CHAPTER 6:

DISCUSSIONS

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From TG curves shown in Figure 4.1, the stages of weight loss of the lithium titanate precursor can be observed between 30 ^oC to 600 ^oC. Jais *et al*., (1996) noted two stages of weight loss in the TG curve where the first stage occurs at ~90 ^oC and may be attributed to the evaporation of residual alcohol and water. The second stage of weight loss in the range of 250-500 ^oC is due to the decomposition of organic compounds such as acetic acid. Chen *et al*., (2003) carried out thermal analysis in dry nitrogen flow to minimize oxidation effects and reported the occurrence of weight loss between 100 ^oC and 400 ^oC. From XRD diffractogram (Figures 4.3 and 4.4), the impurity of Li_2TiO_3 is detected at $2\theta=27.65^o$. The existence of this phase is due the decomposition of $Li_2TiO_7(CH(CH_3)_2)_4$ precursor below 600 ^oC as predicted in Equation (4.5).

Ji *et al*., (2010) calcined $Li_4Ti_5O_{12}$ for five to six hours in order to avoid excessive growth of the grains. Rahman *et al*., (2010) noted the formation of a secondary TiO_2 phase as sintering temperature is increased. The existence of a small amount of TiO_2 in the $Li_4Ti_5O_{12}$ sample is due to lithium evaporation that deviates its molar ratio [Ji *et al*., 2010]. As a result, the amount of titanium element remaining in the sample is more compared to lithium. Shen *et al*., (2002) have detected a small amount of rutile TiO_2 phase derived from the loss of lithium in the precursor fired at 800 ^oC. Peramunage and Abraham (1998) prepared $Li_4Ti_5O_{12}$ in a single step solid state reaction involving TiO_2 and Li_2CO_3 and detected additional peaks due to TiO_2 and Li-Ti-O ternary phases in the XRD profile.

Yuan *et al*., (2008) prepared $Li_4Ti_5O_{12}$ via a combustion technique and found that after calcination at 900 ^oC, the colour of the $Li_4Ti_5O_{12}$ powder changed from white to bright blue that is characteristic colour of Li-deficient $Li_4Ti_5O_{12}$. Such deficiency resulted from a high evaporating pressure of lithium oxide. Kanamura *et al*., (2006) successfully obtained a pure of $Li_4Ti_5O_{12}$ phase at 500 ^oC by emulsion-gel method but further calcination at 800 ^oC is necessary in order to improve the electrochemical behaviour of $Li_4Ti_5O_{12}$ since the low temperature calcined product had poor crystallinity. This is because electrochemical behaviour of $Li_4Ti_5O_{12}$ is typically highly dependent on its crystallinity. Ji *et al*., (2010) noted that short calcination time, within five to six hours was also critical to prevent excessive growth of the grains and in this work, precursors were sintered for one to five hours.

Yuan *et al*., (2008) also noted that, Li-ion intercalation and de-intercalation are dependent on the stable metal oxide structures of the anode. It is possible that some intercalated lithium in the first discharge could not de-intercalate due to defects in the crystallites. After several cycles, the charge and discharge capacity is almost about the same. This indicates stabilization of the structure. Performance of $Li_4Ti_5O_{12}$ anode is also closely related with particle size, particle morphologies and crystallographic structure. The larger grain size and smaller surface area leads to longer diffusion distance of lithium ion and smaller active surface reaction sites which will result in the increase of polarization resistance at high charge-discharge rates. Substituting carbonaceous anodes with lithium titanate is a step towards safety because lithium titanate is chemically compatible with the electrolyte and the total specific energy of the cell is lower compared to carbonaceous anode cells. The voltage of lithium titanate is significantly higher and the capacity is significantly lower than those of graphite-based Li-ion cells [Rahman *et al*., 2010]. Because of such considerations, lithium titanate anode could be considered as complementary to carbonaceous anodes in lithium-ion batteries. Hao *et al.*, (2006) noted that the rapid decrease in discharge capacity after 10 cycles is due to the lower crystallinity of $Li_4Ti_5O_{12}$ and a large amount of anatase TiO_2 phase present in the low temperature calcined material.

Following Allen *et al.*, (2006), the theoretical capacity of $Li_4Ti_5O_{12}$ is 175 mAh g^{-1} based on the following lithium insertion/de-insertion equation:

$$Li_4Ti_5O_{12} + 3Li^+ + 3\bar{e} \rightarrow Li_7Ti_5O_{12} \qquad (6.1)$$

Theoretically 1 gram-equivalent weight of any material delivers 96487 C or 26.8 Ah of charge. Since from the above intercalation/de-intercalation reaction $Li_4Ti_5O_{12}$ releases or gains 3 moles of electrons during intercalation and de-intercalation processes and turn to $Li_7Ti_5O_{12.}$ The theoretical capacity of $Li_4Ti_5O_{12}$ is 175 mAh g^{-1}. In present work, the average discharge capacity is almost 60 mAh g^{-1} for 20 cycles. Hence, the $Li_4Ti_5O_{12}$ anode its expected to release only one mole of electron or one mole of lithium ion during the discharge process. The experimental capacity is therefore lower compared to the theoretical capacity. The intercalation/de-intercalation equation can be expressed as follows:

$$Li_4Ti_5O_{12} + Li^+ + \bar{e} \rightarrow Li_5Ti_5O_{12} \qquad (6.2)$$

The low crystallinity of the $Li_4Ti_5O_{12}$ samples produced in this work may contribute to the low capacity of the half-cell prepared. This has also been claimed by Hao *et al.*, (2006) and Kanamura *et al.*, (2006). From the diffractograms obtained in Figure 4.4, an amorphous hump can be observed at low 2θ angles. Even upon increasing sintering time the sample is still quite amorphous, Figure 4.5. According to Ji *et al*., (2010) during the charge-discharge process if the electrons fail to migrate timely, the electrode is expected to polarize and lithium ion insertion or extraction can be impeded, contributing to low discharge capacity.

Pasquier *et al*., (2004) reported a cell containing $Li_4Ti_5O_{12}$ and poly (methyl) thiophene, PMeT as anode drastically decreased from 55 mAh g^{-1} to 30 mAh g^{-1} for 10000 cycles. The presence of PMeT may have caused the higher capacity fade. In the present work, the initial discharge capacity is ~ 210 mAh g^{-1} and after 10 cycles the discharge capacity is stable and constant (60 mAh g^{-1}) as shown in Figure 4.7.

Amattucci *et al*., (2001) noted that lithium-ion cells with high energy density could not be charged faster than 2 C. Fast charging can induce severe underpotential, resulting in hazardous lithium plating and the subsequent deterioration of cell performance. Further, according to Ji *et al*., (2010) charging process is exothermic and the rate must be kept below C/2 for safety issues.

The higher dielectric loss that occurs at lower frequencies is due to an accumulation of free charge at the electrode/composite interface. Mohan *et al*., (2010) also found that at low temperature the relaxation peaks is not detected. Kobayashi *et al*., (2008) noted that an increase in the volume fraction of the ceramic material can affect the dissipation factor of a composite film.

Polar polymer matrices (i.e., the ones containing a large number of permanent dipoles in their structure) generate high dielectric losses within MHz to GHz frequency range, which become even more pronounced in the presence of a high dielectric constant filler.

Hence, polymers with little or no dipolar functional groups within their structure will form composites with lowest tan δ values at high frequencies. Such polymers usually have low dielectric constant, which will lower the dielectric constant of the composites. However, at GHz frequencies the influence of the polymer matrix on the dielectric constant of high dielectric constant ceramic/polymer composites is not as significant as at low frequencies [Popielarz and Chiang, 2007].

Popielarz and Chiang (2007) noted that composites which have high dielectric constant and low dissipation factor make good materials for application in capacitors. Comparing results from Figures 5.10 and 5.13 with that of Kobayashi and co-workers (2008), the dielectric constant at *f*=100 Hz as reported by Kobayashi *et al*., (2008) is between 35 and 40. At the same frequency the dielectric constant for the present material is between 25 and 30 and reduces drastically below 10 as frequency increases to 1 MHz. In the paper by Kobayashi and co-workers (2008) the dielectric constant value does not decrease below 25. This indicates that the PVA/$Li_4Ti_5O_{12}$ composite is not able to store charge at high frequencies and would exhibit “leaky” characteristics. From Figure 5.10 the PVA film produce by dissolving PVA in 1 % acetic acid has lower dielectric constant compared to that dissolved in water. It also can be observed from Figure 5.10 the addition of a small amount of $Li_4Ti_5O_{12}$ can increase the dielectric constant in the high frequency region. On addition of 8 to 10 wt. % $Li_4Ti_5O_{12,}$ the dielectric constant in the high frequency region drops even below that of the PVA film with water as solvent.

From Kobayashi *et al*., (2008) the dissipation factor from 10^2 to 10^5 Hz lies between 0.05 and 0.12. From the present work, dissipation factor in the same frequency region lies between 0 and 6. This indicates that losses are high compared to the PVDF/$BaTiO_3$

composite and this shows that the present material would not perform as well as PVDF/$BaTiO_3$ composite in capacitor.

PVA is a crystalline polymer. This is due to the strong intermolecular and intramolecular hydrogen bonding in the PVA molecular structure [Gautam and Ram, 2010]. However on increasing addition of $Li_4Ti_5O_{12}$ to the PVA system, the peak representing crystallinity of PVA ($2\theta=23.00^o$) decreases as can be seen in Figure 5.2. This is attributable to presence of $Li_4Ti_5O_{12}$ that decreases the intermolecular hydrogen bonding in the chain of PVA. The intensity of the peak at $2\theta=18.55^o$ is increases with the increasing amount of $Li_4Ti_5O_{12}$.

Migahed *et al*., (2004) noted that modulus formalism has been used widely to analyze the electrical conductivity data in ionic conductors because the interfacial polarization is obscured by the conductivity and dielectric permittivity can be very high at low frequency in systems with conductive component. Besides that Prabakar *et al.,* (2003) had noted that the advantage of adopting complex electric modulus formalism is that it could discriminate against electrode polarization and other grain boundary conduction process. The relaxation process in the material may possibly be immobile species/electrons at low temperatures and defects/vacancies at high temperatures [Barik *et al*., 2008].