalation, LTO based anode shows an almost zero strain properties with good thermal stability and

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can endure of thousands of cycles without significant capacity loss [5]. However, LTO has a low electrical conductivity $(10^{-9} \text{ S.cm}^{-1})$ which is not favorable to high rate capability application [6].

The focus of this study is to increase the electrical conductivity of LTO using the addition acetylene black (AB) during assembly process of Li-ion battery half cells. The LTO in this work was prepared by mixing anatase TiO_2 xerogel with Li_2CO_3 using hydrothermal mechanochemical method. Combination of these methods is expected to produce $Li_4Ti_5O_{12}$ with nanoparticle size with good electrochemical performance. Influence of the AB content (wt.%) in the LTO slurry mixture will be investigated.

2. Experimental

2.1 Materials synthesis and electrode fabrication

 $Li_4Ti_5O_{12}$ powder was prepared through the following steps, i.e. sol-gel, calcination hydrothermal mechanochemical and sintering process. The sol-gel process started with the mixing the primary solution (titanium butoxide + ethanol pH 3) with secondary solution (ethanol pH 3 + distilled water) to form a clear gel using a magnetic stirrer. The obtained gel was dried in the ambient temperature to get xerogel TiO₂. Calcination process was done at temperature of 300 °C for 2 h to obtain anatase TiO₂. Then, hydrothermal process was done at temperature of 120 °C for 15 h. The high energy ball mill was used to mix the hydrothermal result with Li_2CO_3 . Finally, the sintering process was then performed at 750 °C in 1 hour to form LTO spinel phase and ready to be used for the active electrode material.

The electrochemical cycling performance of LTO powder was carried out with a coin cell using a lithium metal foil as anode. The cell had a configuration of Li metal, electrolyte and $Li_4Ti_5O_{12}$ and polypropylene was used as the separator. A combination of acetylene black as conductive agent with various 10 wt.%, 12 wt.%, and 15 wt.%. Polyvinylidene fluoride (PVDF) binder homogeneously mixed with DMAC was prepared into viscous slurries for efficient deposition. The slurries were deposited on current collectors copper foil by Doctor Blade with 6 cm/minutes coating speed. The electrode was then dried under vacuum at 80 °C for 2 h before electrochemical testing. Cell assembly was performed in a glove box filled with pure argon.

2.2 Characterization and Testing

The characterization of LTO powder to know the morphology of sample was observed by scanning electron microscope. The particle size of sample was measured with Image J software. Phase identification was examined by X-ray diffraction analysis (XRD) using Cu K α radiation. BET (Brunaeur-Emmet-Teller) method was used to analyze the surface area of LTO by using Quantachrome Nova instrument.

The Cyclic voltammetry (CV) of coin cell was carried out at scan rate of 100 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) tests was performed to show impedances value. The charge and discharge (CD) testing was conducted to evaluate the cell electrochemical performance from low current (C/3) to high current (10C) discharge rate.

3. Results and discussion

3.1 The structure of $Li_4Ti_5O_{12}$ powder

The morphology of the LTO powder produced from hydrothermal mechanochemical reaction synthesis was examined using scanning electron microscope (SEM). Figure 1. shows representative SEM image of LTO powder with 20000X (A) and 5000X (B) magnification. The grain size is almost uniform distribution, but there is still almost evenly agglomerates.

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Figure 1. SEM image of LTO powder with magnification (a) 20.000X and (b) 5.000X

The LTO powder has diameter approximately 0.34 μ m as seen in Figure 1. (A). The average diameter size of agglomerates was approximately 2.27 μ m as seen in Figure 1. (B) That small particle size can improve the surface area of this LTO solid.

The structure of the synthesized powder was characterized using a X-ray diffraction (XRD). The data is processed using XRD results X'Pert High Score Plus software installed in the instrument and matches to JCPDS 26-1198 reference numbers for the LTO spinel phase and (JCPDS 01-076-0318) TiO₂ rutile [7].

X-ray diffraction patterns of LTO powder after sintering for 2 h is shown in Figure 2. The peaks at the XRD pattern take place at 2θ = 18.42°, 35.44°, 43.30°, 62.89° and 66.19° correspond to the characteristic of crystal peaks of LTO. The TiO₂ rutile phase obtained at 2 θ position are 27.49° and 54.37°. The presence of little amount of TiO₂ rutile compound is considered as an impurities



Figure 2. X-ray diffraction patterns of LTO powder after sintering for 2 h

The existence of these impurities caused by the presence of lithium kation loss [7] and upon mixing with insufficient homogeneity [8]. Peak intensity indicates that rutile content in the amount approximately of 15%. The surface area of LTO powder was $2.26 \text{ m}^2\text{g}^{-1}$ analysed by BET measurement.

3.2 EIS characterization of LTO electrodes

Half-cell measurement of LTO and a lithium counter electrode using electrochemical impedance spectroscopy (EIS) can show the charge transfer resistance (Rct) electrode as seen in Figure 3. as follows.

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Figure 3. Complex impedance plots of the half cell with Li₄Ti₅O₁₂ anode prepared by hydrothermalmechanochemical synthesis calcined at 750 °C for 3 h

The electrode-polarization resistance increased with added acetylene black for the cell with the $Li_4Ti_5O_{12}$ derived from the standard hydrothermal reaction. The results can be seen in **Table 1** shows electrolyte resistance (Re) and resistance charge transfer (Rct) to determine the resistance or impedance at the half cell batteries.

Table 1. Values of Re and Rct of ion exchange the experimental with variation acetylene Black Content

Samples	$\operatorname{Re}(\Omega)$	Rct (Ω)
LTO-HT1-Ac1	15.57	113.09
LTO-HT1-Ac2	46.90	107.85
LTO-HT1-Ac3	9.00	27.56

The electrolyte resistance were inversely proportional with the addition of acetylene black contents. Since resistance is the opposite of the conductivity, therefore the conductivity is proportional with the addition of acetylene black contents.

3.3 Cyclic Voltammetry (CV) characterization of LTO electrodes



Figure 4. CV curve of half-cell, sweep rate 100 mVs⁻¹

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The CV curve shows the initial three cycles of half-cell with potential sweep rate of 100 mV/s is shown in Figure 4. The specific capacity of LTO-HT1-Ac1 is 115.78 mAhg⁻¹ that is higher than others samples. The capacity LTO-HT1-Ac2 and LTO-HT1-Ac3 are 100.50 mAhg⁻¹ and 99.80 mAhg⁻¹ respectively. They showed decreased capacity because in this AB content range, the increase of conductivity has no effect to the specific capacity and the less proportion of LTO as the active material cause decreasing capacity on the battery.

Cycles behavior corresponded to kinetic reaction of highest peak LTO with average potential of 1.55 V which correlated to two phases that is $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ phases in the intercalation and deintercalation process with reaction as follows [7]:

$$\mathrm{Li}_{4}\mathrm{Ti}_{5}\mathrm{O}_{12} + 3\mathrm{Li} + 3\mathrm{e}^{-} \leftrightarrow \mathrm{Li}_{7}\mathrm{Ti}_{5}\mathrm{O}_{12}$$

$$(3.1)$$

All sample had same anodic and cathodic working potential. From the peak potential that indicated acetylene black content did not affect performance of cell battery as seen in the result of cyclic voltammetry test. The working potential is average potential from oxidation and reduction curve [9] can be calculated with equation as below.

$$E^{0} = \frac{E_{p,c} + E_{p,a}}{2}$$
(3.2)

The synthesis obtained from hydrothermal combined with mechano-chemical process generated higher surface area and less aggregation of the $Li_4Ti_5O_{12}$. The smaller grain size suggest a shorter diffusion distance, while a higher surface area means more interfacial sites and both are beneficial for higher reaction rate performance.

3.4 Charge-Discharge (CD) characterization of LTO electrodes

The charge and discharge (CD) test were conducted to evaluate the cell electrochemical performance at different current rate is shown in Figure 5. below. In Figure 5., it shows the discharge capacity of the half-cell at various acetylene black content at 0.3C to 10C with LTO powder synthesis after calcination at 750 °C for 3 h. The capacity from this synthesis techniques has not reached the theoretical value of 175 mAhg^{-1} yet.



Figure 5. The discharge capacity of half-cell with current rate 0.3V to 10C

In the first cycle, the discharge capacity was 108.26 mAhg⁻¹ with 10 wt% AB content. At 10C discharge rate, the LTO-HT1-AC1 has the highest capacity compare to the other with the value of 40.91 mAhg⁻¹, LTO-HT1-AC2 was 26.88 mAhg⁻¹ g and LTO-HT1-AC3 was 17.23 mAhg⁻¹ respectively. From the data obtained, indicating that the discharge rate with the addition of AB will degrade the battery capacity. From columbic efficiency generated by the current ratio variation rate and of AB obtained in Figure 6. The current efficiency obtained was approximately in average almost 100%.

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Figure 6. Columbic efficiency of half-cell during charge and discharge cycling

This is because the used of the active material (LTO) has a zero-strain properties. Columbic efficiency added of the AB content does not have a significant influence to change the columbic efficiency of lithium ion batteries.

4. Conclusion

The present $Li_4T_5O_{12}/LTO$ has been successfully synthesized using hydrothermal-mechanochemical process and obtained a quite high surface area and minimum aggregation of the solid state. Conductivity of the assembled battery with various of acetylene black AB content from 10%, 12% to 15wt% shows that conductivity is proportional with the amount of AB contents in the slurry mixture.

The capacity of the assembled battery with various AB content from 10%, 12% to 15wt% shows the highest capacity at the 10wt%, but decrease at addition of more AB 12% and 15%. Thus, 10% is the best performance for the range of AB content from 10wt% to 15wt%. In this range, the conductivity is inversely proportional with capacity of the half-cell battery.

Finally, quite high capacity at the high current-rate 10C is reached at 10wt% AB, i.e. 40.91 mAhg⁻¹ compared to other AB contents. Accordingly, this LTO compound which could withstand under the high current rate of 10C is certainly well above the anode requirement for Indonesia electric car program which is set to be 4C.

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