Synthesized Li$_4$Ti$_5$O$_{12}$ from Technical Grade Raw Material by Excess LiOH.H$_2$O as Anode Lithium Ion Battery

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Abstract. Li$_4$Ti$_5$O$_{12}$ powder as anode lithium ion battery was synthesized via solid state reaction with excess LiOH.H$_2$O. Technical grades raw materials like LiOH.H$_2$O and TiO$_2$ were used as starting materials. LiOH.H$_2$O excess was varied from 0; 2.5; 5 and 7.5% to get higher optimum phases and capacity of Li$_4$Ti$_5$O$_{12}$. All raw materials were mixed stoichiometry then followed by calcination and sintering process to get final products. The obtained products were characterized by XRD, SEM, and PSA to get properties of active materials and the electrochemical properties were done by cyclic voltammetry and charge-discharge test. The XRD test showed that 5% excess have highest Li$_4$Ti$_5$O$_{12}$ phases. All samples have same in morphology, agglomerate and same in particle size distribution. Sample with 5% excess showed good reversible process and charge-discharge test showed that increasing Li$_4$Ti$_5$O$_{12}$ phase can improve specific capacity.

1. Introduction

Lithium-ion batteries have been widely used as the major power sources for portable electronic devices and are regarded as a promising candidate of power sources for electric vehicles and large scale electricity storage stations [1]. Lithium ion battery is also one important device to store energy, it converts electrical energy to chemical energy when charge and vice versa when it uses. The lithium ion battery research has been done until now which focusing to increase capacity and capability. One application of lithium battery is for electric vehicle, electric energy can reduce CO$_2$ emission [2-3]. Lithium battery more confortable used in electric vehicle than others electrochemical devices. Today, there are two lithium battery technology i.e primary battery (not-rechargeable) and secondary battery (rechargeable). Battery that used for electric vehicle as energy storage system belong to secondary battery.

Battery consists of four components like cathode, anode, electrolyte and separator. Each component was made by different materials. Cathode materials that common used are LiFePO$_4$ and LiMnPO$_4$[4] while Anode material is graphite[5]. LiPF$_6$ [6] or LIBOB [7] are used as electrolyte as ion transfer media from cathode to anode and vice versa. Separator used to separate cathode and anode was made from polyethylene.

In this paper, we focus the research on anode materials. The conventional anode for lithium ion battery is graphite and others carbon based materials. But all these materials weren’t suitable for electric vehicle battery because of safety reason. Graphite and carbon based materials have very low working potential, it cause electrolyte decomposition when charge-discharge process especially in high rate.
Electrolyte will decompose become sharp dendrite lithium on anode surface and will wreck the separator [8][9].

Recently, Lithium titanate had chemical formula Li$_4$Ti$_5$O$_{12}$ or sometime called LTO becomes popular and more suitable candidate to replace carbon as anode material for lithium battery because it has some advantages. LTO has high insertion potential at around 1.55 V (vs. Li/Li$^+$), which can avoid the dendrite lithium growth on the anode surface at high charging rate. It can be almost fully charged within 10 min, exceptional cycle, ‘zero-train’ effect and the flat Li insertion voltage [10]. Besides, LTO has excellent Li-ion insertion and extraction reversibility and structure stability with almost negligible volume change during charge-discharge process [11]. So, LTO is indeed a potential candidate material for high-rate LIBs.

On previous work, it had synthesized Li$_4$Ti$_5$O$_{12}$ with raw materials such as LiOH.H$_2$O or Li$_2$CO$_3$ and TiO$_2$ via solid state method. The XRD results show that Li$_4$Ti$_5$O$_{12}$ phase only about 85-96% and TiO$_2$ phase about 4-15%. These result aren’t optimum. Herein, in this work Li$_4$Ti$_5$O$_{12}$ will be synthesized by vary addition LiOH.H$_2$O to get optimum phases [12][13].

2. Experiment

The Li$_4$Ti$_5$O$_{12}$ powders were synthesized by solid state reaction. LiOH.H$_2$O and TiO$_2$ were as Li and Ti sources. The experiment was done by varying LiOH.H$_2$O added 0; 2.5; 5; and 7.5 % weight. Stoichiometric raw materials were mixed by ball milling for 15 h. then all samples were calcined at 750°C for 2 h in an air atmosphere to remove organic compound. Finally, the products were sintered at 850°C for 4 h to obtain Li$_4$Ti$_5$O$_{12}$ powders. The crystal structure of the prepared samples was identified by XRD using Cu-K-alpha radiation (10° ≤ 20 ≤ 80°). SEM and PSA were used to investigate the morphologies and particle size of the as-prepared powders, respectively.

The electrochemical characteristics were evaluated by half-cell coin cell. The sample slurry was prepared by mixing active materials powders with conductive carbon (acetylene black) and binder (PVDF) at a weight ratio of 85:5:10 in DMAC solution. Subsequently, the slurry was coated on a copper foil using the doctor blade technique and dried at 80°C for 1 h to evaporate the DMAC solvent. The electrode foil was punched to 12 mm diameter disc, which were used to assemble the coin cell in an Ar glove box. Li metal was used as the counter and reference electrode in the cell. Polyethylene was the separator and 1M LiPF6 in EC:DEC solution with composition of 1:1 v/v was used as electrolyte. PE/PP-based film Celgard 2000 was used as a separator between the electrodes.

The charge-discharge experiments were conducted by using battery testing instrument (Wonatech WBCS3000, Automatic Battery Cycler). The cut-off voltage was set to be 1.0 V and 2.6 V for discharge and charge, respectively.

3. Result and Discussion

Fig 1 showed that Each XRD pattern consists of two dominant phases like Li$_4$Ti$_5$O$_{12}$ and rutile TiO$_2$ are respectively marked triangles and circles, respectively. Fig 1 also showed the formation of the phase Li$_4$Ti$_5$O$_{12}$ that the addition of LiOH.H$_2$O of 0%, 2.5%, 5% and 7.5%. Another phase formed is an impurity in the form of rutile TiO$_2$. Analysis by using highscore software obtained that composition Lithium Titanate and rutile TiO$_2$ as shown in Table 1. Results showed that the data processing phase Li$_4$Ti$_5$O$_{12}$ LiOH.H$_2$O formed on the addition of 0% is 94.50%, in increments of 2.5% was 94.70%, in increments of 5% is 95.90% and the addition of 7.5% is 95.50%. Diffraction peaks (20) Li$_4$Ti$_5$O$_{12}$ occur at 18°, 37°, 43°, 47°, 58°, 63°, 66°, 75°, 76° and 79°. Although the main phase have been obtained, but the rutile TiO$_2$ peaks at diffraction angles 27° caused final powder is not a single phase but it is a mixture Li$_4$Ti$_5$O$_{12}$ and rutile TiO$_2$. 
Figure 1. XRD pattern of Li₄Ti₅O₁₂ synthesized by varying LiOH.H₂O excess.

Table 1. Phases composition of Li₄Ti₅O₁₂ with LiOH.H₂O Excess from HIGHSCORE Software analysis.

| Sampel | Li₄Ti₅O₁₂ (%) | TiO₂ (%) |
|--------|---------------|---------|
| 0%     | 94,50         | 5,50    |
| 2,5%   | 94,70         | 5,30    |
| 5%     | 95,90         | 4,10    |
| 7,5%   | 95,50         | 4,50    |

LiOH.H₂O additions in the manufacture of active ingredients Li₄Ti₅O₁₂ managed to cause a phase rutile TiO₂ formed tend to decline until the addition of LiOH.H₂O as much as 5% and increased again in addition LiOH.H₂O as much as 7.5%. This shows that the addition of LiOH.H₂O in the synthesis cause initial mixture more evenly and more homogenous. Each item starting material of TiO₂ mixed with LiOH.H₂O so Li₄Ti₅O₁₂ phase is expected to increase.

Table 2. The particle size of the powder Li₄Ti₅O₁₂ synthesized with LiOH.H₂O excess

| LiOH.H₂O excess | Particle Size (µm) |
|-----------------|--------------------|
| 0 %             | 26,46              |
| 2,5 %           | 32,93              |
| 5,0 %           | 25,29              |
| 7,5 %           | 33,13              |

Figure 2 showed that SEM analysis results also showed a smooth texture on each sample. Li₄Ti₅O₁₂ particles shaped like small pebbles (small particles) that are agglomerate with size uniformly distributed (homogeneous). Whereas small particles have a variety of shapes such as round, oval, square and irregular. Addition of LiOH.H₂O does not affect the shape, texture, and particle size of Li₄Ti₅O₁₂.
Figure 2. SEM image of Li$_4$Ti$_5$O$_{12}$ powder with a magnification of 10k SE with LiOH.H$_2$O excess (a) 0% (b) 2.5% (c) 5% (d) 7.5%.

Figure 3. Cyclic Voltametry of Li$_4$Ti$_5$O$_{12}$ powder with LiOH.H$_2$O excess (a) 0% (b) 2.5% (c) 5% and (d) 7.5%.

Table 2 showed larger particle size as measured by CILAS Particle Size Analyzer Brand (1190). The more the addition LiOH.H$_2$O tend to increase the particle size, despite the increase in the size of the particle is not too significant. Particle size tends to be greater due to the total mass of the material during the milling process become more numerous.
Cyclic voltamograms of all sample obtained at a scan rate of 0.1 mV/s between 1 V and 2.5 V are shown in Figure 3. There are a pair reversible redox peaks for each sample, indicating all sample are rechargeable. Sample a and d have wide redox peak indicating bad electrode kinetic. While, sample b and c show sharp redox peak indicating rapid electrochemical process. It can be seen in Figure 3 that the CV of all sample are similar, suggesting that LiOH.H2O excess in Li₄Ti₅O₁₂ synthesis does not change the electrochemical reaction process of Li₄Ti₅O₁₂.

![Graphs](image)

**Figure 4.** Charge-Discharge Curve of Li₄Ti₅O₁₂ powder with LiOH.H₂O excess (a) 0% (b) 2.5% (c) 5% and (d) 7.5%.

**Table 3.** Half-cell battery capacity of Li₄Ti₅O₁₂ were synthesized by LiOH.H₂O excess

| Sample | Specific capacity (mAh/g) |
|--------|---------------------------|
| 0%     | 85                        |
| 2.5%   | 140                       |
| 5%     | 150                       |
| 7.5%   | 110                       |

Diagrams of voltage Vs capacity from charge-discharge test results are shown in Figure 4. All samples showed good charge-discharge curves. Samples 5% LiOH.H₂O excess showed best curve with flat charge-discharge plateau. Difference between charge-discharge plateau showed polarization. It can be seen that the charge-discharging test results indicate the presence of only one phase with a curve that is not marked with staircase. This is because the amount of TiO₂ rutile phase at each sample is less than 10%. The curve will staircase (mark the 2 phases) if the amount of rutile TiO₂ phase of more than 30%.

Results of analysis of the capacity of the battery cell with charge-discharging test are shown in Table 3. Along with the raw materials LiOH.H₂O capacity battery cells from each sample tended to
increase with increasing Li$_4$Ti$_5$O$_12$ phase is formed. This is caused by increasing of Li$_4$Ti$_5$O$_12$ phase and an impurity phase TiO$_2$ decreased.

4. Conclusion
Synthesis Li$_4$Ti$_5$O$_12$ with LiOH.H$_2$O excess has been successfully carried out by using solid state reaction. Crystal structure analysis by XRD test equipment showed the lowest rutile TiO$_2$ phase composition is shown by samples with the addition of LiOH.H$_2$O as much as 5%. Addition LiOH.H$_2$O in 4 variants of the sample does not alter the crystal structure on the results of XRD analysis but only affects the amount of phase composition and does not affect morphology and particle size. Morphology of each samples were agglomerate and form small particles with diverse forms. LiOH.H$_2$O additions increase the capacity of the battery cell because Li$_4$Ti$_5$O$_12$ phase increase and phase impurities (rutile TiO$_2$) decrease.

References
[1]. Yuuri G, Zhaoxiang W, Liquan C 2014 Stability of spinel Li$_4$Ti$_5$O$_12$ in air J Power Sources 245 684-690.
[2]. Robert F N 2000 Power Requirements for Batteries in Hybrid Electric Vehicles J Power Sources 91 2-26.
[3]. Armand M, Jean M T 2008 Building Better Batteries Nat 451 652-657.
[4]. Zagrib K, Trudeau M, Guerfi A, Trottier J, Mauger A, Veillette R, Julien C M 2012 New advanced cathode material: LiMnPO$_4$ encapsulated with LiFePO$_4$ J Power Sources 204 177-181.
[5]. Aojun B, Li W, Jiaoyang L, Xiangming H, Jixian W, Jianlong W 2015 Composite of graphite/phosphorus as anode for lithium-ion batteries J Power Sources 289 100-104.
[6]. Andreas H, Thomas H 2015 Novel electrolyte mixtures based on dimethyl sulfone, ethylene carbonate and LiPF$_6$ for lithium-ion batteries J Power Sources 298 322-330.
[7]. Noor I S, Majid S R, Arof A K 2013 Poly(vinyl alcohol)-LIBOB complexes for lithium-air cells Electrocim Acta 102 149-160.
[8]. Feng N, Yan B H, Baohua L, Hongda D, Dengyun Z, Feiyu K 2012 Effects of TiO$_2$ crystal structure on the performance of Li$_4$Ti$_5$O$_12$ anode material J. Alloys Compd 513 524-529.
[9]. Yan B H, Ming L, Zhen D H, Biao Z, Yang Y, Baohua L, Feiyu K, Jang K K 2013 Effect of solid electrolyte interface (SEI) film on cyclic performance of Li$_4$Ti$_5$O$_12$ anodes for Li ion batteries J Power Sources 239 269-276.
[10]. Euh D J, Hyun J H, Ok S J, Myoung G H, Chil H D, Min J H, Ho S Y, Hong K S 2012 Characterizations and electrochemical performance of pure and metal-doped Li$_4$Ti$_5$O$_12$ for anode materials of lithium-ion batteries Mater Res Bull 47 2847-2850.
[11]. Qianyu Z, Chengli Z, Bo L, Shifei K, Xi L, Yangang W 2013 Preparation and electrochemical properties of Ca-doped Li$_4$Ti$_5$O$_12$ as anode materials in lithium-ion battery Electrochim Acta 98 146-152.
[12]. Guo Q Z, Wenjuan L, Hongwei Y, Yahui W, Sowjanya B R, Yanli C, Chunbao Z, Keqiang D, Zhanhu G 2013 Influence of Preparation Conditions on the Properties of Lithium Titanate Fabricated by a Solid-state Method J. New Mat. Electrochem Systems 16 025-032.
[13]. Qian Y, Hailei Z, Jie W, Jing W, Chunmei W, Xinmei H 2014 Synthesis parameter dependence of the electrochemical performance of solvothermally synthesized Li$_4$Ti$_5$O$_12$ Mater Renew Sustain Energy 3:24.