



The Effect of Al₂O₃ Doped and Carbon Coated Li₄Ti₅O₁₂ on Structures, Morphology and Electrochemical Performance

Slamet Priyono^{1*}, Kerista Sebayang², Rike Yudianti³, and Lisda Annisa⁴

^{1,3} Pusat Penelitian Fisika-Lembaga Ilmu Pengetahuan Indonesia (LIPI), Kompleks Puspiptek Gedung 442 Serpong Tangerang Selatan Banten 15314, Indonesia

^{2,4} Department of Physics, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara 20155, Indonesia

Abstract. In this research, Li₄Ti₅O₁₂ anode with doping Al₂O₃ and carbon coating was made to determine the effect of doping Al₂O₃ and carbon coating on crystal structure, morphology and electrochemical performance. Li₄Ti₅O₁₂ anode material consisting of LiOH.H₂O and TiO₂ was made with various samples of LTO without doping, LTO doped carbon, LTO doping Al₂O₃ and carbon using the solid state reaction method. All raw materials are mixed and milled using a Planetary Ball Miller for 2 hours then crushed to become a precursor to Li₄Ti₅O₁₂. The Li₄Ti₅O₁₂ precursor was sintered at 850°C for 4 hours. The final product was characterized using X-Ray Diffraction (XRD) to determine the formation of Li₄Ti₅O₁₂ phases, Scanning Electron Microscopy (SEM) to analyze the morphology formed, and Cyclic Voltammetry to determine electrochemical performance. The results of XRD characterization were formed in the Lithium Titanium Oxide (Li₄Ti₅O₁₂), Dilithium Titanate (Li₂TiO₃), and Rutile (TiO₂) phases. The SEM characterization results on LTO doping carbon, LTO doping Al₂O₃ and carbon showed a coarser texture compared to the LTO without doping which had a fine texture. The electrochemical performance produced in LTO coating carbon has a slender redox peak in the first cycle, this shows that LTO coating carbon has good electrochemical performance compared to the Al₂O₃ and carbon doping LTO samples.

Keyword: Li₄Ti₅O₁₂ anode, coating carbon, doping Al₂O₃, solid state reaction method.

Received 18 November 2019 | Revised [10 December 2019] | Accepted [14 February 2020]

1 Introduction

Energy production that relies on fossil fuels is thought to have a dire future impact on the world's economy and ecology. The production of electrochemical energy is being considered as an energy source or alternative power, because it is more sustainable and environmentally friendly [1]. Lithium-ion batteries are the most widely used battery types today [2-3]. Various electronic gadgets such as cellphones, tablets, laptops, watches, as well as applications for electric vehicles are very dependent on the type of Li-ion battery. One of the components that

*Corresponding author at: Kompleks Puspiptek Gedung 442 Serpong Tangerang Selatan Banten 15314, Indonesia

E-mail address: slam013@lipi.go.id

affect the large power capability is determined by the battery anode component. The components that have been used so far are based on graphite materials of various types such as natural graphite, synthetic graphite, soft carbon, and hard carbon. They have a weakness, namely, there is a large enough expansion of crystal changes during the charging and discharging processes at high power conditions [4]. The anode is chosen by considering: efficiency as a reducing agent, high coulomb output (Ah/g), good conductivity, good stability, ease of fabrication, and low cost [5].

LTO has been successfully commercialized because it allows a combination of superior thermal stability, high rate, relatively high volumetric capacity and long cycle life. Despite the higher cost of Ti, the cell voltage is reduced and the capacity is lower. LTO is considered "zero strain" because the phase change caused by lithiation / delithiation only results in a slight change in volume (0.2%) [6-7]. This problem various anode materials with increased reversible capacity and stability over commercial graphite have been proposed for lithium ion batteries, one of which is the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode [8-9]. However, LTO also has considerable disadvantages, such as the low conductivity and diffusion coefficient of lithium specificity, these weaknesses can be eliminated in different ways, for example by creating defective structures, reducing the particle size, coating the particle surface with carbon and doping with metals (copper, tin, and silver) [10]. Carbon Black is a form of elemental carbon produced by partial combustion or controlled pyrolysis of hydrocarbons. One of the commercial products of carbon black is Super P with another name acetylene black or graphitized Carbon Black. Acetylene has a high carbon content (92%) in exothermic decomposition to carbon and hydrogen, thus making acetylene an attractive raw material for conversion to carbon black [11].

In the research conducted by Muhammad aziz and Haryati purwaningsih, the addition of 5 wt% Al to TiO_2 caused a decrease in the size of TiO_2 particles, while the addition of 6 wt% Al led to grain growth. The combination of adding 5 wt% Al followed by sintering 700°C produces TiO_2 material with anatase crystal structure and porous morphology suitable for gas sensor materials [12]. In this research, LTO powder will be made based on $\text{LiOH}\cdot\text{H}_2\text{O}$ and TiO_2 doped with Al_2O_3 and coated with carbon were examined.

2 Methods

Synthesis of LTO powder using solid state reaction method with a mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ and TiO_2 materials and characterization of LTO powder including: Rigaku XRD (X-Ray Diffraction) characterization type SmartLab 3 kW, SEM (Scanning Electron Microscope), CV (Cyclic Voltammetry Testing).

In the anode powder manufacturing process, the active ingredients of LTO are mixed with Al_2O_3 and Carbon Super P. The three ingredients are mixed in the milling chamber. The milling chamber is inserted into the Planetary Ball Miller tool. The milling time is set for 2 hours at a

speed of 20.00 Hz. The material that is finished is milled and crushed using a spatula until smooth. Then the sample was sintered at a temperature of 850°C for 4 hours. After sintering, crush the sample using a pastel until smooth and even. A small sample was taken for characterization using XRD to determine the phase and crystal structure of LTO, SEM to determine the morphology of the sample, and CV to determine the electrochemical performance of LTO powder.

3 Result and Discussion

3.1 X-Ray Diffraction (XRD) Analysis

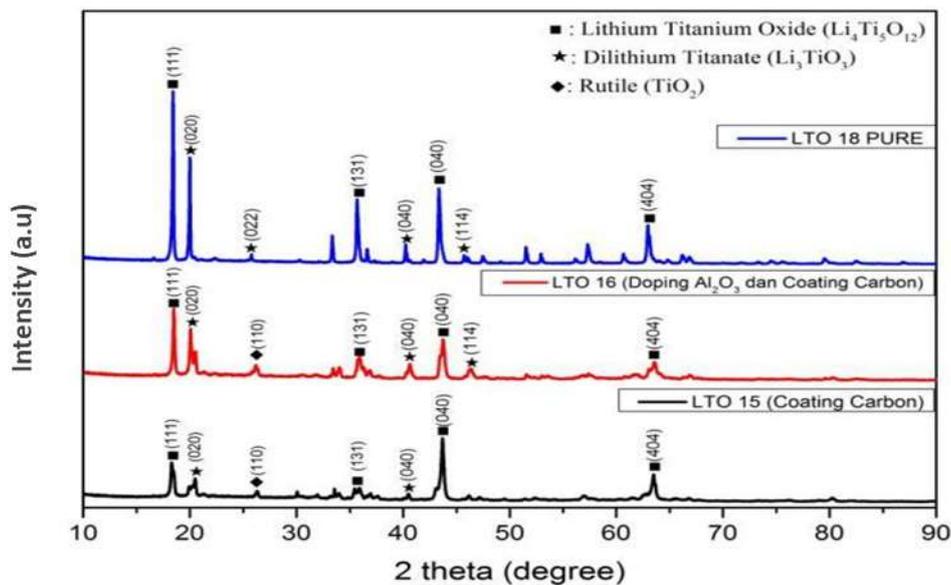


Figure 1. XRD Patterns of LTO

In Figure 1, it can be seen that the phase formed is At LTO 15 the highest peak of the Lithium Titanium Oxide phase is at an angle of 2 theta (2θ) of 18.40°, 35.61° 43.26° and 62.92° while at LTO 16 the highest peak of the phase is at angle of 2 theta (2θ) of 18.38°, 35.64°, 43.26°, and 62.84°. The peak of the Lithium Titanium Oxide phase found in LTO 18 Pure is at the highest angle of 2 theta (2θ) of 18.38°, 35.63°, 43.30°, and 62.83°.

The peak patterns of DiLithium Titanate (Li_2TiO_3) obtained correspond to ICSD 96-151-5996. At LTO 15 the highest peaks are at an angle of 20.14° and 40.18°, while at LTO 16 the highest peaks are at an angle of 20.15°, 40.15°, and 45.55° and at LTO 18 Pure the highest peaks are at an angle of 20.23°, 25.54°, 40.19° and 45.57°.

The peak pattern of Rutile (TiO_2) obtained is in accordance with ICSD 96-900-4144. For the rutile phase found in LTO 15 the highest peak is at 2 theta (2θ) angle of 27.28° while in LTO 16 the rutile phase is at 2 theta angle (2θ) of 27.39°. In LTO 18, there is no TiO_2 impurity

phase. The XRD curve above is not found in the LTO structure which indicates that Al_2O_3 has successfully joined the LTO structure.

3.2 Scanning Electron Microscope (SEM) Analysis

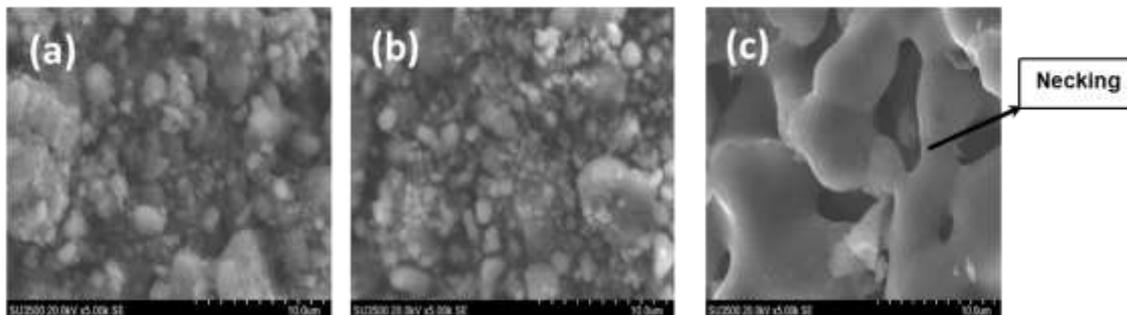


Figure 2. Morphology of (a) LTO 15, (b) LTO 16, (c) LTO 18 with magnification of 5k SE at 850°C

In Figure 2, the results of the morphological characterization of the sample using SEM (Scanning Electron Microscope) with a magnification of 5k SE can be seen in Figure 2. Morphologically, surface area of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample in the LTO 15 and LTO 16 samples has a rough texture, while the LTO 18 pure sample begins to form a smoother surface than the other two samples.

In the LTO 18 Pure sample there were no grain boundaries in the sample. Sample LTO 15 (a) and Sample LTO 16 (b) have the addition of carbon, while in sample LTO 18 (c) there is no additional carbon. In Sample LTO 15 (a) and Sample LTO 16 (b) the granules are separated from one another because the carbon prevents agglomeration. Sample LTO 18 (c) which does not contain carbon causing agglomeration, it is seen that there is a necking between the sintered particles. Necking occurs due to the diffusion process due to high temperature heating.

3.3 Cyclic Voltammetry (CV) Analysis

CV analysis was conducted by using the WBCS3000, Automatic Battery Cycler Version 3.2. In the cyclic voltammetry test, it was carried out by testing a half-cell battery from a coin cell. Where the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material acts as an anode while the cathode is lithium metal. In the LTO 15 sample the resulting graph has a slender redox peak in the first cycle, the next cycle the graph undergoes enlarging polarization which causes the peak to shift. The more cycles that are carried out, the greater the polarization obtained.

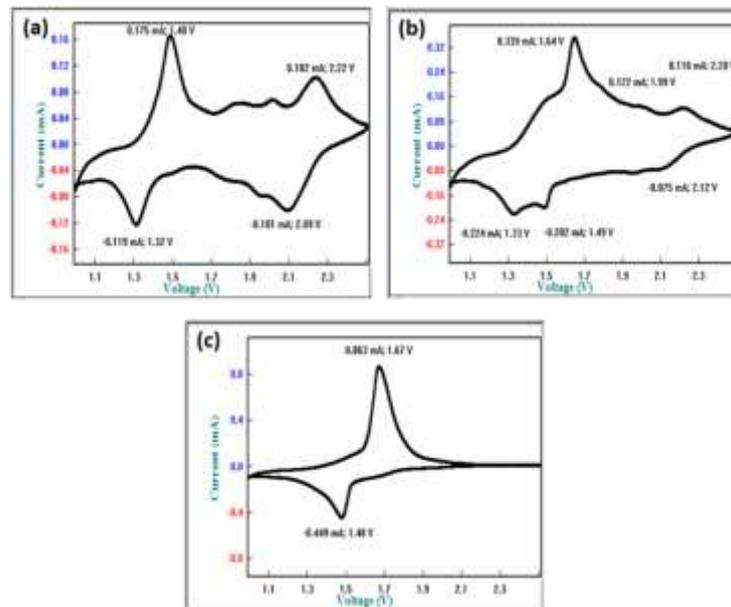


Figure 3. CV of (a) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with P super carbon, (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with Al_2O_3 doped and P super, (c) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ pure

There were reduction peaks at voltage and current of 1.32 V and -0.119 mA, 2.09 V and 0.101 mA, while the oxidation peaks at voltages and currents were 1.48 V and 0.175 mA, 2.22 V and 0.102 mA. For the LTO 16 sample (doping Al_2O_3 and carbon) there were reduction peaks of 1.33 V and -0.224 mA, 1.49 V and -0.202 mA, 2.12 V and -0.075 mA while the peak of oxidation at voltage and current was 1.64 V and 0.339 mA, 1.99 V and 0.122 mA, 2.20 V and 0.116 mA. For sample LTO 18 (without doping) has a slender redox peak, there is a peak reduction in voltage and current of 1.48 V and -0.449 mA, while the oxidation peak at voltage and current is 1.67 V and 0.863 mA. So, it can be said that the LTO 15 (doping carbon) sample has better electrochemical performance than the LTO 16 (Al_2O_3 doping and carbon coating).

4 Conclusion

The synthesis that has been successfully carried out is shown in the XRD analysis results, the XRD shows the formation of 3 phases in each sample. These phases are Lithium Titanium Oxide, Dilithium Titanate and Rutile TiO_2 . For the crystallite size value, LTO coating carbon has a smaller size than LTO doping Al_2O_3 and carbon. The effect of coating and doping on the characteristics of LTO is that when the LTO is coated with carbon the crystallite size is smaller than when the LTO is doped with Al_2O_3 . Morphologically, the granules are separated from one another because carbon prevents agglomeration. The electrochemical performance resulting from the CV analysis shows that the electrochemical performance of the battery cell on LTO doping carbon has a slim redox peak, but in Al_2O_3 doping LTO the redox peak is not slim and widening. So it can be concluded that LTO with doping Carbon has better performance than LTO with doping Al_2O_3 .

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