Journal of Technomaterial Physics Vol. 4, No.12, 2022 | 68 - 72

JoTP
Journal of Technomaterial Physics

XRD Analysis of $Li_4Ti_5O_{12}$ with Post Heat Treatment for Lithium-ion Capacitor (LIC) Applications

Syahrul Humaidi[1], Feby Arianti[2], Slamet Priyono[3*], and Rike Yudianti[4],

[1,2]Department of Physics, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan 20155, Indonesia
[3,4]Physical Research Center, National Research and Innovation Agency (BRIN), Tangerang Selatan, 15314, Indonesia

Abstract. Characterization of XRD-analysis on $Li_4Ti_5O_{12}$ with post heat treatment for applications Lithium-ion Capacitor (LIC) has been conducted. The powder method was used in the analysis, whereas the samples were prepared using the sol gel method. The anode material $Li_4Ti_5O_{12}$ precursor was sintered at 850°C for 4 hours and followed by heat-treatment at 600°C for 3 hours. Characterization of structural (XRD analysis) was applied to determine the formation of $Li_4Ti_5O_{12}$ phase. The results of the characterization were formed Lithium titanate ($Li_4Ti_5O_{12}$) and rutile phase (TiO_2) with crystallite size on LTO I of 82.52 nm and LTO II of 92.07 nm. Overall, post heat treatment of anode $Li_4Ti_5O_{12}$ succeeded in improving the quality and electrochemical performance for Lithium-ion Capacitor (LIC) application.

Keyword: $Li_4Ti_5O_{12}$ Anode, Heat Treatment, Lithium Ion Capacitor, Sol Gel

Received 25 January 2022 | Revised [11 February 2022] | Accepted [25 February 2022]

1 Introduction

The need for energy in the world is increasing every year. Meanwhile, fossil fuels, the main energy source used today, are decreasing. The energy crisis is caused by the gap in demand and supply of energy sources. Several solutions to overcome the energy crisis continue to be carried out, for example the use of fuel cells, hybrids, solar cells, supercapacitor and lithium batteries [1-2].

Lithium-ion batteries and supercapacitors are well-known energy storage technologies for their important role. At present, however, these two devices are not sufficient for applications as diverse as hybrid electric vehicles as batteries have high energy density but low power density. has high power density but low energy density [3-4].

*Corresponding author at: Department of Physics, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan 20155, Indonesia

E-mail address: syahrul1@usu.ac.id

Copyright © 2022 Published by Talenta Publisher, ISSN: 2656-0747 e-ISSN: 2656-0755
Journal Homepage: https://talenta.usu.ac.id/JoTP

Lithium-ion Capacitor (LIC) is an innovative technology that entered the energy storage market more than five years ago. LICs have developed into commercial solutions to address the application gap between lithium-ion batteries and supercapacitors. The anode material in the LIC is the same as the lithium-ion battery or lithium insertion material. The main goal of hybridization is to overcome the gap that exists between supercapacitors and lithium-ion batteries [5-6].

Lithium Titanate ($Li_4Ti_5O_{12}$) is the anode material that has been used in most of the LICs. $Li_4Ti_5O_{12}$ anode has a relatively higher lithiation potential than graphite. Lithium Titanate ($Li_4Ti_5O_{12}$) is a promising graphite replacement anode material, with a strong spinel structure so that during the charge and discharge process there is no change in lattice volume which can ensure high cycle stability and long service time. In addition, $Li_4Ti_5O_{12}$ material has a stable working stress during the intercalation process. This shows that $Li_4Ti_5O_{12}$ is safer to use as anode material than graphite [7]. Another method to synthesize $Li_4Ti_5O_{12}$ anode material is the sol gel method. This method can reduce the sintering temperature, reduce the particle size, the mixture is more homogeneous and the morphology is more uniform. By reducing the particle size, it will reduce the diffusion path of Li ions so that it is expected that the value of the electronic conductivity and the diffusion coefficient of Li ions will increase [8]. $Li_4Ti_5O_{12}$ anode which was synthesized by sol gel technique was then sintered and heat treated to increase the crystallinity of $Li_4Ti_5O_{12}$ anode.

2 Methods

Preparation This research uses materials including $C_2H_3LiO_2$, TBT or $C_{16}H_{36}O_4Ti$, HCl, activated carbon, $Li_4Ti_5O_{12}$ as anode material, PVDF, C_2H_5OH as raw material solvent, DMAC and Super P. The process of synthesizing $Li_4Ti_5O_{12}$ powder was done using the sol gel method. The manufacture of $Li_4Ti_5O_{12}$ powder was synthesized based on the calculation of the stoichiometry of the material as in equation 2.1 as follows:

$$5C_2H_3LiO_2 + 5C_{16}H_{36}O_4Ti + HCl \rightarrow Li_4Ti_5O_{12} + LiCl \quad (2.1)$$

Next, mix the two raw materials in a measuring cup to form a gel solution at room temperature and stirrer for ± 24 hours so that the solution is mixed homogeneously. Each gel formed was left in a toaster at a temperature of 80^{o}C for a duration of 24 hours.

The material sintering process was carried out at a temperature of 850^{o}C for 4 hours using a furnace. Then the material was ground by grinding for 1 hour and then sieved using a 400 mesh sieve to produce the active material $Li_4Ti_5O_{12}$ (I). Furthermore, the process of heat treatment of $Li_4Ti_5O_{12}$ (I) material at a temperature of 600^{o}C for 3 hours, the sample was ground by grinding for 1 hour then sieved with a 400 mesh sieve to produce the active material $Li_4Ti_5O_{12}$ (II).

Samples that have gone through all the steps above are then characterized by XRD to see the crystal form and the phase formed from $Li_4Ti_5O_{12}$ powder.

3 Result and Discussion

3.1 X-Ray Diffraction (XRD) Testing

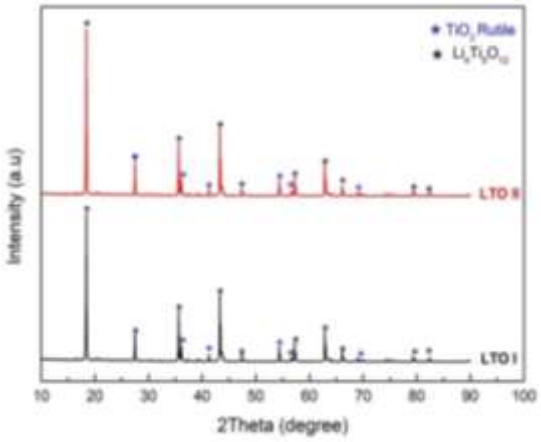
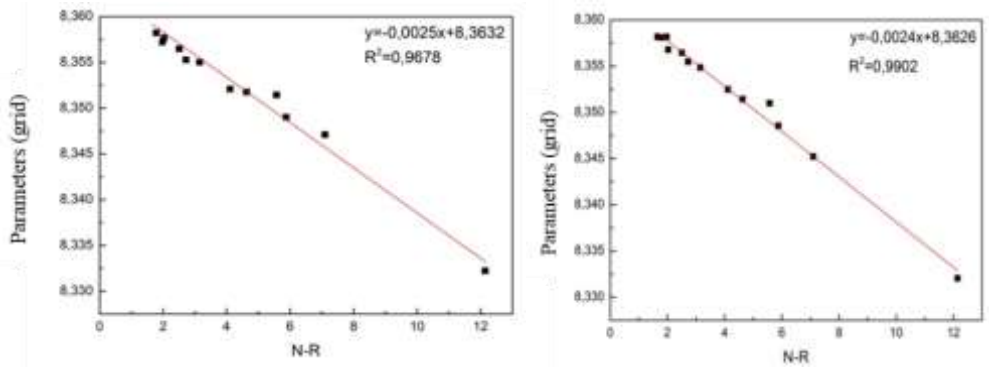


Figure 1. XRD pattern on LTO I and LTO II

The results of the X-ray diffraction pattern are shown in Figure 1. Based on Figure 1, there are two phases formed, namely the $Li_4Ti_5O_{12}$ phase and the TiO_2 (rutile) phase. In LTO I the percentage of the $Li_4Ti_5O_{12}$ phase was 82.6% and the TiO_2 (rutile) phase was 17.4%. While in LTO II the percentage of $Li_4Ti_5O_{12}$ phase is 83.4% and TiO (rutile) phase is 16.6%. In LTO I the highest peak of the $Li_4Ti_5O_{12}$ phase is at angle 2 of 18.41^o while in LTO II the highest peak of the $Li_4Ti_5O_{12}$ phase is at angle 2 of 18.42^o. These results can be concluded that LTO II has the highest intensity seen from its highest peak, meaning that LTO II is the most crystalline compared to LTO I. Then to determine the synthesis process produces the $Li_4Ti_5O_{12}$ phase, the sample lattice parameters are calculated.



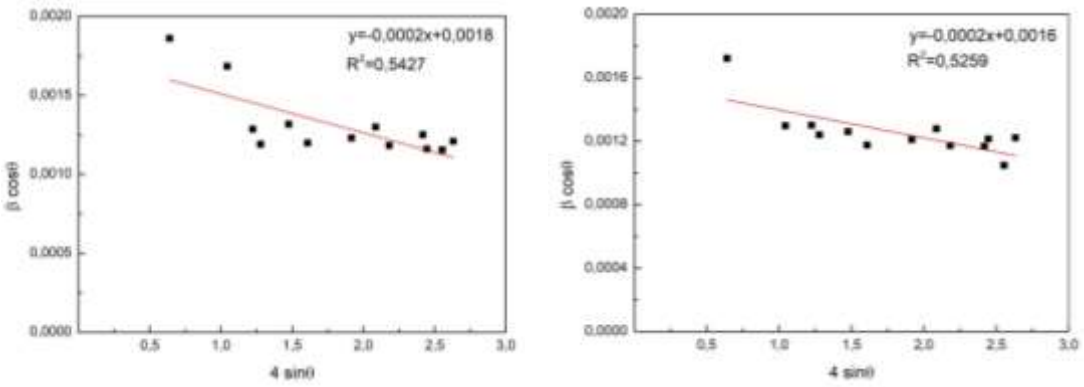
(a) (b)

Figure 2. Graph of Nelson-Riley function on lattice parameters in (a) LTO I (b) LTO II

The lattice parameter values were calculated by the Nelson-Riley method to obtain an accurate lattice parameter value. The equation of the Nelson-Riley function is as follows:

$$NRF = \left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right) \quad (3.1)$$

θ is a Bragg angle [9]. The lattice parameters are plotted against the Nelson-Riley extrapolation function and the lattice parameters can be determined from the intersection point on the y-axis as shown in Figure 2. The LTO I lattice parameter values are 8.362301045 and LTO II are 8.362633359 when compared with the database (ICSD -98-016-0655) LTO I and LTO II lattice parameter values with cubic crystal structure are in agreement.



(a) (b)

Figure 3. Graph of the relationship between cosθ and 4 sinθ in (a) LTO I (b) LTO II

Crystal size was calculated by the Williamson-Hall method using diffraction data and the FWHM value of each peak in the following equation:

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\sigma \sin\theta \qquad (3.2)$$

D is the crystal size, K is the constant (K = 0.9) is the X-ray wavelength (1.5406), is the FWHM value in radians and is the lattice strain. The crystal size is determined from the point of intersection on the y-axis and the lattice strain (σ) is determined from the slope of the straight-line equation [10]. The crystal size for LTO I was 82.52 nm and LTO II was 92.07 nm. Crystal size generally affects the electrochemical performance of the $Li_4Ti_5O_{12}$ anode. The larger the crystal size of the $Li_4Ti_5O_{12}$ anode material, the better the electrochemical performance produced.

4 Conclusion

Post heat treatment succeeded in increasing the crystallinity of $Li_4Ti_5O_{12}$, namely in LTO II, it was proven that the $Li_4Ti_5O_{12}$ phase formed was more than LTO I and the crystal size and lattice parameters of LTO II had a greater value than LTO I. The formed phase could provide good electrochemical performance. This means that the effect of heat treatment at a temperature of 600^{o}C for 3 hours has succeeded in increasing the electrochemical performance of the $Li_4Ti_5O_{12}$ anode material for Lithium-ion Capacitor (LIC) applications.

REFERENCES

[1] I. Dincer, "Renewable energy and sustainable development: a crucial review.", *Renewable and sustainable energy reviews*, vol. 4, no. 2, pp. 157-175, 2000.

[2] S. R. Bull, "Renewable energy today and tomorrow", *Proceedings of the IEEE*, vol. 89, no. 8, pp. 1216-1226, 2001.

[3] A. Jagadale, X. Zhou, R. Xiong, D. P. Dubal, J. Xu, and S. Yang, "Lithium-ion Capacitors (LICs): Development of the materials," Energy Storage Materials, vol. 19, 2019.

[4] C. Zou, L. Zhang, X. Hu, Z. Wang, T. Wik, and M. Pecht, "A review of fractional-order techniques applied to lithium-ion batteries, lead-acid batteries, and supercapacitors", *Journal of Power Sources*, vol. 390, pp. 286-296, 2018.

[5] S. Dsoke, B. Fuchs, E. Gucciardi, M. Wohlfahrt-Mehrens, "The importance of the electrode mass ratio in a Li-ion capacitor based on activated carbon and $Li_4Ti_5O_{12}$," Journal of Power Sources, vol. 282, 2015.

[6] M. Arnaiz, and J. Ajuria, "Pre-Lithiation Strategies for Lithium Ion Capacitors: Past, Present, and Future", *Batteries & Supercaps*, vol. 4, no. 5, pp. 733-748, 2021.

[7] B. Zhao, R. Ran, M. Liu, and Z. Shao, "A comprehensive review of $Li_4Ti_5O_{12}$ based electrodes for lithium-ion batteries: The latest advancements and future perspectives," Materials Science and Engineering: Reports, vol. 98, 2015.

[8] Y. C. Kuo, J. Y. Lin, "One-Pot Sol-Gel Synthesis of $Li_4Ti_5O_{12}$/C Anode Materials for High-Performance LIB," *Electrocimica Acta*, vol. 142, 2014.

[9] C. Suryanarayana, M. G. Norton, "X-ray diffraction: a practical approach," *Springer Science & Business Media*, 2013.

[10] V. D. Mote, Y. Purushotham, B. N. Dole, "Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles," *Journal of Theoretical and Applied Physics*, vol. 6, no. 1, 2012.