

## CHAPTER 1

### INTRODUCTION

#### **1.1 General Introduction**

Energy sources are very important and essential for human daily life. The law of conservation of energy states that energy can neither be created nor be destroyed. When energy is used, it does not vanish but rather converted to another form of energy. A rechargeable battery acts as a transducer that converts chemical energy into electrical energy and vice versa. Living things need energy resources in order to function and perform work. Energy resources maybe divided into two main groups that are renewable energy resources, and non-renewable energy resources.

Renewable resources are available with immediate access; can be replaced and never depleted such as water, wind, and wave energy. Non-renewable resources that include gas, fossil fuels, oil, and coal are non-replenishable.

The global climate issue have become the major concern besides those main resources. That is because the energy generated and the production may cause bad implication to the environment as well as the human health. The energy production may have toxicity, and severe pollutants that might harm our environment. Thus, in order to save our world free from those unwanted phenomenon, using the renewable resources that is readily available may protect our world. Plus, the so-called ‘environmental friendly’ practice may also results production with low cost, that value for climate health.

Alternative method in energy supply is the most studied field for researchers. It is an important challenge to focus on for the sake of the future use. Research on sustainable energy storage has widely become researcher's interest for more practical, quality production, cost-effective and environmental friendly competitive products. To date, there are many type of energy storage system. Batteries, fuel cells, capacitors, solar cells, bio-fuels are the most popular energy storage technology ever made [Wang and Cao, 2008]. Among them, batteries are the most widely used in the form of electricity storage compared with others. Products developed in the market include the primary batteries as well as the rechargeable (secondary) batteries. Technologies especially in consumer electronics such as lithium ion batteries, nickel cadmium (Ni-Cd) batteries, and nickel-metal hydride (Ni-MH) batteries have significantly penetrated the markets for the past decades for its high performance and price competitiveness. Alternative renewable energy that possessed such technology is almost limited by their materials properties. Thus, the usage of developed technologies has not widely spread yet.

Material studies also concerned on economic as well as environmental issues that have been broadly discussed among researchers. Metals, polymers, semiconductors, ceramics, are classes of materials that involves in engineered science. Since then, the extension of materials development has effectively shown great progress and has become worthy to the human lifestyle.

Cathode materials studies for lithium ion battery have become one of the most important subjects in fabricating secondary batteries. The studies have become more interesting due to higher performance of the patented cathodes. Cathodes with high power density and good reversibility for advanced portable devices are the important

criteria on developing new rechargeable batteries. An understanding on cathode materials such as structural and chemical has to be well interpreted for improving the effort on developing new rechargeable batteries.

## 1.2 Work on electrode materials

The rechargeable lithium battery work in the early work used metallic lithium as anode. However, the metallic lithium was never applied in the marketed rechargeable batteries for its safety issues. Lithium was electrochemically coated onto the anode during charging process thus providing high surface area. The lithium reactivity with the electrolyte may be enhanced making it hazardous [Linden, 1994]. Short circuit might occur due to dendrites (uneven) formation on the anode and thus causing thermal runaway reaction and battery explosion [Tarascon and Armand, 2001]. An attempt of substituting the Li metal for an alloy with aluminium (Al) later successfully overcomes the problem [Rao *et. al*, 1977]. However, the alloy electrodes can only withstand for few limited cycles due to abrupt volume changes during the cycling process [Tarascon and Armand, 2001]. Inadequacy of the relevant materials and the suitable electrolyte – electrodes configuration has led in the interruption of the battery development as compared to that of rapid growth in digital technologies. The development of the cathode material considers the  $\text{LiNiO}_2$  system for better specific capacity than the  $\text{LiCoO}_2$  [Dahn *et. al*, 1991]. Nevertheless, the idea of developing such system finally rejected owing to the safety reasons on the collapsing lithiated  $\text{Li}_x\text{NiO}_2$  upon exothermal oxidation on the organic electrolytes [Tarascon and Armand, 2001]. Other layered oxide such as  $\text{LiMn}_2\text{O}_4$  was becoming productive [Armstrong and Bruce, 1996] for having improved on the structural instability by cationic doping with chromium

( $\text{Li}_{1+x}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_2$ ) as the Mn stabilized the chromium oxide layered structure [Ammundsen *et. al*, 2000]. Even so, the toxicity and high cost of chromium had caused major hindrance upon developing such product.

Attempts of synthesizing the inverse spinel vanadium oxides have been reported since 1961 as mentioned by Fey (1995). The study of such product was produced by using conventional solid state reaction. Reports on such material were studied using the same technique until the year 1994 [Fey *et. al*, 1994]. The solid state method typically requires long heating time and energy consuming. Yet, the synthesizing procedure was not favourable and not economically practical. The new method of adapting soft solution technique has created great attention among researchers for more feasible synthesizing. On the other hand, the preparations of solid state method were still discussed using various kinds of starting materials.

The synthesizing method plays an important role for the electrochemical properties and that will be determined by both physical and chemical features such as crystallite size, stoichiometry, homogeneity and etc. Therefore, many attempts on chemical modification were carried out by substituting other metal cations or coating [Kalyani, 2009; Landschoot *et. al*, 2003; Landschoot *et. al*, 2004a; Landschoot *et. al*, 2004b; Fey *et. al*, 2007]. Doping and coating techniques have been implemented in order to improve the performance of the cathode materials. Such structural modification attempts have shown improvement on the cycling capacity [Kalyani *et. al*, 2009; Landschoot *et. al*, 2004b; Fey *et. al*, 2007] as well as reduced particle size [Thongtem *et. al*, 2008; Landschoot *et. al*, 2004b]. Addition of the polymer source and chelating agent has shown the polymerization helps to distributing the metal ions through the

polymeric matrix [Hong *et. al*, 1997; Song and Lee, 2002; Vivekanandhan *et. al*, 2004; Vivekanandhan *et. al*, 2005; Fey *et. al*, 2006b].

The cathode materials such as  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  are both having high cell voltage of 4.8 V and 4.3 V respectively [Fey *et. al*, 1994; Fey and Perng, 1997; Fey and Chen 1999; Fey and Huang, 1999]. Studies on both cathodes have suggested few techniques on the preparation method. Apart from technique used, the structural, physical as well as electrochemical properties are being the major concern among researchers. The sintering temperatures were often discussed studies to obtain the pure phase of inverse spinel products. The concern on preparation technique and the goal on improving the physical and electrochemical properties are mutually important and often mentioned in the reports.

The preparation on the  $\text{LiCoVO}_4$  is unfavorable due to high cost of cobalt material and its toxicity. The  $\text{LiNiVO}_4$  cathode offers better preparation technique as the studies are continuously reported in order to upgrade the cathode performance. This includes the obtained product with smaller particle size upon low firing temperature, the formation of single phase of such structure in easiest technique, as well as lowering the capacity fading upon cycling in the electrochemical process. However, upon reports since the studies commenced, the capacity of the inverse spinel  $\text{LiNiVO}_4$  product practically still does not fit to the theoretical value of 148 mA h/g [Fey and Huang, 1999; Fey *et. al*, 1994; Lai *et. al*, 2001; Kalyani *et. al*, 2002; Subramania *et. al*, 2006]

The slow energy storage advancement cannot be put in square level with the computer advancement as the Moore's Law prediction on doubling memory storage in every 2

years happened in the computer industry. However, the impressive progress achieved on battery sales since past decade has led in developing the lightest battery with high energy density will always be the motivation of researchers for energy storage system.

### 1.3 Objective of the research

Efforts to improve the structure, physical and electrochemical performance are the main goal of this work. Since the studies on the  $\text{LiNiVO}_4$  cathode offers great deal on the cell voltage and high specific capacity, the work on such product will be discussed. Thus, the goal of this work will look forward to the following aims:

1. To prepare the pure phase of inverse spinel  $\text{LiNiVO}_4$  cathode by the sol gel and polymer precursor method at lower temperature and shorter calcination time.
2. To produce nanosized materials by the same soft solution techniques mentioned above.
3. To characterize the synthesized samples and identify their structure.
4. To study the reversibility of the cathode materials by cyclic voltammetry.

### 1.4 Scope of the Thesis

The inverse spinel  $\text{LiNiVO}_4$  work has caught researcher's attention and being widely reported since 1990's. The compound was studied for its great performance of high cell voltage and potential cathode materials. The doped material using manganese, Mn will be discussed in this work.  $\text{LiNiVO}_4$  and  $\text{LiNi}_{1-x}\text{Mn}_x\text{VO}_4$  ( $0 \leq x \leq 1$ ) were prepared by using the sol- gel method and polymer precursor method. The starting material used

for synthesizing the cathode material includes the lithium acetate dihydrate, nickel acetate tetrahydrate, manganese acetate tetrahydrate, and ammonium metavanadate. Lithium acetate dihydrate was used for having cheap and easily available raw material produced in the industry. Besides, the lithium acetate dihydrate is chemically stable and very soluble. Citric acid,  $C_6H_8O_7$  is used to chelate the metal cations during the synthesis. This chelating agent is a weak acid and usually found in the variety amount of fruits and vegetables such as lemons and limes in which having large concentration of the acid. The citric acid is also used as the cleaning agent, an environmentally benign natural source.

The sol- gel and polymer precursor method are promising since they possess several advantages over conventional solid state reaction method. The solid state reaction method would require long heating hours at very high sintering temperature. The solid state was always reported to produce impurities as the cause of the solid may not react completely during the reaction. Inhomogeneity and larger particle size produced is the reason why those drawbacks affect the electrochemical performance of the prepared electrode. Thus, the sol-gel and polymer precursor method has been reported in most works for better performance of the cathode to overcome that unfavourable phenomenon.

The  $LiNiVO_4$  cathode material will be prepared by diluting those starting material with the distilled water separately before those are mixed. This work utilizes the distilled water instead of other inorganic or organic solvent reported for preparing the cathode. This method yields at low sintering temperature of 500 °C for 3 hours with nanosized

particles. The produced nanosized cathode material was successfully synthesized at low heating and sintering hours compared to that of other reported works.

The synthesized  $\text{LiNi}_{1-x}\text{Mn}_x\text{VO}_4$  ( $0 \leq x \leq 1$ ) cathode material was successfully prepared having the single phase of inverse spinel  $\text{LiNiVO}_4$  at  $x = 0.25$ . This result is compared with the reported work for the single phase of the inverse spinel of  $x = 0.4$  at  $750^\circ\text{C}$  [Lai *et. al*, 2002b] sintering temperature for 4 h, then at the same temperature for 3 h after being ground.

An overview of the reported works on the promising cathodes is discussed in Chapter 2. The studies of various kinds of electrode material since they were prepared using diversified numbers of methods are being reported since 1960's. The improvements of the rechargeable lithium ion batteries are deliberate briefly in this chapter towards the commercialization of the energy resources by Sanyo. This chapter mentioned few important issues such as safety.

Chapter 3 discussed the method used in this work to synthesize the  $\text{LiNiVO}_4$  and  $\text{LiNi}_{1-x}\text{Mn}_x\text{VO}_4$  ( $0 \leq x \leq 1$ ) cathodes. There are four systems prepared for the mentioned cathodes. The detailed synthesizing procedures are explained in this chapter for each available system. The prepared cathode for each system are being analysed structurally, thermally and chemically. The synthesized samples were fired at different sintering temperatures from  $500^\circ\text{C}$  to  $800^\circ\text{C}$  in 3 hours using a furnace separately.

The X-ray diffraction (XRD) analyzer was used to provide the cathode information in order to investigate the purity and their product structure. The effect of firing



temperatures on the single phase inverse spinel  $\text{LiNiVO}_4$  was observed based on the obtained diffractogram for all prepared samples. The data obtained from the XRD analysis provide the information of the FWHM (full-half width maximum) of obtained diffractogram. Thus, the crystallite size of the cathode can be calculated by using the Scherrer equation. The obtained crystallite size was acquired to investigate the effect of sintering temperature on the crystal size. The obtained XRD data also enables to investigate the effect upon manganese doped of both cubic lattice constant,  $a$  and cell volume,  $V$  using the Bragg's peak.

The chemical mechanism and the thermal studies on the prepared cathode were also discussed in this work. The chemical mechanism were proposed by considering the mixed solution that might occur during the synthesise process. The thermogravimetric analysis was carried out to study the thermal stability of the obtained precursor. Therefore, the result will help us to estimate the relevant sintering temperature for the precursor. The endothermic peaks which indicates the weight loss in the thermogravimetric curve gives the estimated decomposition process for the formation of the final product.

The morphology studies were done to observe the particle distribution as well as the particle size of the prepared cathode. The scanning electron microscope (SEM) was used to analyse the particle distribution of the prepared cathode. The Transmission electron microscopy (TEM) was held to investigate the actual size of the powder particle upon sintering temperature. The obtained images were then compared to that of calculated crystallite size. The energy dispersive X- ray analysis was obtained to study

the elemental composition of the prepared samples as well as confirms the identity of the material.

This work also considers on the deintercalation and intercalation behaviour of the prepared cathode. Thus, the cyclic voltammetry (CV) test was held to study the electrochemical properties of the cathode material. The voltage of the cathode was observed to analyse the electron gain or loss in the half- cell system. The reversibility of the cell system was recorded upon five respective cycles on each system upon suitable particle size of the cathode.

Chapter 4 deals with the structural studies along with the redox behaviour for prepared pristine  $\text{LiNiVO}_4$  cathode by the sol- gel method. The reports on  $\text{LiNiVO}_4$  system by the polymer precursor method were discussed in Chapter 5. In Chapter 6 and Chapter 7, both physical and chemical properties were analysed for the mixed doped  $\text{LiNi}_{1-x}\text{Mn}_x\text{VO}_4$  ( $0 \leq x \leq 1$ ) by the sol gel and polymer precursor method respectively.

Chapter 8 review the whole results acquired in this work to be discussed. This thesis also includes the conclusion and suggestion on the further work for the  $\text{LiNiVO}_4$  for future consideration in final part in Chapter 9.