

Conference Paper

Substitution of Local TiO_2 on the Synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) for Anodes Lithium Ion batteries

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Abstract Substitution of local TiO_2 on the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for anodes lithium ion battery with solid state reaction method had been done. This study aimed to substitute raw materials TiO_2 and determine the length of sintering time. Synthesis was done by mixing the raw materials like local TiO_2 and $\text{LiOH}\cdot\text{H}_2\text{O}$ in a stoichiometric then milled for 15 hours followed by calcination at a temperature of 600°C with sintering time of 2 hours for each samples. Sintering was done by varying the length of sintering time i.e. 4, 6 and 8 hours at a temperature of 850°C . In this study the effect of sintering time on the material characteristics and performance of battery cells studied in detail. The characterization was conducted by the XRD to determine the structure and the LTO phases, SEM/EDX test to determine the morphology, surface topography and composition of all samples. PSA test was performed to determine the particle size while battery cell performance was tests with automatic charge-discharge battery cyclers. From characterization found that the maximum length of time that is resistant to sintering samples 6 hours. The resulting active material has an LTO phase with spinel crystal structure simple cubic, but not produced a single phase, there are some impurity phases. The results of SEM/EDX provides irregular morphology, have pores, many impurities and varying sizes. Charge-discharge measurement showed that optimum sintering was got at 6 h which gave specific capacity about 50 mAh/g.

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1. Introduction

Lithium ion battery has advantage in high energy and power density, this advantage make battery technology is suitable for portable electronics, power tools, and hybrid/full electric vehicle [1]. If electric vehicles (EVs) replace the majority of gasoline powered transportation, Li-ion batteries will significantly reduce greenhouse gas emission [2]. Beside these, Lithium ion battery has certain fundamental advantages rather than other chemistries such as lead acid and Ni-cd batteries. Firstly, Li has the lowest reduction potential of any element; its allowing Li based batteries to have the highest possible cell potential. Also, Li is the third lightest element and has one of the smallest ionic radii of any single charged ion. These factors allow Li-based batteries to have high gravimetric and volumetric capacity and high power density [3].

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For some practical applications like hybrid electric vehicles (HEV) or electric vehicles (EV), lithium ion batteries have to be re-charged very fast, and therefore the relevant electrode materials have to work at high rates, while maintaining the excellent capacity and cycling stability [4,5]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is found to be a promising material for negative electrodes in lithium-ion batteries because it has good structural stability, considered to be extremely safe, low cost, and zero strain material (negligible volume change during charge/discharge) and the theoretical capacity is 175 mAh/g. LTO can be synthesized by various techniques such as solid state reaction, sol-gel, microwave, combustion, hydrothermal methods, etc. The main disadvantages of LTO are that it has a poor rate capability and low electronic conductivity [6].

Generally, LTO synthesized with TiO_2 (technical) as Ti sources and $\text{LiOH}\cdot\text{H}_2\text{O}$ (technical, Germany) as Li sources which all raw materials are imported from overseas. In this research, LTO was made from local TiO_2 and $\text{LiOH}\cdot\text{H}_2\text{O}$ using solid state reaction with varying sintering time. Local TiO_2 was extracted from ilmenite by certain process. The use of local TiO_2 to substitute TiO_2 (technical) will affect the synthesis process of LTO especially at sintering time. Therefore this research will be focused on determining long time sintering and to know the influence on the characteristics both materials and electrochemical properties of LTO.

2. Experiment

LTO was prepared by using the solid-state reaction method from stoichiometric mixture of raw materials. The starting materials were lithium hydroxyl hydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, Germany) and titanium dioxide (TiO_2 , local product, 97%). All materials were ball milled by planetary ball mill for 15 h. The precursor was calcined at 600°C for 2 h and then sintered at 850°C for 4, 6, and 8 h to get optimum sintering time. All heat treatment was done under atmosphere with heating rate of $3^\circ\text{C}/\text{min}$. The synthesized materials were characterized by using the conventional x-ray diffractometer (XRD, Rigaku) and scanning electron microscope (SEM, Hitachi) and particle size analyzer (PSA, Cilas 1190).

The electrochemical characteristics were evaluated by means half test. The sample slurry was prepared by mixing active material powders (LTO) with binder (PVDF) and conductive carbon (acetylene black) at a weight ratio of 85:10:5 in N-N dimethylacetamide (DMAC). Subsequently, the slurry was coated on a copper foil using the doctor blade technique and dried at 80°C for 1 h to evaporate DMAC solvent. The electrode foil was cut to 14 mm diameter discs, which were used to assemble the coin cell in glove box. Li metal foil was used as the counter electrode and reference electrode in the cell. LiPF_6 was used as electrolyte. Charge discharge test was done by automatic battery cycler WBCS3000 to get capacity materials.

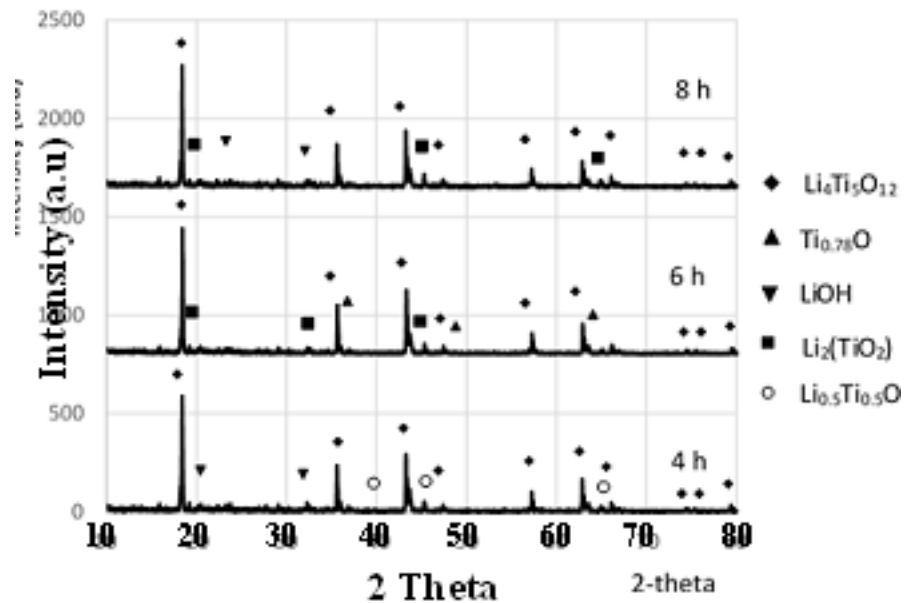


Figure 1: XRD spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which synthesized with different sintering time (a) 4 h, (b) 6 h, and (c) 8 h.

Sintering time	Lattice constant (Å^3)	Unit cell Volume (Å^3)	Calculated density (g.cm^{-3})
4 h	8.3564	583.51	3.484
6 h	8.3542	583.06	3.568
8 h	8.3586	583.98	3.553

TABLE 1: Lattice information of LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$).

3. Result and Discussion

Fig 1 shows the spectra of XRD diffraction pattern with different sintering times. The main phase, LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), denoted by diamond sign. Fig 1.a where the sample sintered for 4 h showed that LTO phase is formed by chemical formula ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), and the small other phases like $\text{Li}_{0.5}\text{Ti}_{0.5}\text{O}$ and LiOH phases which denoted by circle and inverted triangle respectively. The presence of LiOH phase indicated that sintering time is not enough for chemical reaction between $\text{LiOH.H}_2\text{O}$ and local TiO_2 . Fig 1.b where the sample sintered for 6 h shows LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) phase and still appear impurity phases like $\text{Li}_2(\text{TiO}_3)$ and $\text{Ti}_{0.78}\text{O}$. Although it still contains impurity phase but this sample has no LiOH phase. It indicated that 6 h sintering time is enough for this process. While in the sintering time for 8 h, LTO is formed but it contained LiOH again. So, the optimum sintering time for synthesis of LTO using local raw material TiO_2 is 6 hours at a temperature of 850°C . The number of phase obtained in XRD analyze due to so many elements impurities contained in TiO_2 local as raw materials.

Basically sintering process is densification or solidification process of compound that formed in calcination process. Longer time for sintering makes material denser and more solid. In atomic scale, density of material is not only affected by mass but also lattice

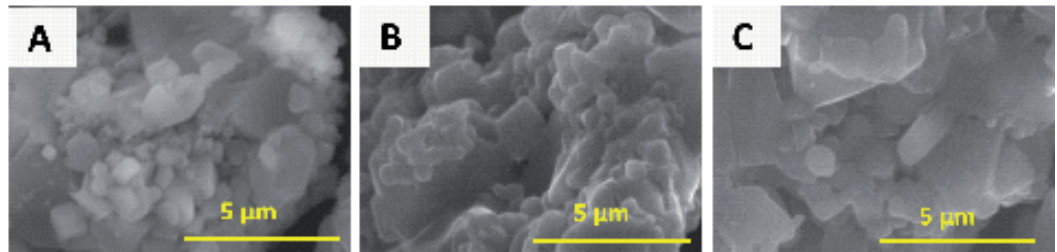


Figure 2: SEM images of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders which synthesized with different sintering time (a) 4 h, (b) 6 h, and (c) 8 h.

constant, because density also determined by unit cell volume. Table 1 shows sintering time make material denser especially in 6 h sintering time than others sample. Samples which sintering time for 4 and 8 h have lower density than 6 h because they contain LiOH phase which have higher mass.

Fig. 2 shows SEM images with a magnification of 10 K SE of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders which synthesized with different sintering time (a) 4 h, (b) 6 h, and (c) 8 h. SEM analyze was done to know the effect of varying sintering time on morphology of material surface. It is apparent that all powders have similar morphologies. All samples have polyhedral shape, smooth texture, no porous and agglomeration. The particles that were synthesized at 6 h looked bigger than 4 h and the particles that were synthesized at 8 h bigger than 6 h due to grain growth at long sintering time. Normally, sintering process will increase the rate of grain growth and indirectly reduce porosity and make material denser. But, this result is not shown like that because impurity phases contained in materials.

Particle size is one importance factor which affect electrochemical properties of electrode material because the small and uniform particle was good for contact between active materials and electrolyte[7]. The resulting powder particle size of the old sinter 4, 6, and 8 hours are $46.66\ \mu\text{m}$, $52.05\ \mu\text{m}$ and $52.67\ \mu\text{m}$, respectively. Increased long sintering causes the particle size increased due to the grain growth during high temperature diffusion and a longer length of time. In the process of grain growth occur crystal growth aggregate grain size increases. Long sintering influence both the level crystalline a material and diameter of the particle size.

Fig. 3 shows the charging-discharging profile of synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) 4 h, (b) 6 h and (c) 8 h with 0.1 C-rate for coin cell against Li metal. The cell was charged to 3.0 V and discharged to 0 V vs. Li/Li+. According the charge-discharge graphs, the sample which has lowest capacity is sample 4 h. Its sample has capacity about 45 mAh/g. While the 6 h and 8 h samples have capacity about 52 mAh/g. All capacities are very low compared by theoretical values about 175 mAh/g because synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ have many impurities and big particle size (50 μm). The data indicated that charge/discharge characteristics for all battery samples are about same. Thus, the sintering time does not significantly affect the performance of battery. In charge-discharge curve, all graphs seem as staircase curves. These graph have two working potential at 1.5 V and 1.6 V. It means that all samples have two dominant phases. Potential at 1.5 V correspond with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase while potential at 1.65 V correspond with Li_2TiO_3 phase. Others phases

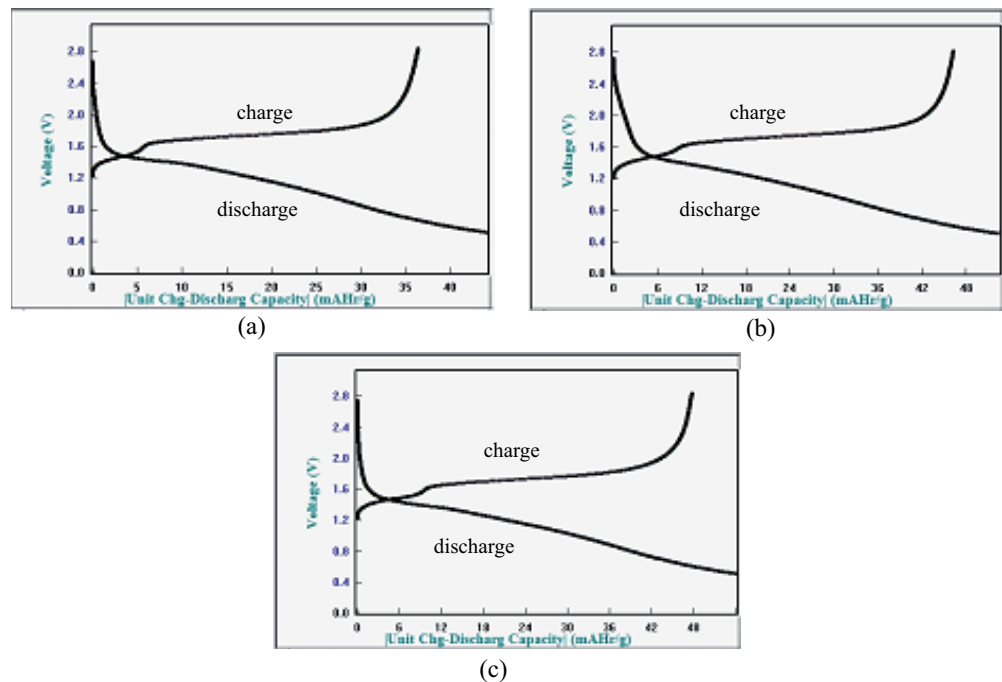


Figure 3: Charge/discharge characteristics of synthesized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) 4 h, (b) 6 h and (c) 8 h.

like LiOH , $\text{Ti}_{0.78}\text{O}$ and $\text{Li}_{0.5}\text{Ti}_{0.5}\text{O}$ are not appearing in CD curves because of very little. Charging potential of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is longer than charging potential of Li_2TiO_3 , it means that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ more dominant than Li_2TiO_3 phase.

4. Conclusion

Substitution of local TiO_2 on the synthesis of LTO has been successfully done by solid state process at 6 h sintering process. Synthesized LTO still have other phases like Li_2TiO_3 , LiOH , and $\text{Ti}_{0.78}\text{O}$ that caused from element impurities from local TiO_2 . All samples have polyhedral shape, smooth texture, no porous and agglomeration. Increasing sintering time cause the particle size increase due to the grain growth during high temperature diffusion. The biggest material was $52.67 \mu\text{m}$ that sintered at 850°C for 8 h. In charge-discharge curve, all graphs seem as staircase curves because of presence two dominant phase such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li_2TiO_3 . The best capacity is 52mAh/g obtained by sintering for 6 h. The specific capacity is very determined by impurity contain, phases and particle size.

References

- [1] H. Li, Z. Wang, L. Chen, and X. Huang, Research on Advanced Materials for Li-ion Batteries, *Adv Mater*, **21**, 4593–4607, (2009).
- [2] H. Zhang, Y. Chen, J. Li, C. He, and Y. Chen, $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ composite anode material for large capacity and high-rate lithium ion batteries, *Int J Hydrogen Energy*, **39**, 16096–16102, (2014).

- [3] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, Li-ion battery materials: present and future, *Mater Today*, **18**, 252–264, (2015).
- [4] X. Chen, X. Guan, L. Li, and G. Li, Defective mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12-y}$: an advanced anode material with anomalous capacity and cycling stability at a high rate of 20 C, *J Power Sources*, **210**, 297–302, (2012).
- [5] C. C. Yang, H.-J. Hwu, S. J. Lin, W.-C. Chien, and J.-Y. Shih, Preparation of High-rate performance $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ Anode Material in $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ Batteries, *Electrochim Acta*, **125**, 637–645, (2014).
- [6] V. D. Nitya, R. K. Selvan, K. VEDIAPPAN, S. SHARMILA, and C. W. Lee, Molten salt synthesis and characterization of $\text{Li}_4\text{Ti}_5-x\text{Mn}_x\text{O}_{12}$ ($x=0.0, 0.05$ and 0.1) as anodes for Li-ion batteries, *Appl Surf Sci*, **261**, 515–519, (2012).
- [7] F. Gu and G. Chen, Carbon coating with Oleic Acid on $\text{Li}_4\text{Ti}_5\text{O}_{12}$, *Int J Electrochem Sci*, **7**, 6168–6179, (2012).