CHAPTER 8

DISCUSSION

The study of the lithium incorporated cathode material using the transition metal oxides has been the objective of this thesis. The nano-crystalline $LiNiVO_4$ is the most attractive candidate to be studied as the intercalation compound for the cathode active materials. This is because, the inverse spinel $LiNiVO_4$ not only exhibit high potential of 4.8 V [Fey *et. al,* 1994; Fey, 1995; Fey *et. al,* 1997; Fey and Wu, 1997; Fey and Perng, 1997; Fey and Huang, 1999; Chitra *et. al,* 2000; Subramania *et. al,* 2006; Kazakopoulos *et. al,* 2008] and is the first known Li intercalation observed near 5 V, but it is also the first material with inverse spinel structure to be patented as potential cathode material for rechargeable lithium cells [Fey and Dahn, 1996]. The other cathode material having 4.8 V versus Li/Li^+ active material is the $LiCoPO_4$. $LiCoPO_4$ has olivine structure and is also a strong candidate for high voltage cathodes having high theoretical capacity of about 170 mA h/g [Amine *et. al,* 2000]. However, rapid capacity fading was often observed during the redox process in which the cell only gained 60-80 % of capacity value during initial intercalation [Wolfenstine *et. al,* 2005; Bramnik *et. al,* 2004; Jin *et. al,* 2008; Li *et. al,* 2009; Wang *et. al,* 2010; Tan *et. al,* 2010]. The toxicity of cobalt and its high cost are other reasons why studies on alternatives to cobalt have been carried out to produce cathode materials [Liu *et. al,* 1999; Chen *et. al,* 2003b].

Synthesis method for preparing the active cathode material has also to be considered apart from physical appearance and performance of the fabricated cell upon using the material. Firstly, the method should be easy and economical. Rapid advancements in performance of the cathode materials have triggered the development of the most practical and efficient synthesis methods to enhance the electrochemical performance. Reports on $LiNiVO_4$ have been presented ever since until 1995 using the same solid state reaction method [Ito, 1979; Chang and Wang, 1988; Wang, 1995]. The solution co-precipitation preparation method has been proposed by Wang (1995) for an effective reduced heating rate. The combustion method has been reported [Prabaharan *et. al,* 1997] using glycine as the fuel source. Later, the ceramic route method [Orsini *et. al,* 1998] has been used followed by hydrothermal synthesis using the isopropanol as the solvent [Lu *et. al,* 1999]. Subsequently, another solution precipitation method was introduced using acetylacetonate as the reagent [Fey and Chen, 1999]. Complexation-precipitation and gelation (CPG) method was then suggested [Lai *et. al,* 2001; Lai *et. al,* 2002a] and later, Liu's group proposed the sol-gel method using citric acid [Liu *et. al,* 2002] as the chelating agent. A few other synthesis method were then introduced including the starch-assisted combustion method (SAC) [Kalyani *et. al,* 2002], glycerol-assisted gel combustion (GAGC) method [Vivekanandhan *et. al,* 2004] and combustion method using gelatine as the fuel source [Subramania *et. al,* 2006].

The solid state reaction method has major drawbacks in which the method is no longer favourable to prepare cathode materials. It has been found that the solid raw materials may not react completely. The incomplete reaction of solid particles obtained from the solid state reaction may produce impurities [Fey and Huang, 1999]. Therefore, the sintering temperature must be high and will enhance the size of the particle [Momchilov *et. al,* 1993]. The preparation of $LiNiVO_4$ using the high temperature solid state process may affect the cycling and electrochemical behavior [Fey *et. al,* 1994]. The cathode prepared by such method exhibit only ∼45-50 mA hg^{-1} during initial discharge capacity [Fey *et. al,* 1994]. Apart from poor control of chemical homogeneity the solid state reaction method also imposes high cost for heat treatment [Huang *et. al,* 1998].

Thus, the solution technique namely sol–gel, hydrothermal, soft combustion, etc was performed [Kwon *et. al,* 1998; Hon *et. al,* 2002, Vivekanandhan *et. al,* 2004; Laberty-Rebert *et. al,* 2001; Monoharan *et. al*, 1990; Fey *et. al*, 1997; Lu and Liou, 2000; Liu *et. al,* 2002; Fey and Perng, 1997; Kalyani *et. al*, 2002]. These methods are favorable for not having to sinter the powder at very high temperature for long reaction time. The solution technique is rather simple and less costly than conventional solid state reaction. The final products obtained from the solution reaction method produce smaller particles as a result of better dispersion on the colloid solution. In this work, the single phase of $LiNiVO_4$ was successfully prepared by sol-gel method and polymer precursor method at minimum temperature as low as 600 °C in 3 hours and 500 °C in 3 hours, respectively.

The sol-gel method has been used since 1990's [Larcher *et. al,* 1997; Barboux *et. al,* 1991; Garcia *et. al,* 1995]. The sol-gel method which is one of the soft chemistry solution methods was chosen to develop the cathode material. In this work, the cathode material was prepared by the sol-gel method. The sol-gel method is the wet chemical technique that is widely used in the materials science field. The synthesis of materials is used primarily to obtain the precursor. The process initially starts from the formation of the colloidal solution (sol) that behaves as the intermediate for an integrated network by low temperature to form a viscous gel. The solid nanoparticle will be dispersed in the solution, undergoes agglomeration to form the 3D network that extends throughout the liquid (gel). The solution technique has been widely applied for its promising behaviour over conventional solid state processing method. Besides having good stoichiometric control, the sol-gel provides low synthesis temperature and shorter heating time. The product obtained from using such method offers homogeneous mixing at the atomic or molecular level, good crystallinity, uniform particle size and producing smaller diameter even at the nanometer scale [Klein, 1988; Brinker and Scherer, 1990]. Therefore, the sol-gel method has been proposed to prepare materials for energy conversion and storage system [Liu *et. al*, 2004].

The systems prepared in this work have been added with citric acid. The citric acid was used as the chelating agent and carbon source [Li *et. al*, 2007]. Other acids that have been used to prepare the inverse spinel precursor include oxalic acid [Lai *et. al*, 2001; Lai *et. al*, 2002a], tartaric acid [Thongtem *et. al*, 2007a], and malic acid [Thongtem *et. al*, 2007b]. Citric acid was chosen due to its popularity in the preparation of various kinds of sub-micron particles [Alcantara *et. al*, 1997; Chen *et. al*, 2003a] and these include $LiNiVO_4$ [Liu *et. al*, 2002; Vivekanandhan *et. al*, 2004; Xu *et. al*, 2007; Li *et. al*, 2007; Landschoot *et. al*, 2004b; Landschoot *et. al*, 2003; Vivekanandhan *et. al*, 2005; Fey *et. al*, 2006; Fey *et. al*, 2007]. According to Song and Lee (2002), chelating agent has ligands which can combine positive ions; the positive ions are distributed homogeneously in the gel precursor. The ligand in citric acid (carboxylic functional group) binds with the metal cations to form metal complexes. Citric acid has been used in several reported works for preparing the cathode material [Liu *et. al*, 2002; Vivekanandhan *et. al*, 2004; Li *et. al*, 2009]. $LiNiVO_4$ produced using tartaric acid as chelating agent produced particle size ranging from range of 10 to 30 nm [Thongtem *et. al*, 2007a; Phuruangrat *et. al*, 2007a]. With malic acid as chelating agent, the synthesis yielded particle size of ~20 nm. The use of citric acid by hydrothermal method [Lu and

Liou, 2000], combustion method [Vivekanandhan *et. al*, 2004] and citric acid complex method [Liu *et. al,* 2002] has obtained particle size of 90 nm, 39 nm and < 5 μm, respectively. The acquired inverse spinel $LiNiVO_4$ in this work by sol-gel and polymer synthesis has yielded particle size ranging from 33 nm to 68 nm. Thus, the particle size obtained in this work is comparable to that of reported by other researchers.

The polymer precursor method also has the same advantage as that of the sol-gel reaction method. The synthesis is also based on the solution technique and the polymer source was added during the preparation process. The polymer precursor method was also selected in this work for its efficiency and for providing the special characteristics as gelling agent [Liu *et. al*, 1996; Park *et. al,* 1997; Sun and Oh, 1997]. In this work, the esterification process of the metallic citrates with the ethylene glycol defines the polymer precursor mechanism by chelation of the metallic cations within the lattice of the polymer [Souza *et. al*, 2005]. The chelated metal ions that are uniformly distributed throughout the polymer gel are attached to the polymer molecules by the COOH functional group [Subramania *et. al*, 2007]. According to Fey et. al, (2007), the polymerization synthesis between the PEG and the citric acid promotes the formation of nanosized particle with larger surface area. Therefore, the product formed will enhance the Li^+ de/intercalation as well as lowering the synthesizing temperature [Fey *et. al,* 2007]. Several researchers have attempted such polymer solution method using different types of the polymerizing sources like gelatine [Subramania *et. al*, 2006], poly (ethylene glycol) (PEG) [Fey *et. al,* 2006a], ethylene glycol [Vivekanandhan *et. al,* 2005], and glycerol [Vivekanandhan *et. al*, 2005]. The principle of using the polymer source is based on the ability of the carboxylic acids to chelate in which the metal cations will be confined by the polymer chains, inhibiting the metal salt precipitation during the evaporation [Hong *et. al*, 1997]. In other words, the polymer matrix will undergo complexation between the metal cation with the citric acid resulting better dispersity of metal ion distribution [Fey *et. al,* 2006a; Fey *et. al,* 2006b].

The co-doped transition metal vanadates for $LiNiVO_4$ cathode using manganese, Mn as the doping material have been demonstrated [Lai *et. al,* 2002b]. Manganese, was chosen as the dopant material to substitute the amount of nickel that to reduce the toxicity of Ni. The doping material does not change the inverse spinel structure but can improve the electrochemical properties of the synthesized cathode by having improved reversibility and cycle efficiency [Lai *et. al,* 2002b].

Ito prepared $LiNiVO_4$ by reacting $LiVO_3$ and NiO at 1000 °C for 4 days [Ito, 1979]. Heating cost is incurred. Chang and Wang (1988) synthesized $LiNiVO_4$ by reacting Li_2O, 2NiO and V_2O_5. The products have been prepared by the applied solid state reaction method is highly possible that impurities are produced. Later, Fey et. al, (1994) proposed the new preparation method for $LiNiVO_4$ by reacting $LiNiO_2$ and V_2O_3 or V_2O_5 at 700 °C for 2 hours in air. Lu et. al, (1999) have developed $LiNiVO_4$ by reacting $LiOH \cdot H_2O$, Ni $(CH_3COO)_2 \cdot 4H_2O$ and NH_4VO_3 as starting materials by using isopropanol as the solvent. The reaction between LiOH, V_2O_5 with nickel nitrate promotes the formation of an amorphous product [Lu and Liou, 2000]. According to Lu and Liou (2000), the NO_3^- anions in nickel nitrate impede the crystallization of $LiNiVO_4$ while NH_4VO_3 possessed higher reactivity than V_2O_5. Therefore, by considering previous literature by Lu and Liou (2000), lithium acetate dihydrate ($LiCH_3COOH.2H_2O$), nickel (II) acetate tetrahydrate (Ni $(CH_3COOH)_2$. $4H_2O$), and ammonium metavanadate (NH_4VO_3) were chosen as the starting materials for preparation of the undoped $LiNiVO_4$. As for the doped $LiNi_{1-x}Mn_xVO_4$, the compounds were prepared using lithium acetate dihydrate ($LiCH_3COOH.2H_2O$), nickel (II) acetate tetrahydrate (Ni $(CH_3COOH)_2$. $4H_2O$), manganese acetate tetrahydrate (Mn $(CH_3COO)_2.4H_2O$) and ammonium metavanadate (NH_4VO_3) as the starting raw materials. The acetates materials were chosen as starting materials because the acetate anion in the acetate salt is one of the carboxylate groups. The carboxylates (salts of carboxylic acid) can easily be dissociated into conjugated base CH_3COO^- anion that combines with metal cations to form a homogeneous mixture in the gel precursor. The solubility in water is another reason why the acetates and NH_4VO_3 starting materials were chosen for preparing the inverse spinel. Therefore, the synthesis of $LiNiVO_4$ and $LiNi_{1-x}Mn_xVO_4$ in this work becomes easier and a shorter time is required and less energy consumed for preparing the final inverse spinel product.

The compounds $LiNiVO_4$ synthesized by the sol-gel and polymer precursor methods and $LiNi_{1-x}Mn_xVO_4$ by the sol-gel and polymer precursor methods were all prepared using distilled water as the solvent. Lu et. al (1999) prepared $LiNiVO_4$ by hydrothermal reaction by using LiOH, $Ni(CH_3COO)_2·4H_2O$, and NH_4VO_3 dissolved in isopropanol. Ethanol was used during ball milling process for 48 hours to prepare $LiNiVO_4$ after the mixing of Li_2CO_3, NiO and V_2O_5 starting materials [Lu and Liou, 1999]. $LiNO_3$, $Ni(NO_3)_2·$ $6H_2O$ and $V(C_5H_7O_2)_3$ were dissolved in *n*- butanol at 60 °C by solution precipitation method to prepare $LiNiVO_4$ [Fey and Chen, 1999]. The alcohols were used to ensure homogenous mixing in the solution [Gao *et. al,* 2008]. Phuruangrat et. al, (2007b) also found that the use of deionized water as a solvent is essential to prevent the presence of toxic medium. By considering the previous literature for the solvent used and the raw materials reported during the synthesis process, it is very important to choose the simplest and less costly materials to obtain the final product.

In this work, the starting materials were dissolved separately in distilled water. Subsequently, the dissolved solutions were mixed into a beaker. The homogenizer was used to ensure homogenous mixing in the solution. The solution was heated under continuous stirring process at 120 °C for 4- 5 hours. The heating process continues until a loose powder form was obtained from the reacted compound. The intermediate compound obtained, which is called precursor was calcined at different temperatures to obtain the final inverse spinel product.

The formation of inverse spinel $LiNiVO_4$ and $LiNi_{1-x}Mn_xVO_4$ must undergo firing procedure from the synthesized intermediate. The intermediate or precursor will go through TGA analysis to determine the relevant heating temperatures. Lu and Liou (1999) have demonstrated the thermal study of $LiNiVO_4$ precursor by TGA experiment. The solid state reaction employed to prepare the precursor suggests that the thermal reaction stops after 400 °C with the total weight loss of 10 % [Lu and Liou, 1999]. Lai *et. al*, (2001) and Lai *et. al*, (2002a) used wet chemical synthesis method and their proposed reaction equations show that the dry gel were the mixture of complexes and precipitates. The total weight loss obtained was around 82 % by TGA thermogram analysis using the oxalic acid as complexant during the synthesized process [Lai *et. al*, 2001; Lai *et. al*, 2002a]. Subramania's group has acquired a total weight loss from TGA analysis of around 28 % by product synthesized by combustion method [Subramania *et. al*, 2006]. Kazakopoulos et. al, (2008) prepared $LiNiVO_4$ by solid state method at 650 °C for 18 hours and obtained 0.8 % of weight loss, but based on the proposed chemical reaction, the weight loss was 80.4 % [Kazakopoulos *et. al*, 2008]. Lai et. al, (2002a) related a weight loss of 82 % in their TGA analysis and their proposed final decomposition reaction the weight loss was 80.4 %. The final proposed chemical reaction for the dry gel by Lai's group was as follows [Lai *et. al*, 2002a]:

$$x\mathrm{VO_2} + (5-x)\ \mathrm{LiVO_3} + \mathrm{NiCO_3} + \frac{x}{2}\,\mathrm{Li_2CO_3} + \frac{x}{4}\mathrm{O_2} \longrightarrow \mathrm{Li\ Ni}^{3+}_{x}\ Ni^{2+}_{1-x}\ V^{4+}_{x}\ V^{5+}_{1-x} + \frac{2+x}{x}\,\mathrm{O_4} + x\,\mathrm{CO_2}$$

These results are comparable and acceptable. However, the proposed chemical reaction by Kazakopoulos et. al, (2008) suggests a weight loss of 80.4% but from the thermal studies only 0.8 % of weight loss was observed. Kazakopoulos's group proposed chemical reaction was as follows [Kazakopoulos *et. al,* 2008]:

$$\mathrm{Li_2CO_3} + 2\mathrm{NiO} + \mathrm{V_2O_5} \longrightarrow 2\mathrm{LiNiVO_4} + \mathrm{CO_2}\uparrow$$

Therefore, the result of their proposed chemical reaction and the total weight loss does not seem to be comparable with the TGA results.

In this work, the TGA study for $\mathrm{LiNiVO_4}$ suggests that the precursor for synthesis of $\mathrm{LiNiVO_4}$ can be calcined at the minimum temperature of 500 °C with the total weight loss of 68.76 %. This reaction was comparable to that of Liu et. al, (2002) who obtained 63.6 % of total weight loss by TGA analysis. The proposed total reaction of the precursor in air is:

$$4\ \mathrm{LiNiC_6H_5O_7}\cdot(\mathrm{VO})\cdot(\mathrm{NH_4})\ \mathrm{C_6H_5O_7} + 37\ \mathrm{O_2} \longrightarrow 4\ \mathrm{LiNiVO_4} + 48\ \mathrm{CO_2} + 22\ \mathrm{H_2O} + 4\ \mathrm{NH_3}$$

Liu et. al, (2002) did proposed chemical reaction of the dried gel precursor $\mathrm{LiNiVO_4}$ as follows;

$$4\ NiC_6H_5O_7 \cdot (VO) \cdot (NH_4)\ C_6H_5O_7 + 37\ O_2 \longrightarrow 4\ LiNiVO_4 + 48\ CO_2 + 22\ H_2O + 4\ NH_3$$

From the proposed reaction mechanism published by Liu's group, the chemical reaction was noticed unbalance on the reactant part on the left hand side of the chemical equation. The calculated weight loss from the proposed decomposition reaction of the dried precursor by Liu's work was reported having 65.9 %. Unless the chemical reaction published was having typing error, the final reaction mechanism of the proposed decomposition process was similar with this work but the sectional reaction equations was different due to different raw materials used in this work and the actual weight loss calculated should be 69.5 %.

The thermogram of $LiNiVO_4$ by the polymer precursor method displays three major endothermic peaks. The overall decomposition reaction exhibits a weight loss of 57.3 %. The TGA curve shows a constant line at nearly 500 °C. The reaction undergone by the precursor to form $LiNiVO_4$ was assumed complete at this temperature.

The $LiNi_{1-x}Mn_xVO_4$ precursor prepared by sol-gel method demonstrates a few main endothermic peaks located at 80 °C, 371 °C, and 573 °C in the DTGA thermogram. The TGA thermogram does not show any prominent saturated line. This may due to the reacted excess gases that continue the reaction decomposition upon increasing temperature to obtain stable vanadate [Lai *et. al,* 2002a]. Again, the same consideration of chemical expression as the previous systems was applied for the first reaction mechanism. The complexation of metal citrates may occur upon mixing solutions and heating. In this system, three kinds of metal cations (Li^+, Ni^{2+} and Mn^{2+}) were involved in the reaction. The total reaction can be written as:

$$4\ LiNi_{0.75}Mn_{0.25}C_6H_5O_7 \cdot (VO) \cdot (NH_4)\ C_6H_5O_7 + 37\ O_2 \longrightarrow 4\ LiNi_{0.75}Mn_{0.25}VO_4 + 48\ CO_2 + 22\ H_2O + 4\ NH_3$$

Phuruangrat et. al, (2007a) acquired no impurities for their work using the carbonates and nitrates as starting materials with tartaric acid at 450 °C for 12 hours. The work using carbonates, acetates and tartaric acid by the same research group has reported that there were no impurities upon sintering at 450 °C for 6 hours with further calcination at 550 °C for 12 hours. Improved crystallinity was obtained upon increasing temperature [Thongtem *et. al*, 2007a]. According to Fey (1995), the tetrahedral Li^+, Ni^{2+}, and V^{5+} has caused an increase in [220] peak at expense of [111] peak. The coordination of V^{5+} at tetrahedral 8a sites leads to higher intensity [220] peak and lower intensity [111] peak in the XRD results [Chitra *et. al*, 2000; Kalyani *et. al*, 2002; Chen *et. al*, 2003a]. The Li^+ and Ni^{2+} ions equally and randomly occupies in the octahedral interstices while V^{5+} occupies in tetrahedral interstices [Fey and Huang, 1999]. Similar [220] and [111] peak behaviour are also reported in most works on $LiNiVO_4$ inverse spinel [Fey, 1995; Lu and Liou, 1999; Lai *et. al*, 2001; Thongtem *et. al*, 2007a; Subramania *et. al*, 2006; Thongtem *et. al*, 2007b].

The structural properties of the prepared samples were also analyzed by the X-ray diffraction (XRD) technique. The $LiNiVO_4$ compound prepared by the sol-gel (SG) method revealed the identity of the pure inverse spinel for the sample fired at 600 °C. The diffractogram of the sample fired at 500 °C (Figure 4.2 in Chapter 4) demonstrates mixed phase of $LiNiVO_4$. From the XRD peaks, small amounts of NiO impurities are present at 37.3°, 43.3° and 62.9°. The XRD result for sample at higher temperatures (600 °C to 800 °C) display the [111] crystalline single phase of $LiNiVO_4$. This result shows that the firing technique removes the presence of impurities at elevated temperatures in the system. As expected, the position of [220] peak is located at 30.6° as confirmed by the JCPDS diffraction data for cubic $LiNiVO_4$. The diffractogram obtained for all treated samples indicates that the XRD profiles of each sample are temperature dependent. The peak at [311] plane ($2\theta = 36.2°$) remains the most intense peak for the system. The peak at $2\theta = 18.6°$ (representing the [111] plane) was too small and sometimes could not be observed in the diffractogram obtained. The intensity of the peak from the JCPDS data is only 3%.

The information on the XRD analysis is very useful to determine the lattice constant. In this work, the lattice constant, *a* for undoped $LiNiVO_4$ by sol-gel and $LiNiVO_4$ by polymer precursor method system are 8.231Å and 8.215 Å, respectively. These values are comparable to the work done by Fey et. al, (1994), Subramania et. al, (2006), and Phuruangrat et. al, (2007a) for $LiNiVO_4$. This shows that using acetate raw materials and distilled water as solvent can also produce comparable lattice constants.

The TGA of the undoped $LiNiVO_4$ prepared by the polymer precursor method revealed that the minimum sintering temperature to produce the pure phase is about 500 °C. This result shows that the polymer source added during the preparation led to the formation of a single phase without NiO contaminant at a temperature lower than the sol-gel method. The increased intensity of the strongest peak of the [311] plane indicates the improved crystallinity upon increasing firing temperature. The advantage of the polymer precursor method is that it does not produce impurities at 500 ºC while the sol-gel method still contain NiO after sintering the precursor at 500 ºC for three hours.

The diffraction peaks of the $LiNi_{1-x}Mn_xVO_4$ ($0\leq x \leq 1$) is similar to that of inverse spinel $LiNiVO_4$ profile. The single phase of the product was observed at x = 0.25 mole ratio of

Mn for all sintering temperatures. There was no trace of any impurities for all heating treatment from 500 °C to 800 °C. The strongest peak for the XRD profile remains at the [311] plane. However, the strongest peak was less sharp and slightly broader at the highest heating temperature suggesting the particle size is suppressed upon higher sintering temperature [Khomane *et. al,* 2008]. As for the XRD analysis for the $LiNi_{0.75}Mn_{0.25}VO_4$ prepared by polymer precursor method, the diffractogram displays similar behaviour of inverse spinel $LiNiVO_4$ as that of $LiNi_{0.75}Mn_{0.25}VO_4$ by sol-gel system.

The increased peak intensity with increasing calcination temperature indicates improved crystallization. Chitra et. al, (2000) proposed that the high crystallinity nature of $LiNiVO_4$ is acceptable if the $I_{[220]}/ I_{[311]}$ intensity ratio is 0.5. Later in 2007, the work from Phuruangrat et. al (2007a) was used for determination of crystallinity. In this work, the intensity ratio of the [220] peak over the strongest peak at [311] plane is calculated. The calculated intensity ratio of $I_{[220]}/ I_{[311]}$ for single phase $LiNiVO_4$ by sol-gel method obtained in this work is 0.42, 0.49 and 0.57 for sample treated at 600 °C, 700 °C, 800 °C, respectively. The calculated intensity ratio of $I_{[220]}/ I_{[311]}$ for inverse spinel $LiNiVO_4$ prepared by polymer precursor method was observed at 500 °C, 600 °C, 700 °C, 800 °C, is 0.57, 0.34, 0.56 and 0.57, respectively. The calculated intensity ratio of $I_{[220]}/ I_{[311]}$ for sample $LiNi_{0.75}Mn_{0.25}VO_4$ by the sol-gel method was at 500 °C, 600 °C, 700 °C, 800 °C, is 0.52, 0.50, 0.43 and 0.65, respectively. The calculated intensity ratio of $I_{[220]}/ I_{[311]}$ for inverse spinel $LiNi_{0.75}Mn_{0.25}VO_4$ prepared by polymer precursor method is 0.42, 0.54, 0.34 and 0.58 for sample treated at 500 °C, 600 °C, 700 °C, 800 °C, respectively. These result shows that the inverse spinel cathode materials are in general crystalline material.

The crystallite size of prepared samples for all systems was calculated using the Scherrer equation. This equation is often used by almost all researchers [Rashad *et. al,* 2009; Bakoyannakis *et. al,* 2003; Subramania *et. al,* 2006; Barreca and Massignan, 2001; Ryu *et. al,* 2005; Tsang *et. al,* 2006; Kumar and Mouli, 2010]. The nanosized material is favourable in developing the desirable cathode materials because of the larger total surface area to volume ratio. The larger surface area to volume ratio will shorten the diffusion path of Li^+ ion and electron within the particles during the intercalation/deintercalation processes. The nanosized particles improve the transport charge carrier while preserving the large surface area to the volume ratio and thus, enhancing the contact with electrolyte and the reaction kinetics. Thus, such properties may improve the capacity of the electrode [Subramania *et. al,* 2006]. Since the new solution precipitation process using acetylacetonate in preparing the nanoscale material is proposed [Fey and Chen, 1999], various kinds of methods such as hydrothermal process [Lu *et. al,* 1999; Lu and Liou, 2000], combustion techniques [Kalyani *et. al,* 2002; Vivekanandhan *et. al,* 2004; Subramania *et. al,* 2006] have been reported to produce nanosized cathode materials.

The particle size of $LiNiVO_4$ are often mentioned in the literature (Fey and Perng, 1997; Prabaharan *et. al,* 1997; Fey and Chen, 1999; Lu *et. al,* 1999; Lai *et. al,* 2001; Liu *et. al,* 2002; Kalyani *et. al,* 2002; Vivekanandhan *et. al,* 2004; Subramania *et. al,* 2006; Phuruangrat *et. al,* 2007; Thongtem *et. al,* 2007a; Thongtem *et. al,* 2007b). The synthesis by solid state reaction method by Fey and Perng (1997) obtained $LiNiVO_4$ with crystallite size of ~ 20 μm. The combustion reaction method was employed using various kinds of fuels [Prabaharan *et. al,* 1997; Kalyani *et. al,* 2002; Vivekanandhan *et. al,* 2004; Subramania *et. al,* 2006]. The crystals obtained using starch and glycine produced micrometer range of particle size [Prabaharan *et. al,* 1997; Kalyani *et. al,* 2002], Later, the size of particle was improved by using glycerol and gelatine as fuel source that obtained 39 nm and 40-60 nm, respectively [Vivekanandhan *et. al,* 2004; Subramania *et. al,* 2006]. The size obtained using combustion method maybe due to the fuel source that behaves as good dispersing agent [Subramania *et. al,* 2006] that ensures the well mixing in the solution during the synthesis. Lu et. al (1998) prepared inverse spinel $LiNiVO_4$ by the hydrothermal process which yielded particles size between 0.2 and 0.3 μm. Phuruangrat et. al (2007b) prepared $LiNiVO_4$ by hydrothermal technique and acquired particle size between 19 and 69 nm. The use of acids in the synthesis has been very useful to acquire nanosized material cathodes. $LiNiVO_4$ processed in acidic media has been prepared by reacting nitrate starting materials with addition of nitric acid [Fey and Chen, 1999]. The powder obtained has acquired 343 nm of particle size [Fey and Chen, 1999]. Thongtem and his research group have attained 10-30 nm using tartaric acid and ~ 20 nm using malic acid for preparing $LiNiVO_4$ nano powder in solution method at 450 °C for 6 hours [Thongtem *et. al,* 2007a; Thongtem *et. al,* 2007b]. Therefore, the use of acids for preparing the inverse spinel $LiNiVO_4$ promotes the formation of nanosized powder since the acid behaves like a chelating agent. In this regards, the metal ions complexes with the acid to form homogenous and well dispersed matrix in the solution. In this thesis, the work on the $LiNiVO_4$ by the sol-gel and polymer precursor method has attained the crystal size ranging from 33 nm to 68 nm by using the XRD spectra and Scherrer equation.

Generally, the growth of the particle is dependent on the heating temperatures. This behaviour was also found in the calculated crystallite size for $LiNiVO_4$ by sol-gel and polymer precursor method**.** The single phase inverse spinel $LiNiVO_4$ for undoped sample by sol-gel method was obtained starting from 600 °C for 3 hours. The calculated size obtained for the sample prepared by such method is around ~ 43 nm obtained from the XRD data. The calculated particle size increases with increase in sintering temperature for the undoped sample prepared by polymer precursor method. The smallest average particle size calculated using Scherrer equation for the undoped system is around ~ 33 nm. This was obtained at 500 °C sintering for 3 hours through the polymer precursor method. This result shows that PEG helps to suppress particle growth.

However, upon addition of Mn dopant material, the particle size obtained decreases with increasing of firing temperature. This behaviour may be due to the different sizes of the nickel and manganese atoms and the space available for expansions. The expansion rates could also be different. The growth of the particle was observed having particle size of around ~ 33 nm and ~ 35 nm for 500 °C and 600 °C, respectively. At these temperatures, there may be space available for expansions. Subsequently, the particle size decreased to ~ 32 nm and ~ 23 nm at higher temperature at 700 °C and 800 °C, respectively for the sol-gel doped compound. The shrinkage for the doped system happened as the result of the doped system has achieved better thermal stability than the undoped system. Therefore, the growth of the particle restrains at elevated temperature. Similarly, the particle size was also observed to decrease upon increasing firing temperature for the doped material prepared using the polymer precursor method. The particle size was observed to drop from around ~ 39 nm at 500 °C to ~ 19 nm at 800 °C. The size of the particles became even smaller due to the polymer source (PEG) that helps to inhibit the particle growth besides the assistance of citric acid as chelating agent.

Even though Lai et. al, (2002b) had prepared the same doped $LiNi_{1-x}Mn_xVO_4$ ($0 \leq x \leq 0.4$) at 750 °C for 4 hours, there was no report on the crystal size in their work.

According to Lai's work, the XRD spectrum of $LiNi_{0.6}Mn_{0.4}VO_4$ is identical to the XRD spectrum of undoped inverse spinel $LiNiVO_4$. Lai's group have prepared the doped $LiNi_{1-x}Mn_xVO_4$ ($0 \leq x \leq 0.4$) using moist chemical method by mixing the stoichiometric amount of $LiOH \cdot H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and NH_4VO_3 raw materials in distilled water and ethanol solution and dissolved under grinding [Lai *et. al,* 2002b]. The $LiNi_{0.6}Mn_{0.4}VO_4$ precursor obtained was calcined at 750 °C for 4 hours and another subsequent 3 hours to obtain the single phase of the inverse spinel structure. On the contrary, the doped $LiNi_{1-x}Mn_xVO_4$ ($x=0.25$) in this work prepared by sol-gel and polymer precursor method were successfully prepared with no trace of impurity calcined at temperature as low as 500 °C for 3 hours. This probably showed the better choice of raw materials used.

The cubic lattice constant, a and the crystal cell volume, V obtained by using Braggs formula as presented in subsection 3.3 (equation 3.1) of Chapter 3 are compared with the work by Lai *et. al,* (2002b). The values were taken from the XRD data at sintering temperature of 600 °C. The peak chosen was that of the [311] plane. The difference in the lattice constants obtained for each composition was the consequence of the change in the scattering angle with x in $LiNi_{1-x}Mn_xVO_4$ although all $LiNi_{1-x}Mn_xVO_4$ ($0 \leq x \leq 1$) samples have the $LiNiVO_4$ XRD pattern [Lai *et. al,* 2002b]. The lattice constants and the crystal cell volume increase with the increasing amounts of manganese molar ratio in $LiNi_{1-x}Mn_xVO_4$ because the ionic radii of Mn^{2+} (0.83 Å) is larger than that of Ni^{2+} (0.69 Å) in the tetrahedral sites and this might be related to the manganese substitution for nickel [Shannon, 1976].

The morphology analyses of all four systems in this work are deliberated in the Chapter 4 to Chapter 7. The fluffy and fragile-looked $LiNiVO_4$ particles prepared by the sol-gel were obtained at firing temperature of 500 °C. The SEM micrographs at lower temperature (500 °C) depict flakey-looking with large voids for the $LiNiVO_4$ samples prepared by polymer precursor method. As for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ by sol-gel method, the surface morphology exhibits flakey particle composed of the powder treated at 500 °C. The SEM image shows the brittle-like $LiNi_{0.75}Mn_{0.25}VO_4$ particles at 500 °C prepared by polymer precursor method. The micrographs for all treated samples prepared using both methods in this work show the growth of the particle with visible particle boundaries upon treatment at higher temperatures. The porosity of the undoped sol-gel method was observed at highest calcined temperature of 800 °C.

The particle growth is also observed for both sol-gel and polymer precursor doped compounds. The particles increase in size upon increasing calcination temperature as shown in SEM results. In addition, formation of polyhedral particles was obtained at the highest firing temperature of 800 °C for both sol-gel and polymer precursor compounds.

The TEM studies offer higher resolution and depict the actual crystal size of the prepared product. The preparation before TEM viewing requires one to sonicate the powder to agitate the particles under ultrasonic (sound) energy. In this manner, the particles will be much more dispersed and thus, a close comparison can be made for the crystallite size with the calculated value using Scherrer equation as tabulated in Table 4.1, Table 5.1, Table 6.2 and Table 7.2 in Chapter 4, Chapter 5, Chapter 6 and Chapter 7, respectively. From the values calculated using the Scherrer equation, the crystallite size for the undoped system increased as the sintering temperature increased. As mentioned, smaller particles are formed at elevated temperatures for both doped systems TEM results support the calculated crystallite size obtained by the Scherrer equation as explained in subsection 3.3 (equation 3.1) of Chapter 3.

The TEM result and the SEM micrographs for the doped systems sintered at different temperatures did not suggest the same morphology. This behaviour could possibly be due to the presence of the doped material that has been treated at different sintering temperatures. The precursor that may contain impurities was calcined initially at 500 °C. After three hours of sintering, contaminants were removed as proven by XRD. The dopant material from the doped system (manganese) prevents the particle from growing. At higher sintering temperature (600 °C, 700 °C, and 800 °C) more materials will be released producing smaller particle size. The reason for this may be due to the polymer source that acts to prevent more weight loss and forming the material quicker. Since 0.25 mole ratio of Mn was used in this work, the polymer will entrap the Mn making them closer to each other and thus promotes a small weight loss in process of formation of the inverse spinel product and at the same time prevents growth of the material. This is supported by the thermal studies obtained for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ systems which acquired 18.9 % and 14.37 % of weight loss by sol-gel and polymer precursor method respectively.

The elemental studies using the EDAX analyzer demonstrated the material content of the prepared compounds in subsection 4.6 of Chapter 4. EDAX results show that the $LiNiVO_4$ samples are quite homogeneous based on the Ni:V ratio since EDAX could not detect Li. The best ratio that is closest to the 1:1 ratio was obtained at sintering temperature of 800 °C. Based on these results, it may be deduced that nickel in the sample exists as Ni^{2+} and vanadium as V^{5+}. Similarly, the calculated ratio of the Ni:Mn ratio from EDAX results in the doped $LiNi_{1-x}Mn_xVO_4$ ($0\leq x \leq 1$), x = 0.25 system is almost equal to the Ni:Mn ratio of 3:1. At the sintering temperature of 500 °C, the ratio shows that the sample is Ni rich, but for precursors sintered at 600 °C and 700 °C the

Ni:Mn ratio is closer to 3:1. However, for the precursor heated at 800 °C is slightly deficient in Ni. It may be inferred that, based on this work, the most suitable minimum temperature for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ sample is 600ºC and the highest is 700ºC.

The reversibility of the fabricated $Li/LiNiVO_4$ and $Li/LiNi_{0.75}Mn_{0.25}VO_4$ ($0\leq x \leq1$) half-cells were analyzed at 1 mV/s scan rate to observe the intercalation and deintercalation properties form identification of the oxidation and reduction peaks in the CV studies. The voltage scan was cycled between 3 and 5 V versus Li^+/Li. From the CV measurements, there were features of oxidation and reduction peaks which correspond to the single electron transfer in the lithium extraction/ insertion [Kalyani *et. al,* 2002; Kalyani *et. al,* 2005]. The open circuit voltage of undoped and doped materials prepared by both sol-gel and polymer precursor methods were around 3.0 V and 3.5 V, respectively. The redox couple of Ni^{2+}/ Ni^{3+} coexist with the Li^+ ion deintercalation/ intercalation processes.

The cyclic voltammogram for the undoped system $LiNiVO_4$ by sol-gel method registers a broad reduction peak at ~ 4.5 V on the reverse scan. The result shows that the system has capacity fading upon cycling and weak Li^+ intercalation during subsequent scans. On the other hand, the peaks on the anodic and cathodic scans were better for the compound sintered at higher temperatures. The voltage difference between anodic and cathodic peaks during the initial scan was smaller to that of the compound calcined at lower temperature. Therefore, better reversibility is achieved for samples sintered at higher temperatures as a result of improved crystallinity for the sample treated at higher temperature.

The cell containing the undoped compound $LiNiVO_4$ by polymer precursor method depicts similar behavior on the cathodic scan on the CV plots. However, there was a slight shift on the potential and even broader peak present at the 5th scan of the cathodic curve for the compound fired at low temperatures. The oxidation and reduction peaks were even well defined for the compound sintered at higher temperatures. There was a slight shift in the redox potential for sample calcined at higher temperature prepared by the polymer precursor method and a small increase on the voltage difference between the forward and reverse peaks. This result suggests that slight capacity decay occurs upon cycling to the 5th scan on the cell system. The redox peaks are better defined than the compound sintered at lower temperatures, which suggests that the redox processes occurred more efficiently in the compound prepared using the sol-gel system.

The CV plots on the doped system $LiNi_{0.75}Mn_{0.25}VO_4$ prepared by the sol-gel method revealed the noticeable peaks on the oxidation and reduction curve. This behavior suggests that upon Li^+ extraction, Ni^{2+} oxidized to Ni^{3+} and reduces back on Li^+ insertion. This result was similarly obtained even at higher calcined temperatures where broader redox peaks are observed after a few subsequent cycles, which suggests the slow kinetics on the Li^+ de/intercalation [Landschoot, 2005]. The potential separation was better for compound sintered at lower temperatures for the doped system. Therefore, reversibility of compound fired at low temperature is better.

As for the doped system $LiNi_{0.75}Mn_{0.25}VO_4$ prepared by the polymer precursor method, the voltammogram suggest identical behavior of improved reversibility at lower temperatures for the doped sol-gel system. The peaks for redox processes are reduced as the cycling process took place for sample treated at 800 °C. The peaks were not well defined which suggests the weak intercalation of Li^+ in the system. Therefore, cyclic voltammetry showed better reversibility at lower calcination temperature (600 °C) for the doped system prepared by the polymer precursor method. This may be attributed to the Mn dopant in the system that has increased the thermal stability of the compound since TGA experiments showed a lower weight loss than the undoped materials.