Synthesis of Li$_4$Ti$_5$O$_{12}$ (LTO) by Sol-Gel Method for Lithium Ion Battery Anode

Yustinus Purwamargapratala$^{1*}$, Agus Sujatno$^1$, Yohanes Lugas Sabayu$^2$, Evvy Kartini$^1$

$^1$Centre of Advanced Materials Science and Technology, National Nuclear Energy Agency, South Tangerang 13310, Indonesia
$^2$Physical Engineering, Faculty Of Engineering, Surya University Tangerang, Indonesia

pratala_yustinus@yahoo.com

Abstract. Li$_4$Ti$_5$O$_{12}$ (LTO) is one of the material that has the potential as anode in lithium ion battery that is safe to use and has a long life cycle. In this research, LTO was synthesized by sol-gel method using oxalic acid as chelating material, it is expected to produce materials with smaller particles and homogeneous distribution. The LTO sol-gel compared to commercial LTO. Characterization was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS). The measurement of LTO battery performance is carried out by charge discharge and electron impedance spectroscopy. The sol-gel LTO has a purity of 99%, which is higher than 57% commercial LTO. The average particle size is 1 μm, and the conductivity is 7.6x10$^{-7}$ S.cm$^{-1}$. While commercial LTO has a purity of 57%, the average particle size is 30 μm and conductivity is 7.4x10$^{-7}$ S.cm$^{-1}$. Batteries with synthesized LTO anodes have a capacity of 25.9% higher in the first cycle and 110% higher in fifth cycles in comparison with batteries used commercial LTO anodes.

Keywords: Li$_4$Ti$_5$O$_{12}$, LTO, oxalic acid, sol-gel

1. Introduction

The development of technology has created a lot of equipment requiring electrical energy, especially batteries. A battery is a device that can convert the chemical energy it has into electricity. Batteries can be divided into two, namely primary and secondary batteries. Primary batteries are batteries that cannot be recharged while batteries that can be recharged and can be used again are called secondary batteries [1].

Lithium ion batteries are batteries that have great potential for the future. The existence of lithium ion batteries in the sales market began with Sony’s company announcing its new product called lithium ion batteries in 1991 [2]. The demand for lithium ion batteries continues to increase. The price of lithium ion batteries in 2016 has decreased by 73% since 2010. Although the price has decreased, the growth in demand for lithium ion has increased throughout the year [3]. Lithium ion batteries have energy density, efficiency, and a high life cycle, can store a lot of energy in the smallest volume, and can work well for a long time [4].

Anode is a negative electrode that functions as an electron release which then moves to the external circuit and undergoes oxidation when the electrochemical reaction occurs. Anode material affects the nature of the battery [1]. The ideal properties of anodes are low atomic weights, cheap, high ionic and...
electrical conductivity [5]. With safety considerations, lithium ion batteries use lithium metal as an anode, hence the type of carbon anode, mixed metal, metal oxide and sulfide is developed [5-6]. Graphite is an anode material that is most widely used in the manufacture of lithium ion batteries because it has a high energy density, however it has the disadvantage of having a short life cycle and short circuit prone characteristics, an alternative anode is Li$_4$Ti$_5$O$_{12}$. The use of Li$_4$Ti$_5$O$_{12}$ has the advantage of safe batteries and a long life cycle [4,7-10].

Li$_4$Ti$_5$O$_{12}$ can be synthesized by solid state, sol-gel, hydrothermal, and so on. The synthesis method that is often used in the manufacture of Li$_4$Ti$_5$O$_{12}$ is solid state synthesis because it is easier, and cost-effective, but it is difficult to adjust particle size, particle size distribution, and lack of stoichiometric control [7,11-13]. Particle size can affect the performance of the anode, therefore alternative synthesis is needed that can overcome the problem. Sol-gel synthesis is a synthesis that can make particles smaller and spread more homogeneously [7]. In the sol-gel synthesis the number of chelating agents can affect the end result of the [11-12]. Chelating agent plays a major role in the formation of Li$_4$Ti$_5$O$_{12}$ because it affects particle size. Oxalic acid is one of the chelating agents that can be used in the synthesis of Li$_4$Ti$_5$O$_{12}$ [11].

The aim of this study to synthesis LTO with sol-gel method by titanium butoxide and compared the results with commercial Li$_4$Ti$_5$O$_{12}$ both in the form of anode material. The performance of the lithium batteries will be characterized.

2. Experimental method

Sol-gel synthesis was carried out according to the steps of Qiu [14] but using titanium butoxide as a source of titanium and lithium acetate dihydrate as sources of lithium. The lithium dihydrate acetate is dissolved in ethanol and deionized air with the ratio of ethanol and deionized air to 5:1. Oxalic acid is added to the solution with the ratio of oxalic acid and ethanol to 1. The dissolved titanium butoxide is added to the solution and stirred for 4 hours, then left for 12 hours. The material that has reached maturity is dried at 80 °C for 6 hours. Then it is crushed and put into a container and heated at 200 °C for 30 minutes, at a temperature of 500 °C for 30 minutes and calcined at a temperature of 800 °C for 1 hour. The product from Li$_4$Ti$_5$O$_{12}$ synthesis by the sol-gel method is called solgel LTO and from commercial materials called commercial LTO [13].

Observation of the morphology and particle size of LTO was carried out by scanning electron microscopy (SEM), while the crystalline phase was measured by X-ray diffraction (XRD). LTO sheet was produc by LTO mixing with PVDF and NMP using a vacuum mixer. The LTO mixture is coated on a copper sheet. The electrochemical profiles was measured by LCR and a battery tester.

3. Results and discussion

Observation of the crystal structure was carried out using X-ray diffraction and analyzed using the High Score Plus method on the sol-gel LTO and commercial LTO, as shown in Figure 1.

The results of X-ray diffraction with the main peaks at 2.3°, 18.3°; 35.5°; 43.2°; 47.2°; 57.1°; 62.7°; 65.9°; 74.2°; and 79.2° shown in Figure 1. Data were analyzed using the High Score Plus method. In accordance with the database, high scores plus used numbers 98-008-4973 and number 98-026-1239, sol-gel LTO and commercial LTO contain Li$_4$Ti$_5$O$_{12}$ and Li$_2$Ti$_3$O$_7$.

Table 1 shows the refinement results of XRD data by HighScore Plus (HSP). It is shown that sol-gel LTO and commercial LTO have 2 phases with different compositions. LTO sol-gel resulted about 99% Li$_4$Ti$_5$O$_{12}$ and 1% Li$_2$Ti$_3$O$_7$, whereas commercial LTO contained 57.7% Li$_4$Ti$_5$O$_{12}$ and 42.3% Li$_2$Ti$_3$O$_7$. The analysis also shows that Li$_4$Ti$_5$O$_{12}$ corresponds to a space group F-3 m with a cubic while Li$_2$Ti$_3$O$_7$ belongs to a space group C 1 2/c 1 with a monoclinic.
Figure 1. X-ray diffraction pattern from LTO (a) sol-gel LTO (b) commercial LTO.

Table 1. X-ray Refinement results of sol-gel LTO and commercial LTO.

|            | Chemical Formula | Space group | QPA wt% | Crystallite Size (nm) | Strain (%) | Lattice Parameters | R_{ref}^2 (%) | R_{exp}^2 (%) | \chi |
|------------|------------------|-------------|---------|-----------------------|------------|--------------------|---------------|---------------|-----|
| **Sol-gel LTO** | Li_{4}Ti_{5}O_{12} | F d -3 m    | 99.0    | 561.50                | 0.000403   | 8.3561             | 8.3561        | 8.3561        | 7.61| 5.05| 1.43 |
|            | Li_{2}TiO_{3}    | C 1 2/c 1   | 1.0     | 855.03                | 0.000416   | 5.0700             | 8.9000        | 9.5900        |    |    |     |
| **Commercial LTO** | Li_{4}Ti_{5}O_{12} | F d -3 m    | 57.7    | 396.42                | 0.000143   | 8.3590             | 8.3590        | 8.3590        | 7.48| 5.08| 1.47 |
|            | Li_{2}TiO_{3}    | C 1 2/c 1   | 42.3    | 383.30                | 0.000136   | 5.0650             | 8.7900        | 9.7670        |    |    |     |

Figure 2. SEM Observation Results 1000x magnification from LTO (a) Sol-gel LTO (b) Commercial LTO.

Analysis uses a scanning electron microscope (SEM) to study sample morphology, both in shape and size. In Figure 2 shows the SEM photo with a magnification of 1000 times, from LTO synthesized by the commercial sol-gel and LTO method. Figure 2(a) shows that the particles of sol-gel LTO appear to be in the form of sheets with an average particle size of 1 μm. The sheet form will improve to
material conductivity, because it will facilitate the distribution of lithium ions. Figure 2(b) shows granular commercial LTO particles with an average size of 30 μm.

![Graph showing conductivity comparison](image)

**Figure 3.** The Conductivity of sol-gel LTO and commercial LTO.

**Table 2.** Conductivity of sol-gel LTO and commercial LTO.

| Sample         | Conductivity       |
|----------------|--------------------|
| Sol-gel LTO    | $7.6 \times 10^{-7}$ S.Cm$^{-1}$ |
| Commercial LTO | $7.4 \times 10^{-7}$ S.Cm$^{-1}$ |

The conductance measure by EIS with a voltage of 1V in the frequency range 42 Hz - 5M Hz as shown in figure 3 and Table 2. Table 2 shows conductivity sol-gel LTO is $7.6 \times 10^{-7}$ S.cm$^{-1}$ and the commercial LTO is $7.4 \times 10^{-7}$ S.cm$^{-1}$. This conductivity value is not quite different in the same order. This shows that the sol-gel LTO conductivity is similar to the commercial LTO.

The charge discharge of battery measurement with a rate of 0.05C and a voltage range of 0.2 V to 3.0 V for battery cell systems sol-gel LTO/LiFePF$_6$/LiFePO$_4$ and commercial LTO/LiFePF$_6$/LiFePO$_4$ were shown in Figure 4.

![Graph showing charge discharge comparison](image)

**Figure 4.** Charge discharge of Sol-gel LTO and Commercial LTO anode battery curves at (a) cycle 1st and (b) cycle 5th.
Figure 4 shows the result of first cycle charge discharge battery with the sol-gel LTO as anode material and using a commercial LTO. In cycle 1, the battery of sol-gel LTO as anode has the first output voltage of around 1.75 V and capacity is 170 mAh.g\(^{-1}\) and capacity of commercial LTO as battery is 135 mAh.g\(^{-1}\), this means capacity of the sol-gel LTO as battery was 25.9% higher than commercial LTO as battery. Figure 4(b) shows the status of batteries in the fifth cycle around high voltage 1.4 V - 1.6 V. The capacity of sol-gel LTO as anode battery is 160 mAh.g\(^{-1}\) and the capacity of commercial LTO as anode battery is 75 mAh.g\(^{-1}\), this means capacity of the sol-gel LTO as battery was 110% higher than commercial LTO as battery.

**Figure 5.** Battery performance of sol-gel LTO anode and commercial LTO anode.

Figure 5 shows the 1\(^{st}\) to 5\(^{th}\) cycle of the battery performance. In the 1\(^{st}\) cycle it can be seen that sol-gel LTO anode batteries have a higher capacity than commercial LTO anode batteries. As cycles increase, sol-gel LTO anode batteries have a more stable capacity when compared to commercial LTO anode batteries. The sol-gel LTO anode battery has a slope of -2.3 and a commercial LTO anode battery of around -15.4. The more flat the battery performance cycle, the longer the battery life cycle [11].

**Table 3.** Capacity of the sample.

| Ciclus | Sol-gel LTO anode battery | Commercial LTO anode battery |
|--------|---------------------------|-------------------------------|
|        | Charge (mAh.g\(^{-1}\)) | Discharge (mAh.g\(^{-1}\)) | Coloumbic Efficiency (mAh.g\(^{-1}\)) | Charge (mAh.g\(^{-1}\)) | Discharge (mAh.g\(^{-1}\)) | Coloumbic Efficiency (mAh.g\(^{-1}\)) |
| 1      | 204.05                    | 171.94                       | 84.27                                | 197.59                     | 135.62                      | 68.64                                |
| 2      | 173.30                    | 167.30                       | 96.54                                | 131.69                     | 121.00                      | 85.93                                |
| 3      | 170.86                    | 166.06                       | 97.19                                | 115.48                     | 98.15                       | 88.81                                |
| 4      | 167.55                    | 162.92                       | 97.24                                | 96.76                      | 85.93                       | 88.81                                |
| 5      | 164.15                    | 162.63                       | 99.07                                | 87.78                      | 76.20                       | 86.81                                |

Table 3 shows battery capacity with both LTO anodes. In the first cycle, the sol-gel LTO anode battery had Coulumbic Efficiency (CE) of 84.27% and for the next cycle above 96%. The commercial LTO anode battery in the first cycle has CE 68% and the next cycle is above 85%. The results show that the battery performance of sol-gel LTO anode has higher capacity and has a longer life cycle [15].
4. Conclusion
The synthesis of LTO with the sol-gel method has been carried out and the results was compared with commercial LTO. LTO synthesized using the sol-gel method has a purity of 99%. The sol-gel LTO has average particle size 1 μm, and conductivity 7.6x10⁻⁷ S.cm⁻¹. While commercial LTO has a purity of 57%, the average particle size is 30 μm and conductivity is 7.4x10⁻⁷ S.cm⁻¹. Batteries with a sol-gel LTO anode has a capacity of 25.9 % higher in the first cycle and 110 % higher in fifth cycles using with commercial LTO anodes batteries.

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