

CHAPTER 4:

**STUDIES ON LITHIUM
TITANATE**

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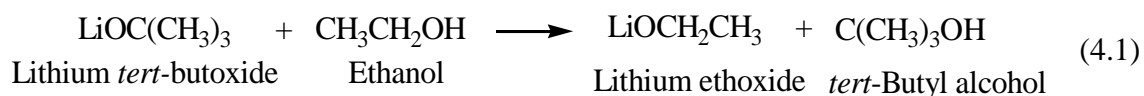
4.1 Introduction

Many experiments have been carried out in order to study the physical and chemical properties of the samples prepared. In this study, lithium titanium oxide was prepared by the sol-gel method and characterized using thermo gravimetric-mass spectroscopy (TGMS), fourier transform infrared (FTIR) spectroscopy and x-ray diffraction (XRD). The performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material is tested out in an electrochemical cell.

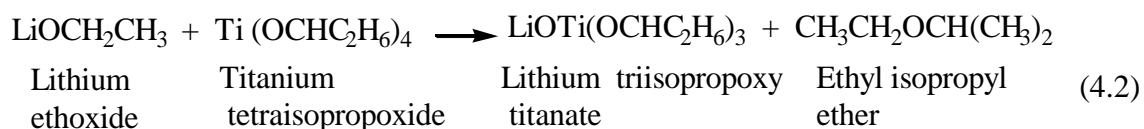
4.2 Thermo gravimetric-mass spectroscopy (TGMS)

The lithium titanium oxide precursors were synthesized by the sol-gel technique. 0.05 mol lithium *tert*-butoxide (LTB) and 0.03 mol titanium isopropoxide (TIP) were dissolved in a solvent containing a mixture of water and ethanol with water to ethanol volume ratio of 1:1.6. Due to the complex chemical reaction of lithium titanate preparation, TGMS analysis was first performed to analyze the thermal stability and composition of the compound.

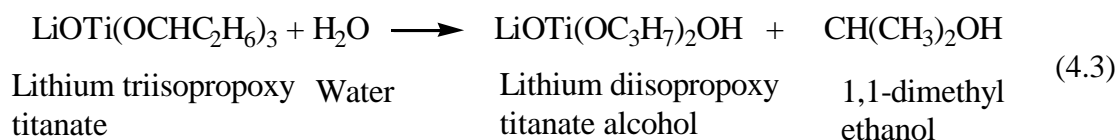
Let *et al.*, (2008) reported that metal alkoxide is highly reactive towards nucleophilic attack. A nucleophilic species is an electron rich species and can donate its electron to the electron hungry counterpart. Lithium *tert*-butoxide, $\text{LiOC}(\text{CH}_3)_3$ in powder form dissolves in ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ to yield lithium ethoxide, $\text{LiOCH}_2\text{CH}_3$ and *tert*-butyl alcohol, $\text{C}(\text{CH}_3)_3\text{OH}$. The potential reaction is shown in Equation (4.1).



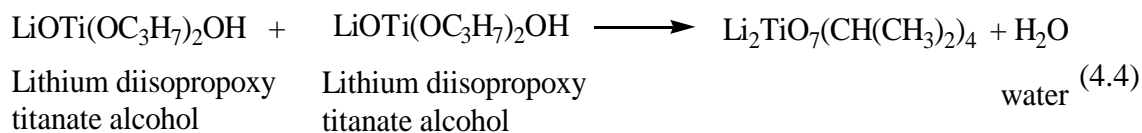
Lithium ethoxide, $\text{LiOCH}_2\text{CH}_3$ then reacts with titanium tetraisopropoxide, $\text{Ti}(\text{OCHC}_2\text{H}_6)_4$ according to Equation (4.2) yielding a clear yellow solution. In the reaction C_3H_7 from one of the $-\text{O}-(\text{CH}_2)_2-\text{CH}_3$ branches attached to Ti exchange places with Li from the ethoxide. Oxygen in $-\text{O}-\text{Ti}-$ reacts with Li^+ and C_3H_7 that is partially positive reacts with $-\text{OCH}_2\text{CH}_3$ in which the oxygen atom is partially negative.



Due to the presence of water, lithium triisopropoxy titanate, $\text{LiOTi}(\text{OCHC}_2\text{H}_6)_3$ undergoes hydrolysis. The hydrolysis reaction substitutes the alkoxide with a hydroxyl group [Let *et al.*, 2008; Nouwen *et al.*, 1996]. The nucleophilic group in water will bond with the more positive titanium and cause ethanol to form when $\text{O}-(\text{CH})-\text{C}_2\text{H}_6$ reacts with a proton from the water molecule. The possible chemical reaction is shown in Equation (4.3).



Nouwen *et al.*, (1996) has reported that, alcoholates acts as bridging ligands to form oligomers. The hydrolyzed group will further react by condensation reaction to form an isopropoxide with Ti-O-Ti bridging bonds [Let *et al.*, 2008]. The possible mechanism for reaction is shown in Equation (4.4).



Madarasz *et al.*, (2007) reported that excess of organics in the prepared sample can be removed by thermal treatment. The $\text{Li}_2\text{Ti}_2\text{O}_7(\text{CH}(\text{CH}_3)_2)_4$ precursor was heated at 100 °C for one hour to remove the water formed during the reaction. Figure 4.1 shows the TGMS profile for the powder precursor after heated in an oven at 100 °C for one hour.

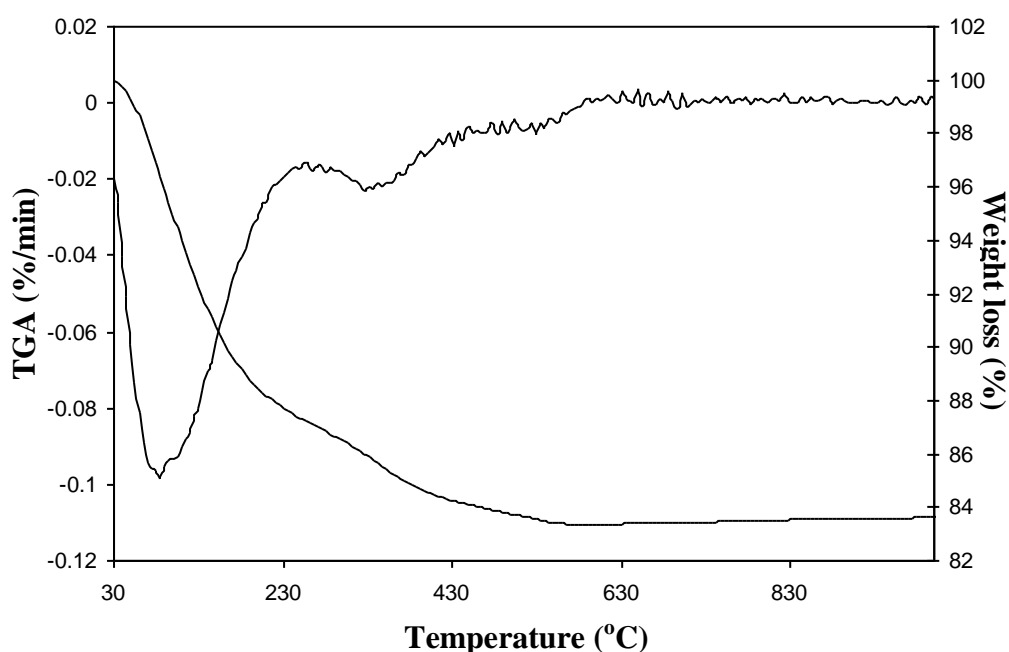


Figure 4.1: TG-MS profile for the powder precursors of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated in oven at 100 °C for one hour.

It can be observed that, phase transitions occurred from 30 °C to 600 °C. Two main regions of weight loss can be observed where the first region of weight loss was detected at 90 °C to 230 °C. This is due to water evaporation which is thermally stressed at 100 °C [Let *et al.*, 2008; Ibrahim and Abu-Ayana, 2008; Jais *et al.*, 1996] and weight loss is 12.98 %. Weight loss at temperatures 250 °C to 600 °C is due to the decomposition of organic compounds since many organic compounds such as ethers

and alcohols can be formed during hydrolysis and condensation reactions [Mullens *et al.*, 2002]. The weight loss for this region is 3.38 %.

Depicted in Figure 4.2 is the mass spectroscopic gas evolution curve of some selected fragments of the decomposition as released from the precursor that has been heated in oven at 100 °C for one hour. It can be observed that the decomposed product with $m/z=18$ (H_2O) exhibit two peaks at 353 °C and 540 °C. Likewise the fragment with $m/z=44$ (CO_2) exhibits two peaks at 357 °C and 536 °C. Methyl-methoxide with $m/z=46$ exhibits a distinct peak at 357 °C and 536 °C.

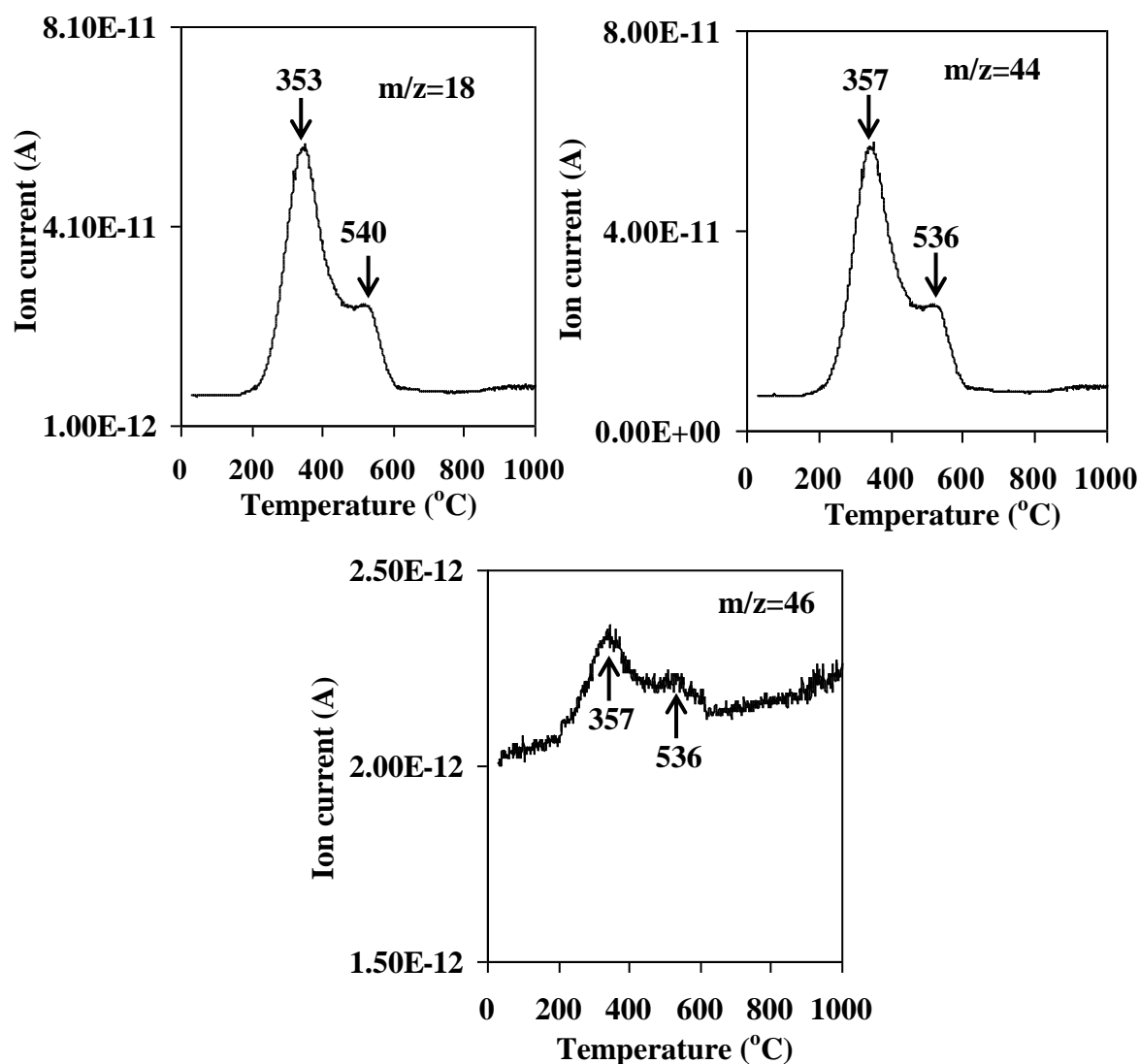


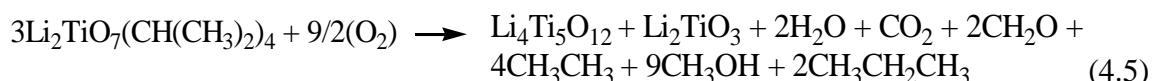
Figure 4.2: Thermal degradation of powder precursors of $Li_4Ti_5O_{12}$ heated in oven at 100 °C for one hour.

Table 4.1 lists the mass loss with the corresponding chemical compounds released in the gaseous form from 30 °C to 1000 °C. All the respective compounds are organic with boiling point lower than 600 °C.

Table 4.1: List of weight losses for sample pre-heated at 100 °C.

Mass (g/mol)	Compounds
18	H ₂ O
30	CH ₃ CH ₃ (ethane) CH ₂ O (formaldehyde)
32	CH ₃ OH (methanol) O ₂
44	CO ₂ CH ₃ CH ₂ CH ₃ (propane)
46	CH ₃ -O-CH ₃ (methyl methoxide)

From Figure 4.1 the wanted product can be expected to form if the precursor is heated at 600 °C and above. From the results obtained, it may be inferred that if the precursor were to be heated in air at 600 °C and above the following reaction occurs.



The reaction suggests that two forms of lithium titanate maybe produced.

4.3 X-ray diffraction (XRD)

Identification and purity of the products can be determined by matching the diffractogram of the prepared samples with the diffractogram of good-quality single phase pattern of powder data file. Shown in Figure 4.3 are the diffractograms of the precursor pre-heated at 100 °C and 600 °C for one hour. Broad peaks can be observed at $2\theta=43.70^\circ$ and $\sim 64.15^\circ$.

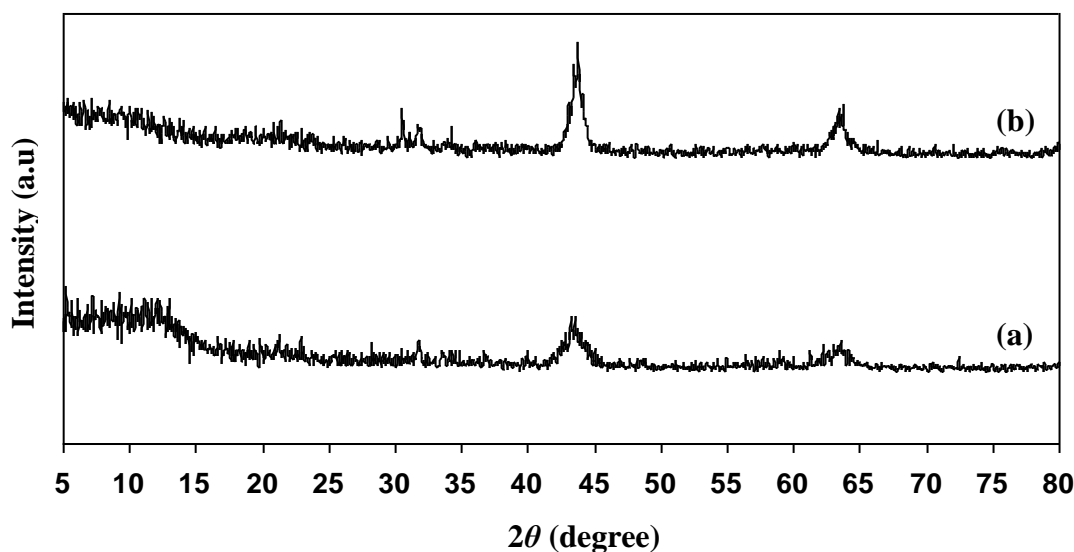


Figure 4.3: XRD profile for the powder precursors of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated in oven at (a) 100 °C and (b) 600 °C for one hour.

The x-ray diffractograms for the precursor sintered for one hour at the temperatures 700 °C, 800 °C, 900 °C and 1000 °C are shown in Figure 4.4. It is observed that, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is formed but at temperatures above and equal to 700 °C. All peaks present in diffractogram reported by Raja *et al.*, (2009) are also present in the diffractogram of the present work except for the peak at $2\theta=27.65^\circ$ which is the (220) plane in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and 55.57° which is an impurity rutile TiO_2 phase. In the diffractogram of this work, there is a small peak at $2\theta=20.35^\circ$ which is not present in the diffractograms of Raja *et al.*, (2009) and Zaghbi *et al.*, (1999). This small peak is attributed to Li_2TiO_3 [Wang *et al.*, 1999]. Previous works on the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ reported that the optimum sintering

temperature for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is $800\text{ }^\circ\text{C}$ in order to avoid the loss of lithium elements by evaporation process [Yuan *et al.*, 2008] and formation of impurities [Yan *et al.*, 2009]. As the sintering temperature is increased to $900\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$ additional peaks are observed between $2\theta=22^\circ$ to 23° and following Wang *et al.*, (1999) is attributed to Li_2TiO_3 . Thus the prepared mechanism where $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compound is expected to form maybe true.

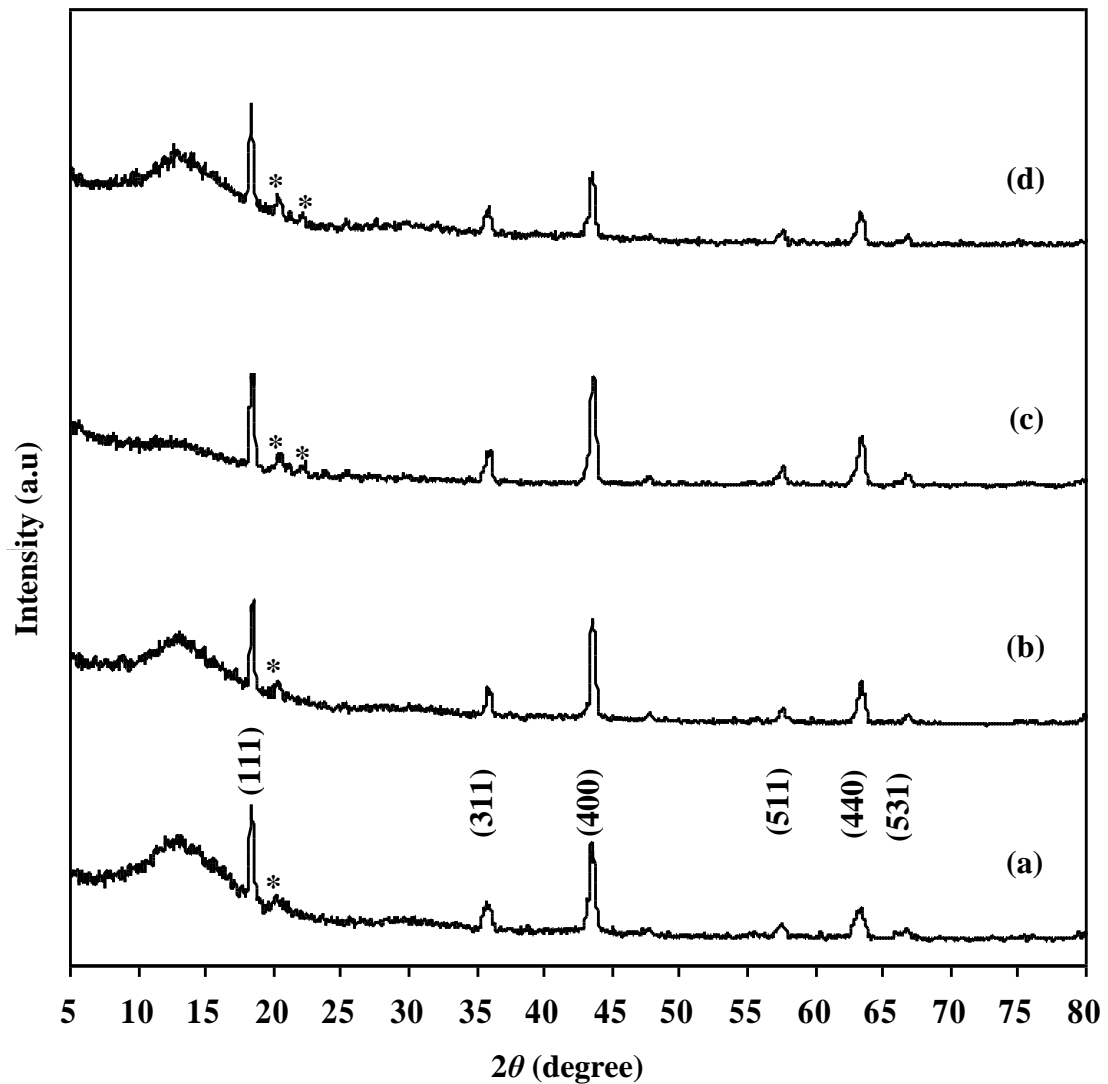


Figure 4.4: XRD pattern for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at (a) $700\text{ }^\circ\text{C}$, (b) $800\text{ }^\circ\text{C}$, (c) $900\text{ }^\circ\text{C}$ and (d) $1000\text{ }^\circ\text{C}$ for one hour. (*) indicates impurity due to Li_2TiO_3 .

The temperature of $800\text{ }^\circ\text{C}$ was chosen to heat fresh precursor samples for one, two, three, four and five hours. Results are shown in Figure. 4.5. It can be observed that the hump at low 2θ angles have decreased with increasing sintering time. Raja *et al.*, (2009)

have obtained $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with anatase TiO_2 impurity on heating the precursor at 800°C for 10 hours. Although Yuan *et al.*, (2008) have stated that the optimum sintering temperature for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is 800°C , they have successfully synthesized pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by combustion synthesis followed by sintering at 850°C for 17 hours. There were no impurities due to TiO_2 anatase phase.

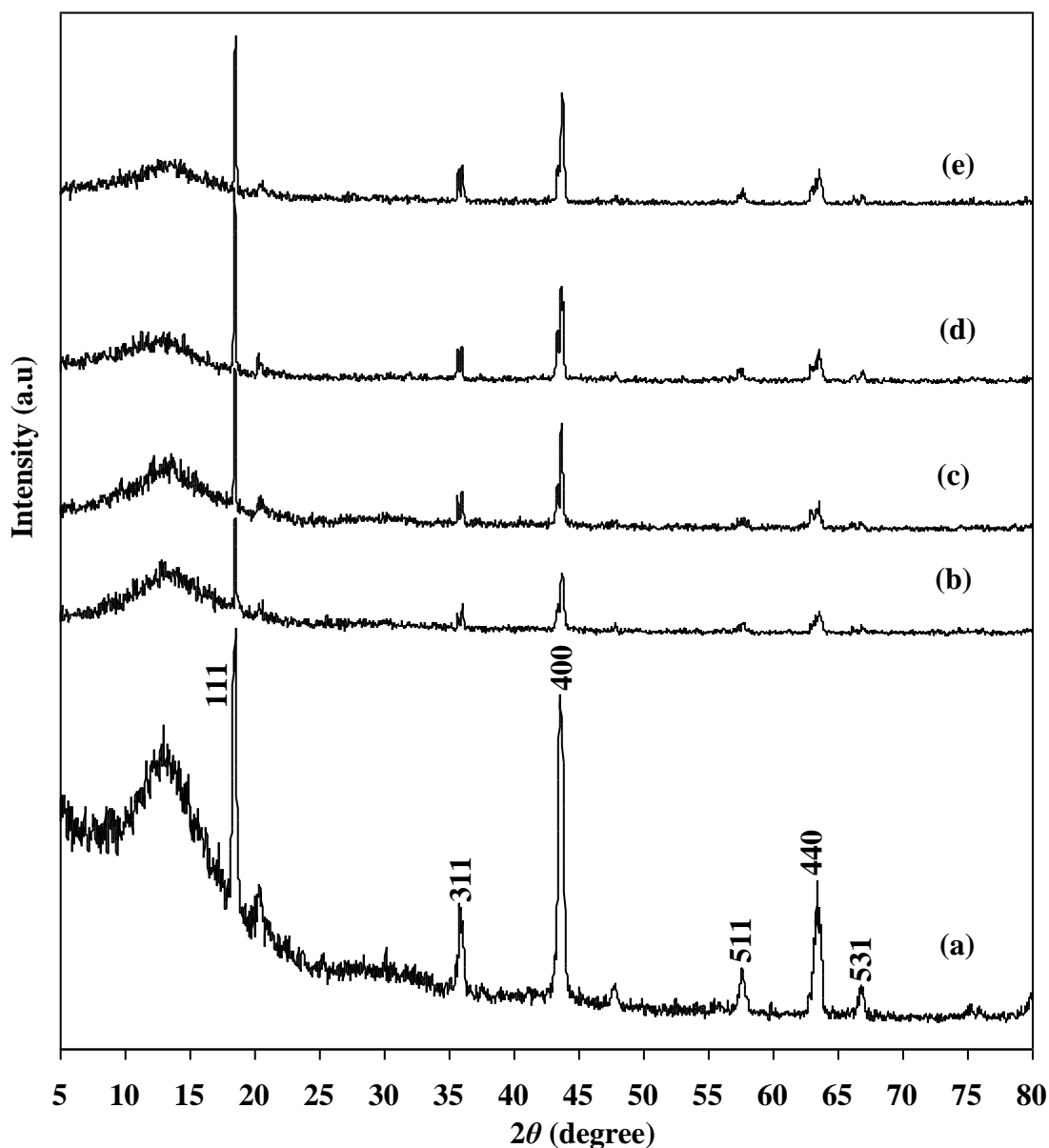


Figure 4.5: XRD profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at 800°C for (a) one, (b) two, (c) three, (d) four and (e) five hours.

Tabulated in Table 4.2 are lattice parameter and volume of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ unit cell sintered at different temperatures. Our results for lattice parameter differ by 0.6–0.8 % from that reported by Kataoka *et al.*, (2008). Tabulated in Table 4.3 is density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at different sintered temperatures from 700 °C to 1000 °C for one hour. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at 700 °C and 1000 °C have lowest density.

Table 4.2: The list of lattice parameter and volume at different sintered temperatures.

Sintered temperature, T (°C)	Lattice parameter, a (Å)	Volume, $V(=a^3)$ (Å ³)
700	8.31	574
800	8.30	572
900	8.29	570
1000	8.31	574

Table 4.3: Density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different sintered temperatures.

Temperature (°C)	Density, ρ (g cm ⁻³)
700	10.65
800	10.67
900	10.72
1000	10.65

Data in Table 4.4 are lattice parameter and volume of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at 800°C at various sintering times from one to five hours. There are no significant changes of lattice parameter of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ after sintering for two, three, four and five hours. The density for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at one, two, three and five hours is the same which is 10.67 g cm^{-3} as tabulated in Table 4.5. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sintered at four hours shows 0.67 % deviation from the list.

Table 4.4: The list of lattice parameter and volume at different sintered times.

Sintered time, (Hour)	Lattice parameter, a (Å)	Volume, $V(=a^3)$ (Å ³)
1	8.30	572
2	8.30	572
3	8.30	572
4	8.32	576
5	8.30	572

Table 4.5: Density of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at different sintered times.

Time (Hour)	Density, ρ (g cm^{-3})
1	10.67
2	10.67
3	10.67
4	10.60
5	10.67

4.4 Battery performance

Figure 4.6 depicts the charge-discharge characteristics for the $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$ cell. The charging and discharging currents were fixed at 0.5 mA. The cell was cycled 25 times from 3.0 to 0.0 V. The characteristics are quite similar to that reported by Shenouda and Murali (2008), Pasquier *et al.*, (2004), Shu (2009) and Hao *et al.*, (2006). The discharge plateau is found to be at approximately 1.5 V versus Li^+/Li and this is showed in Figure 4.6.

The voltage plateau is the result of a two-phase reaction based on the redox couple of $\text{Ti}^{4+}/\text{Ti}^{3+}$ during lithium-ion extraction and insertion processes [Zhao *et al.*, 2009; Yang *et al.*, 2008]. A voltage plateau located at 1.55 V corresponds to the reversible insertion of 0.95 lithium ions in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ without damaging the structure [Bach *et al.*, 1999].

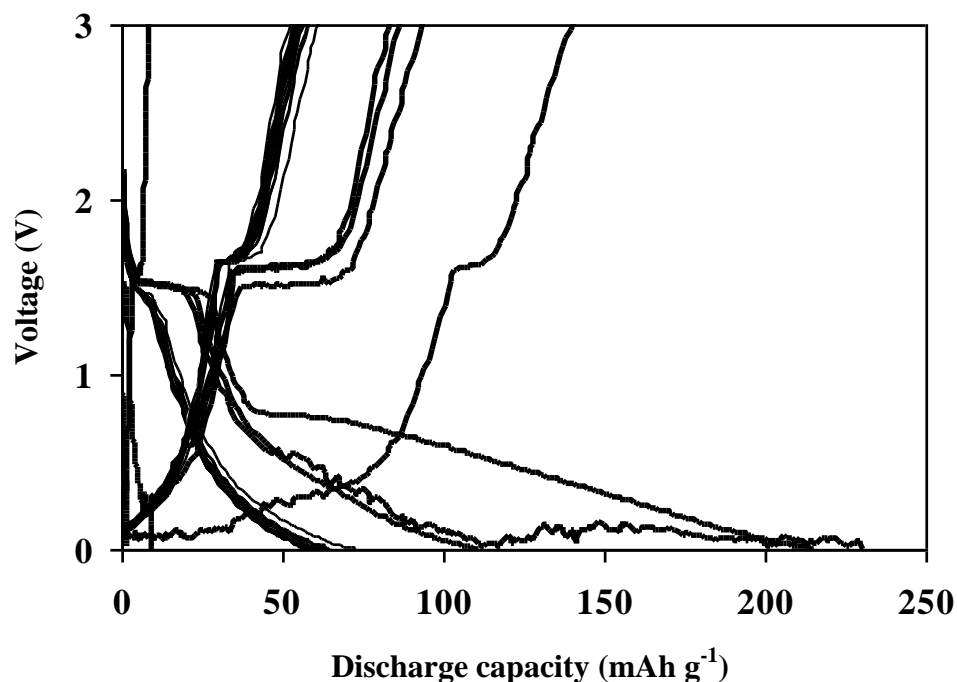


Figure 4.6: The charge-discharge profile for the Li//Li₄Ti₅O₁₂ cell.

Shown in Figure 4.7 is the discharge capacity of the fabricated cell for 25 cycles. The average discharge capacity taken over 20 cycles is $\sim 60 \text{ mAh g}^{-1}$. The first five cycles were attributed to conditioning of the cell for the complete formation of the solid electrolyte interface (SEI) layer. Hao *et al.*, (2006) reported the discharge characteristics for the cell employing Li₄Ti₅O₁₂ powders synthesized at 800 °C for 20 hours. The cell exhibited a discharge capacity of 70 mAh g^{-1} over 25 cycles. Yuan *et al.*, (2008) observed that the initial discharge capacity is higher than the theoretical capacity (175 mAh g^{-1}). They attributed this observation to the nano-crystallinity of the particles, presence of small amount of carbon residues and impurities due to anatase and rutile TiO₂ phase and spinel Li_{1.14}Ti_{1.8}O₄.

According to Ju and Kang (2009), the post-treatment temperature is important in determining a high initial discharge capacity. A lower post-treatment is not able to remove existing impurities which according to them lowers the discharge capacity of

the Li//Li₄Ti₅O₁₂ cell. In this work, the Li₄Ti₅O₁₂ powders used in the anode preparation was the product of sintering at 800 °C for one hour.

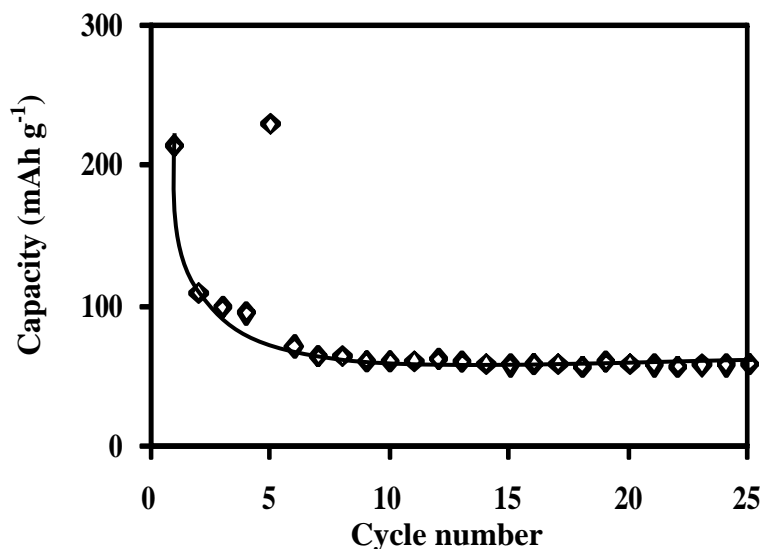


Figure 4.7: Discharge capacity of Li₄Ti₅O₁₂ at a constant current density of 21.37 mA g⁻¹.

4.5 Summary

Lithium titanate is successfully obtained via the sol-gel method followed by heat-treatment. From TGMS studies, it was found that Li₄Ti₅O₁₂ is thermally stable at temperature of 700 °C and above. XRD patterns show peaks due Li₄Ti₅O₁₂ exhibited at $2\theta=18.55^\circ$, 35.90° , 43.60° , 47.85° , 57.80° , 63.40° and 67.00° . The lattice parameter and density of Li₄Ti₅O₁₂ sintered from 700 to 1000 °C are approximately $\sim 8.3 \text{ \AA}$ and $\sim 10.7 \text{ g cm}^{-3}$. After Li₄Ti₅O₁₂ sintered at 800 °C for longer times, the peak intensity corresponding to Li₂TiO₃ is decreasing. The lattice parameter and density of Li₄Ti₅O₁₂ after sintered at 800 °C for five hours are approximately $\sim 8.3 \text{ \AA}$ and $\sim 10.7 \text{ g cm}^{-3}$. The charge-discharge cycling was carried out for Li//Li₄Ti₅O₁₂ cell and the average discharge capacity is $\sim 60 \text{ mAh g}^{-1}$ for 20 cycles.