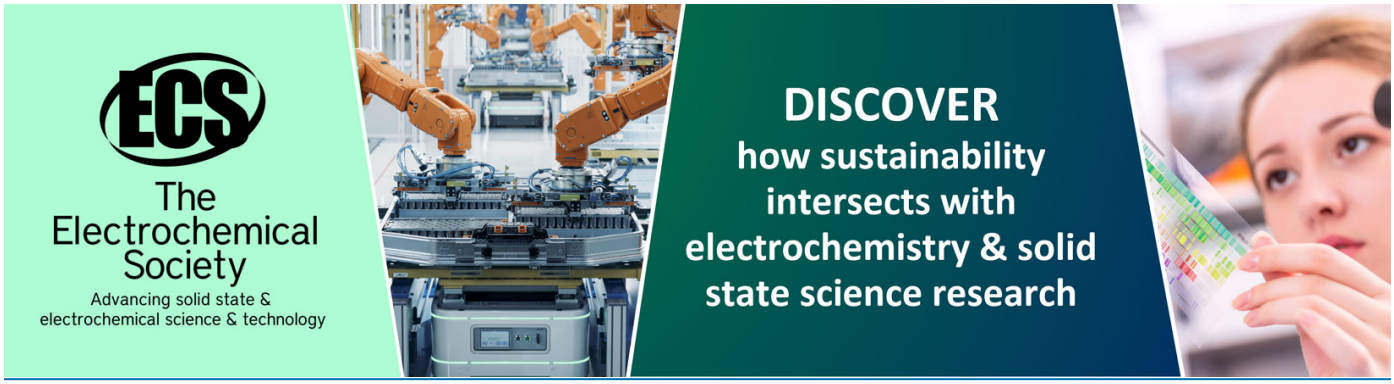
# Facile and rapid method of synthesizing Lithium Titanate for the use in energy storage





# Facile and rapid method of synthesizing Lithium Titanate for the use in energy storage

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Batteries are an important facet in today's world. With smaller devices being produced, the challenge to power it with long lasting batteries continue to be quite the task. Recently, a new compound has proved its usefulness in battery fabrication that is Lithium Titanate (LTO). In this study a facile method of producing LTO via hydrolysis of Lithium Nitride and Titanium n-Butoxide. The method used in this study produced LTO in under 7 hours, much quicker than the standard processing time for LTO. The produced LTO is characterized using Raman Spectroscopy.

## 1. Introduction

Batteries make the world turn around. As the source of portable electricity most devices in the modern time, if not all, are fitted with at least one battery. With many form factors and capacities, current research is geared towards improving the battery, from its capacity density, to shorter recharging times and increasing the number of charge-discharge cycles it can go through.

### *1.1 Batteries as energy storage devices*

Batteries were first proposed and fabricated by a Alessandro Volta, following the observation of the generation of electricity by contact of two different metals with a liquid interface between them [1]. Following that, various other scientists and researchers found that by changing the metal contacts, the voltage of the electricity generated could be changed, which now is understood as the electrochemical series. From then until now, research has been devoted to create increasingly minute batteries with ever increasing capacity. Some commercially available batteries in modern times are alkaline batteries, zinc and carbon batteries, lead batteries, and lithium based batteries.

### *1.2 Lithium based batteries*

Lithium based batteries are advantageous for a number of reasons, that is, high capacity density [2] , good life cycle, good thermal stability, commercially available, and economical in costs [3]. Lithium ion batteries were made to rectify the shortcomings of lithium batteries, which were relative instability, prone to catching fire, and were mostly primary batteries [4]. These batteries typically had a manganese dioxide cathode that were fashioned into a button cell.

Lithium ion batteries were first proposed in 1973 [5] and produced in 1977 [6] by different researchers. Lithium ion batteries seek to improve stability, while maintaining or improving battery capacity, providing rechargeability by the intercalation of the lithium ions with electrodes, and reducing costs. Other compounds as well have been researched to be used with lithium ion batteries, some being commercially available, such as Cobalt Dioxide [7], Lithium Nickel Manganese Oxide [8], Lithium Iron Phosphate Oxide [9] and many others [10–12].

One such compound that is the focus of this research is Lithium-Titanate (LTO). LTO has two separate compounds, one $Li_2TiO_3$ and one $Li_4Ti_5O_{12}$, also referred to as spinel LTO from its surface structure. Spinel LTO, hereon referred to simply as LTO, will be fabricated in this study using a low cost and fast hydrolysis method.

## 2. Background of Experiment

LTO has been synthesized in laboratories by various researches through various methods, for example, hydrothermal method [13–15], sol-gel method [16–18], solid-state route[19] and spray drying [20]. While they certainly are successful in synthesizing high quality LTO, most synthesizing methods require durations of 12 hours and above. That was the driving force of this research, that is, to reduce the duration for synthesizing LTO.

A hydrothermal route was chosen for this study, with some modification to the method to reduce to sintering temperatures, at 500°C in this study, as well as total length of time to synthesize LTO, which was at the most 7 hours including preparation of reactants and processing. This also was to reduce manufacturing costs as longer synthesizing durations meant less output over time, which is vital in a modern industry where mass production processes would need to be streamline and effective to compete on the global market.

## 3. Methodology

LTO was synthesize from the hydrothermal route following hydrolysis reactions and the combination of Lithium Hydroxide (LiOH) and Titanium Dioxide ($TiO_2$). The equation for the reaction is as follows:

$$4LiOH(aq) + 5TiO_2(s) \longrightarrow Li_4Ti_5O_{12}(s) + 2H_2O(aq)$$

The LTO were synthesized in the lab with the procedure outlined, following Figure 1 below:

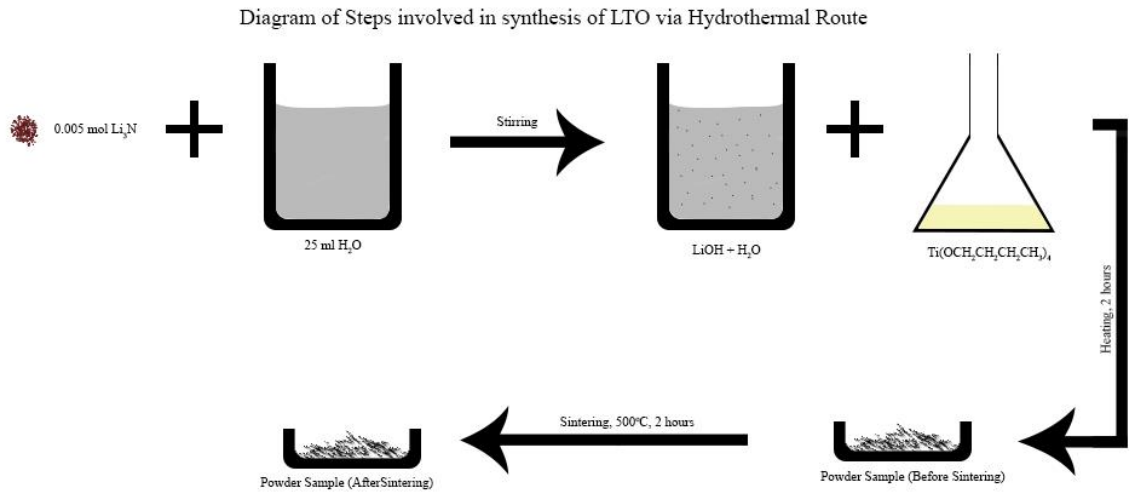


**Figure 1.** Diagram of steps involved in the synthesis of LTO via hydrothermal route.

*3.1 Synthesis of Lithium Hydroxide*

Lithium hydroxide was synthesized by the hydrolysis of Lithium Nitride ($Li_3N$) which releases ammonia as the equation below:

$$Li_3N(s)+3H_2O(aq)\rightarrow 3LiOH(aq)+NH_3(g) \quad (1)$$

0.005 mol of Lithium Nitride reacted with 25 ml of water to make 0.015 mol of aqueous Lithium Hydroxide. As Lithium Nitride is known as explosive in its reaction to water, the powder was added carefully in small amounts to the water to prevent accidental ignition or explosions from occurring. The final solution is slightly cloudy, indicating the presence of Lithium Hydroxide.

*3.2 Hydrolysis of Titanium Dioxide*

Titanium Dioxide was hydrolysed from a Titanium n-Butoxide precursor. This precursor reacts instantaneously with water to produce Titanium Dioxide precipitate and butanol as shown below:

$$C_{16}H_{36}O_4Ti(aq) + 2H_2O(aq) = TiO_2(s) + 4C_4H_9OH(aq) \quad (2)$$

10 ml of Titanium n-Butoxide was added slowly into the Lithium Hydroxide synthesized earlier. A white precipitate of Titanium Dioxide was formed as a film on the surface of the water.

*3.3 Thermal removal of water and synthesizing Lithium Titanate*

The solution was heated at 90°C for 2 hours to remove aqueous ammonia (boiling point : 37.7 °C), before the temperature was increased to 150°C for another 2 hours. This was done in order to remove the water and butanol from the solution, and to facilitate the synthesis of LTO. After 2 hours, the aqueous solution was dried and a cloudy white powder remained.

The white powder, which may contain traces of unreacted Titanium Dioxide and Lithium Hydroxide, was annealed at 500°C for 2 hours. Raman spectroscopy before and after the final sintering process was performed on the sample and was detailed in the following chapter.

**4. Results and discussions**

In this study, Lithium-Titanate was synthesized by the hydrolysis of Lithium Nitride and Titanium Dioxide, and then sintered at 500°C for 2 hours. Characterization of the LTO was done by using Raman spectroscopy as shown below.

*4.1 Before sintering at 500°C*

Before sintering at 500°C, the sample LTO was characterized by Raman Spectroscopy to determinethe presence of LTO if any. The peaks noted from the sample were at 134 $cm^{-1}$, 193 $cm^{-1}$, 283 $cm^{-1}$, 431 $cm^{-1}$, 484 $cm^{-1}$, 587 $cm^{-1}$, 641 $cm^{-1}$, 704 $cm^{-1}$ and 868 $cm^{-1}$ with the spectroscopy data shown in Figure 2 below:

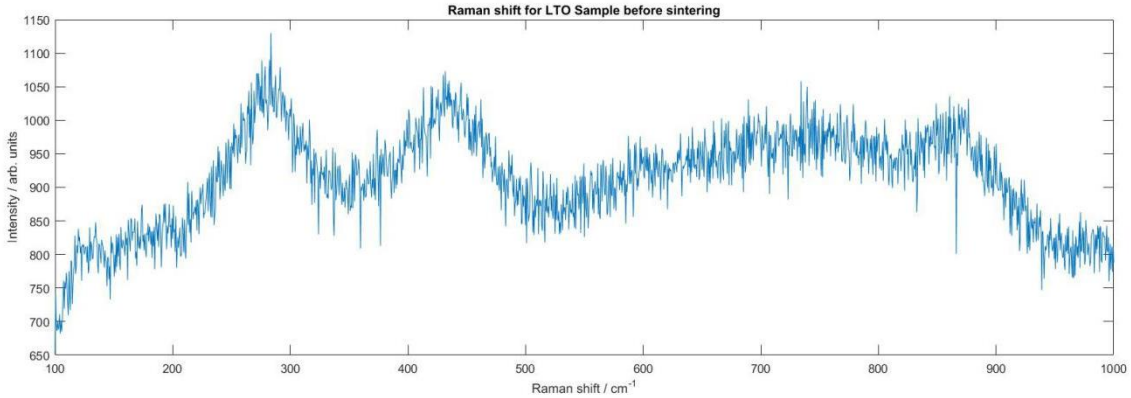


**Figure 2.** Raman shift data for the sample before sintering.

From the graph we can note that there is a shift about 50 $cm^{-1}$ in each of the peaks from the corresponding peaks of LTO.Thus, we hypothesized that the shift was due to an instable bond length of the powder, caused by the incomplete composite of LTO/LiOH/$TiO_2$. Therefore, sintering at temperatures above 500°C is vital in the completion of the reaction towards LTO.

*4.2 After sintering at 500°C*

After sintering at 500°C for 2 hours, the appearance of powder remains unchanged, even though there were a shift of the peaks at 220 $cm^{-1}$. 293 $cm^{-1}$, 349 $cm^{-1}$, 402 $cm^{-1}$, 418 $cm^{-1}$, 564 $cm^{-1}$, and 693 $cm^{-1}$. This is indicative of the 3 main vibrational modes of LTO, that is $F_{2G}$, $E_G$, and $A_{1G}$ modes. The more prominent peak of 693 $cm^{-1}$ can be attributed to Ti-O stretches of $TiO_6$ [21]. At the other end, the 220 $cm^{-1}$ peak can be attributed to O-Ti-O bonds [22]. The central 418 $cm^{-1}$ peak indicates stretching of the Li-O bonds in $LiO_4$ and $LiO_6$ [23].

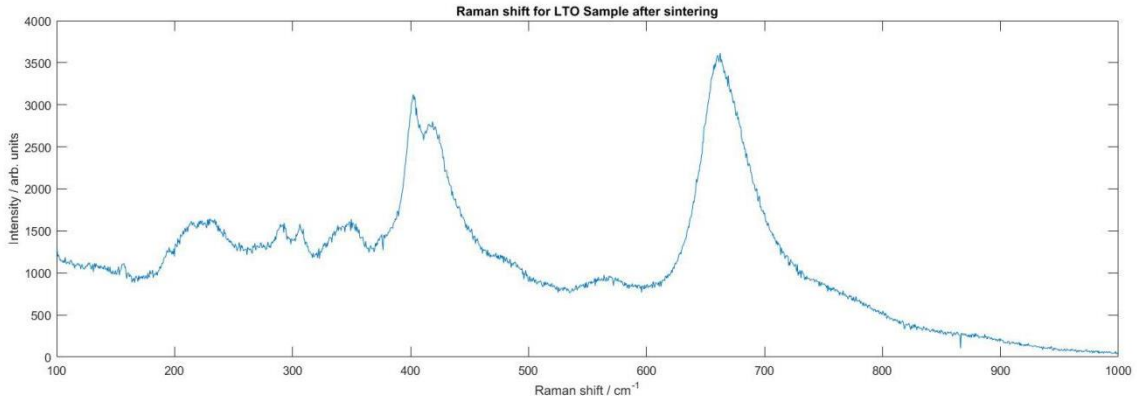


**Figure 3.** Raman shift data for LTO samples after sintering.

Shifting of the Raman peaks can only be observed when there are some changes of atomic properties in the material, such as bond length. The shifting of the peaks to the left is attributed to a decreasing bond length between the Lithium, Titanium and Oxygen, forming a spinel LTO structure.

Sintering temperatures of about 500°C is vital for the formation of spinel LTO, as the calcination of LTO occurs at a temperature of 350°C and above[24]. Another thing noted is the process time. Past literature denotes a hydrothermal process for 8 hours or more [21, 22, 24], but in this study LTO was successfully formed after only 2 hours. A possible factor would be the use of Titanium n-butoxide instead of Titanium Tetraisopropoxide (TTIP) in this study. Lower durations were also recorded in similar research using Titanium n-butoxide [25]. Thus, the use of different precursors could influence the overall process duration of the LTO synthesis.

## 5. Conclusion

In this study, LTO was synthesized with a complete process duration of under 7 hours using Titanium n-butoxide, indicating using other precursors may shorten the duration of synthesizing LTO. Raman Spectroscopy analysis validated the presence of LTO, and that sintering at 500°C or more is necessary in producing the final LTO product.

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