CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The oil crisis in mid-1970s has driven the demand of high-energy power sources for light electronics, alternative materials to avoid the poisonous Pb and Cd for environmental protection. Thus, the commercialization of lithium battery was finally achieved in late 1980s [Liu *et. al,* 2004]. Matsushita had developed Li/Carbon- Fluorine (CF) battery which was the earliest concept used mainly in Japan [U.S. Patent *3,536,532,* 1970]. Today's largest manufacturer for both lithium rechargeable and nickel metal hydride batteries [Ikeda *et. al,* 1975], Sanyo was once come out with one of the earliest lithium ion batteries and that are Li/MnO_2 system that they initially sold in solar rechargeable calculators [Sanyo, Model *CS-8176L*].

The demand for the lithium ion batteries has created everyone attention since their commencement in the market in 1991. To date, the necessity for portable power sources with high energy density has tremendously increase due to the advancement of the portable power sources such as cell phones, notebook computers, camcorders and so on [Lu and Liou, 1999; Zou *et. al,* 2001; Mai *et. al,* 2000; Chen *et. al,* 2002; Lu *et. al,* 1999; Chen *et. al,* 2003a]. The famous cathode materials such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ are among various transition metal oxides used in most reported work.

The 'rocking chair batteries' includes the non- lithium materials anode such as carbon, the lithium metal oxide or lithium alloy [Fey and Huang, 1999]. Such batteries are often recalled to have problems with dendritic growth of lithium metal. On the other hand, the cell can be intercalate lithium ion reversibly and enhance the safety of such secondary batteries [Fey and Huang, 1999]. Figure 2.1 demonstrates the dendrite growth of the Li surface in the cell system. In order to increase the energy density of the battery, the anode can be replaced by the lightweight of metallic lithium [Fey and Huang, 1999]. Thus, such battery system must utilise the high potential to achieve high energy density as well as increasing the cell potential.

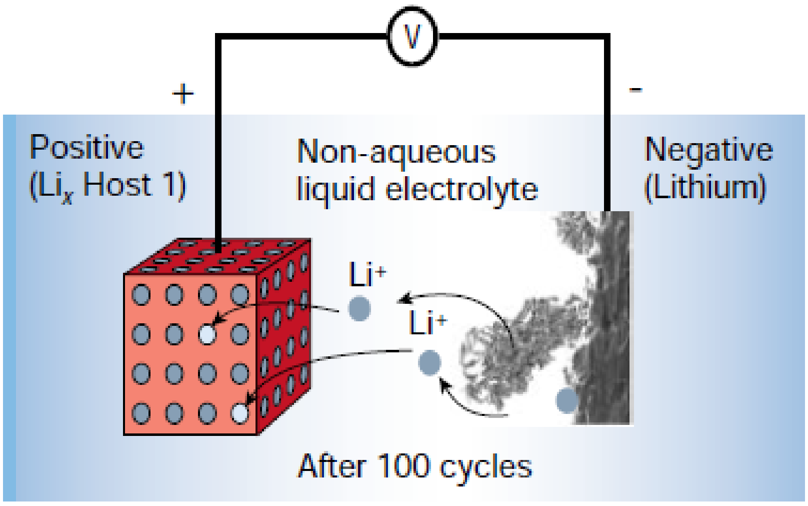


Figure 2.1: Dendrite growth on the Li surface [Tarascon and Armand, 2001; Orsini *et. al*, 1999]

Succeeding the invention of these materials, the $LiNiVO_4$ and $LiCoVO_4$ are found to exhibit high cell voltage of over than 4.3 V. These new materials have been proposed as attractive candidate cathode material for recent rechargeable batteries [Lu and Liou, 2000; Fey *et. al*, 1997].

Such lithium transition metal oxides have inverse spinel structure are very promising cathode owing to their high cell potential at 4.8 V [Fey and Huang, 1999; Vivekanandhan *et. al*, 2005]. Nevertheless, such cathode had facing some drawbacks [Fey *et. al*, 2007] such as:

(a) low discharge capacities,
(b) abrupt capacity drop during even at initial cycle, and
(c) large capacity fading during continuous cycling.

Table 2.1 Advantages and disadvantages of Li-ion batteries [Linden and Reddy, 2001]

Advantages	Disadvantages
Sealed cells; no maintenance required	Moderate initial cost
Broad temperature range of operation	Degrades at high temperature
Long shelf life	Need for protective circuitry
Rapid charge capability	Capacity loss or thermal runaway when overcharged
High rate and high power discharge capability	Venting and possible thermal when crushed
High coulombic and energy efficiency	Cylindrical designs typically offer lower power density than NiCd or NiMH
High specific energy and energy density	
Long cycle life	
No memory effect	

These problems are believed to be associated with the diffusion and electrode dissolution in the acidic electrolyte [Fey *et. al,* 2007]. Table 2.1 show some pro and cons of lithium ion batteries reported in 2001 [Linden and Reddy, 2001].

2.2 Vanadium Oxide Cathode Materials

Research on cathode materials has been continuously studied since early 1960’s. The cathode materials prepared were focused mainly on the preparation method, as well as the structural analysis. Those $LiMVO_4$ cathode where M=Cu, Ni, Co, Zn, Cd, Mg, and Be [Kazakopoulos *et. al,* 2010] are the most cathode materials that have been synthesized using various types of techniques.

TABLE 2.2

$LiMVO_4$ Compound Structures [Fey, 1995]

Structure	Compounds
Spinel	$LiCuVO_4$, $LiNiVO_4$*, $LiCoVO_4$*
Olivine	$LiMnVO_4$, $LiCdVO_4$, $LiMgVO_4$
Phenacite	$LiBeVO_4$, $LiZnVO_4$

Both $LiNiVO_4$ and $LiCoVO_4$ are found to have inverse spinel structure, proved by [Fey *et. al,* 1994].

According to the early reported results, the $LiMVO_4$ compounds have been classified into 3 different types of structure namely olivine, spinel, and phenacite [Paques-Ledent and Tarte, 1974; Kanno *et. al,* 1980]. Both $LiNiVO_4$ and $LiCoVO_4$ have been widely thought having to be spinel structure for decades.

However, Fey and Dahn have proved the contrariwise fact. Instead of having spinel structure, both compounds possess the inverse spinel structure based on their calculation on the powder XRD results [Fey *et. al,* 1994]. On the other hand, both $LiMgVO_4$ and $LiZnVO_4$ structures can be converted from olivine or phenacite to spinel by high-pressure modification [Blasse, 1963]. Table 2.2 summarize the $LiMVO_4$ compound structures presented by [Fey, 1995].

2.3 Inverse spinel lithium transition metal vanadium oxide

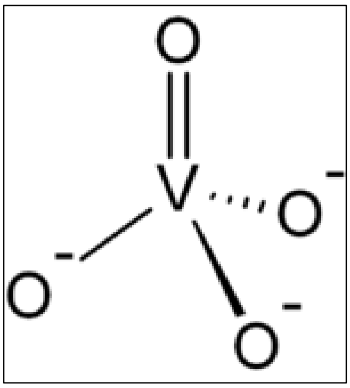


Figure 2.2 The vanadate diagram [http://en.wikipedia.org/wiki/Vanadate]

Materials for positive electrode in lithium ion cell vanadates have the highest oxidation state of +5. The material consisting VO_4^{3-} anions has become attention for the high energy density for enhanced electrochemical performance of the cell. These compounds have demonstrated high cell potential; a way of achieving high energy density [Liu *et. al,* 2001; Phuruangrat *et. al,* 2007a]. Figure 2.2 shows the arrangement of vanadate, VO_4^{3-}.

2.3.1 Lithium Cobalt Vanadate, $LiCoVO_4$

$LiCoVO_4$ has an inverse spinel structure which has high cell potential of more than 4.3 V versus metallic Li [Landschoot *et. al,* 2004a; Landschoot *et. al*, 2004b] with capacity of 71 mA h/g [Fey *et. al*, 2008]. The $LiCoVO_4$ cubic occupies in $Fd\bar{3}m$ space group, the same structure as the inverse spinel $LiNiVO_4$. Such lower cell potential has made the product is more suitable for some oxidation- resistant electrolytes [Fey *et. al*, 2008]. However, the high cost of cobalt and negative impact to the environment for its toxicity has made a turn to the other alternatives for free-cobalt cathode material.

2.3.2 Lithium Nickel Vanadate, $LiNiVO_4$

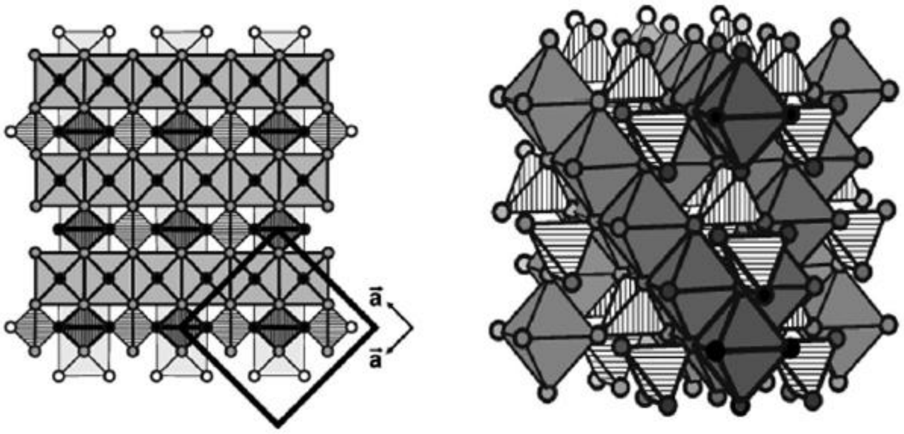


Figure 2.3: Crystallographic representation of $LiNiVO_4$ structure. Li, Ni ions are in octahedral site and V ions in tetrahedral site [Reddy *et. al,* 2008]

The $LiNiVO_4$ is a face centered cubic crystal where all the atoms in the inverse spinel structure occupy special position in the $Fd\bar{3}m$ space group [Gonzalez *et. al,* 1994] with 8.22Å of unit cell value [Liu *et. al,* 2001] . The positive electrode material having the VO_4 is located in the tetrahedral sites. According to Prabaharan and his research group, the Li and Ni atoms may be bonded to each oxygen atom of VO_4 tetrahedron [Prabaharan *et. al,* 1997]. This behaviour suggests that asymmetry in the VO_4 unit without perturbing the whole cubic symmetry [Li *et. al,* 2009]. Figure 2.3 displays the inverse spinel $LiNiVO_4$ cubic structure.

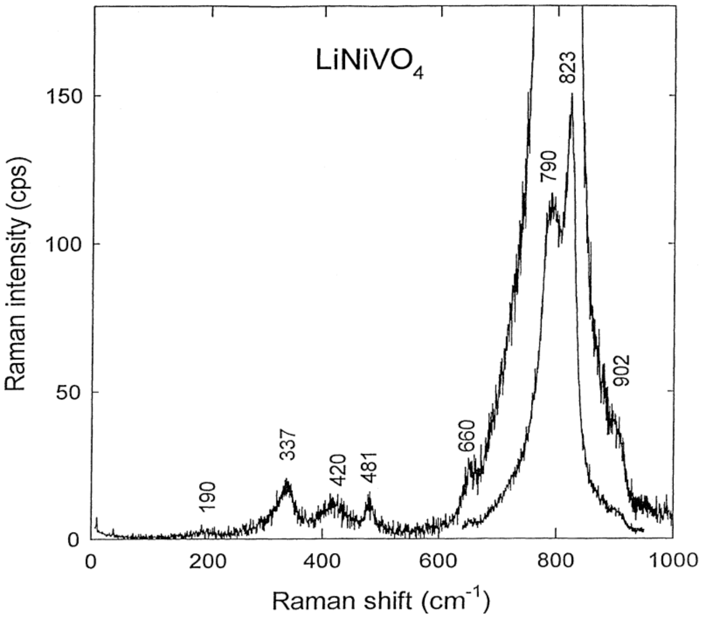


Figure 2.4: Raman scattering spectrum of $LiNiVO_4$ [Chitra *et. al,* 2000]

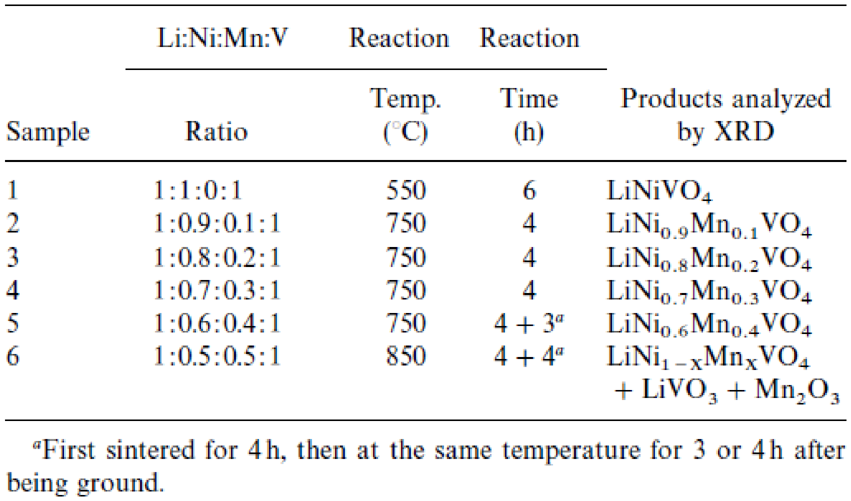
Liu and his research group have reported that the Li and Ni atom are arbitrary allocated in the octahedral sites while the pentavalent vanadium atom occupies in the tetrahedron sites [Liu *et. al,* 2001]. The proposed explanation suggests that the V−O bonds behave in stretching vibration mode [Premudhomme and Tarte, 1972]. Chitra and co-workers have demonstrated the stretching mode of the VO_4 tetrahedron with A_1 symmetry in the broad high frequency Raman spectra shown in Figure 2.4 [Chitra *et. al,* 2000]. Lithium in the host lattice relatively tightly bound and that is the reason of high insertion potential of the inverse spinel compound [Kazakopoulos *et. al,* 2008].

The $LiNiVO_4$ compound was the first known Li- intercalation reaction near 5 V and patented inverse spinel as potential cathode material for rechargeable Li-ion cells [Fey and Dahn, 1996].

2.3.3 Lithium Nickel Manganese Vanadate, $LiNiMnVO_4$

Lai and his co-workers report the study of the doped $LiNi_{1-x}Mn_xVO_4$ [Lai *et. al*, 2002b]. Generally, the aim of the doping in the system is to enhance the electrochemical properties [Xie and Zhou, 2006]. The other systems having the inverse spinel host structure was doped by various types of dopant material usually the 3*d* dopant material (Cu, Cr and Fe) manifest enhanced initial capacity [Landschoot *et. al*, 2004b]. However, the large capacity fading was observed upon few cycling. Fey and his group have prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}VO_4$ by citric acid assisted with the polyethylene glycol (PEG) and obtained improved cycle stability on the cycle test [Fey *et. al*, 2006]. The doped $LiNi_{1-x}Mn_xVO_4$ mentioned earlier [Lai *et. al*, 2002b] have been synthesized by the moist chemical method. They have prepared series of doped compound as shown in Table 2.3.

Table 2.3: The reaction conditions and the resulting products for preparation of $LiNi_{1-x}Mn_xVO_4$ [Lai *et. al*, 2002b]



	Li:Ni:Mn:V	Reaction	Reaction	
Sample	Ratio	Temp. (°C)	Time (h)	Products analyzed by XRD
1	1:1:0:1	550	6	$LiNiVO_4$
2	1:0.9:0.1:1	750	4	$LiNi_{0.9}Mn_{0.1}VO_4$
3	1:0.8:0.2:1	750	4	$LiNi_{0.8}Mn_{0.2}VO_4$
4	1:0.7:0.3:1	750	4	$LiNi_{0.7}Mn_{0.3}VO_4$
5	1:0.6:0.4:1	750	4 + 3[a]	$LiNi_{0.6}Mn_{0.4}VO_4$
6	1:0.5:0.5:1	850	4 + 4[a]	$LiNi_{1-x}Mn_xVO_4$ $+ LiVO_3 + Mn_2O_3$

[a] First sintered for 4 h, then at the same temperature for 3 or 4 h after being ground.

The xerogel obtained was dissolved by the distilled water and ethanol under grinding. Although they have successfully prepared the single phase similar to that of undoped $LiNiVO_4$ structure over suitable range of $(0 \leq x \leq 0.4)$ mole ratio, the additional 3 hours was still needed in order to obtain the desired product for $LiNi_{0.6}Mn_{0.4}VO_4$. Moreover, upon few studies reported by Lai's group [Lai *et. al*, 2002b], there was no evidence on the morphology of the particle to support the explanation on the electrochemical performance obtained. The reversible capacity initially obtained at only 64 mA h/g; the value was much lesser than the reversible capacity of undoped work reported by Kalyani et. al, (2002), and Subramania et. al, (2006). Therefore, more understanding should be focused on the structural behaviour upon doping to give clearer view on the electrochemical performance.

2.4 Methods

Few attempts on engineered chemical modification had possessed microstructure or even nanostructured materials that may contribute for better power properties. The electrochemical energy sources have been intensively studied for energy storage and conversion system. New systems of diversified materials have been prepared to suite current developed technology. However, some materials produced may have some drawbacks either in structural or electronic properties. Thus, such problems may be overcomes by implementing various methods of synthesizing. As being emphasized by previous researchers, the performance of improved battery relies on the materials refinement on different kinds of cell component [Hassoun *et. al*, 2007; Whittingham, 2008; Patil *et. al*, 2008; Shukla and Kumar, 2008].

2.4.1 Solid state reaction

The typical method such as solid state reaction method is very famous during the commencement of vanadium oxide studies. However, such method can give undesirable properties for the prepared cathode [Vivekanandhan *et. al*, 2005, Vivekanandhan *et. al,* 2004].

This conventional reaction method for preparing the cathode materials are often reported to produce impurities. As a result, the compound may affect the electrochemical performance of the prepared cathode. Other disadvantages [Fey and Huang, 1999; Fey and Dahn, 1994; Prabaharan *et. al,* 1997; Ohzuku *et. al,* 1990; Masquelier *et. al,* 1996; Momchilov *et. al,* 1993; Huang *et. al,* 1998] that may have occur could possibly be:

i. solid particles may not react completely, producing impurities, and so that sintering temperatures must be high.
ii. affect the cycling properties /electrochemical features
iii. poor control of chemical homogeneity as well as high cost for heat treatment
iv. long range diffusion of reactants
v. inhomogeneous composition
vi. larger particle size
vii. longer particle size

The solid state method was used as conventionally used to prepare the $LiCoVO_4$ and $LiNiVO_4$ products. As the method consumed much energy and time, the approach of having soft solution technique was applied [Chen *et. al,* 2003a].

The studies have been focused on the preparation method in synthesizing the $LiNiVO_4$. According to Fey and Huang, they have reviewed the work that was started since early 1960's which have been reported using the conventional solid state method where the compound has been fired for 7 days at 500 °C by using the $LiVO_3$ and $NiCO_3$ as the starting materials [Fey and Huang, 1999]. On the other hand, $LiNiVO_4$ was prepared at 1000 °C for 4 days by using NiO as the raw material instead of $NiCO_3$ [Ito, 1979]. The same compound have been synthesized by reacting $LiNiO_2$ with V_2O_5 or V_2O_3 at 400 °C in 4 hours and subsequently at 800 °C for 8 hours [Fey and Perng, 1997]. A new method for preparing $LiNiVO_4$ have been proposed using the LiOH, V_2O_5, and $Ni(CH_3COO)_2$ as the starting materials [Lu *et. al,* 1999].

2.4.2 Wet chemistry method / Soft solution technique

Attempts on preparing the cathode materials have been suggested for preparing the convenient way of synthesize method. As the studies have been widely performed, the discovery of the new inverse spinel cathode materials for rechargeable lithium batteries has increased due to their high voltage behavior with methods implemented to improve the cathode. In past few years, much attention have been directed to the preparation using the soft solution techniques [Fey and Huang, 1999; Fey and Perng, 1997; Landschoot *et. al,* 2004a; Landschoot *et. al,* 2004b; Fey *et. al,* 1994; Fey *et. al,* 1997; Orsini *et. al,* 1998; Chitra *et. al,* 2000]. Orsini group have suggested such method for the preparation of amorphous and cyrstallized $LiNiVO_4$ [Orsini *et. al,* 1998].

The solution techniques have been proposed such as hydrothermal, sol-gel, combustion method and et cetera [Larcher *et. al,* 1997; Barboux *et. al,* 1991; Garcia *et. al,* 1995; Amatucci *et. al,* 1996; Garcia *et. al,* 1997]. On the other hand, there were a lot of works on $LiNiVO_4$ assisted with the carboxylic acid group reported to chelate the metal ions in the solution during their synthesize processes.

2.4.2.1 Combustion method

The combustion method is a complex succession of chemical reactions involving the fuel and an oxidant followed by the heat formation and light in either a glow or flames. The work on combustion process using the immediate thermal degradation of the precursor with the oxygen has been efficiently used for developing the nanoscale products by various kinds of metal oxides [Purohit *et. al,* 2001; Guo *et. al,* 2004; Hwang and Wu, 2004; Biswas *et. al,* 2007; Jeong *et. al,* 2007].

The fuel- oxidant combustion comprise of an exothermic decomposition fuel oxidant precursor such as urea-nitrate, glycine nitrate, DHF- nitrate and et-cetera held in lower temperatures [Chick *et. al,* 1990; Li *et. al,* 2002; Zhang *et. al,* 2004a]. This technique employs quick and exothermic reaction between the metal precursors and organic fuels. The method does not involve the external source but combustion reaction itself supplies the required heat for the phase formation. A large volume of gasses will be acquired throughout the combustion process. The resultant for the reacted product will inhibit agglomeration and serve formation of the nanostructured powders.

The product yield from the combustion method annealed at 500 °C acquired < 1 μm [Prabaharan *et. al*, 1997] of average grain size coexist with the controlled particle growth. Kalyani and her research group have adopted the combustion method using starch and metal nitrates as the starting materials [Kalyani *et. al,* 2002]. They have gained an average grain size of 1.5 μm with mono dispersed particles from the SEM analysis. Vivekanandhan and his group have prepared inverse spinel $LiNiVO_4$ cathode by using glycerol for the combustion method [Vivekanandhan *et. al,* 2004]. Even though they obtained 39 nm nanosized powders; the firing rate was still high at 12 hours. The inverse spinel synthesis of $LiNiVO_4$ was proposed by using gelatin as the fuel source [Subramania *et. al*, 2006]. The gelatin acts as good dispersing agent yields an ultrafine particles range from 40 nm to 60 nm with uniform distribution.

Apart from having low cost and low temperature process, better stoichiometry control, nanometer ranged particles, instant exothermic reaction; there are still some drawbacks that might occur during synthesizing process. The contamination caused by carbonaceous residue, better understanding to run a controlled combustion reaction for expected final product with favourable properties, the safety precaution should be taken into account for the potentially unwanted hazard throughout the process.

2.4.2.2 Hydrothermal Synthesis

Among various types of ionic compound, water is the suitable candidate for the solvent source. Usually, water can dissolve diversified compounds at high pressure and high temperature. The use of water is less hazardous even at raising temperatures and high pressure than other conventional ceramic methods in solid state route. Thus, the water characteristics mentioned above have been manipulated for development of metal oxide fine powders can be utilized by using such method [Whittingham *et. al,* 1995; Adschiri *et. al,* 2001; Burukhin *et. al,* 2002]. The hydrothermal method is associated on liquid and solid reagent upon heating accompanied by appropriate solvent in fastened chamber (autoclave) at temperature as high as 250 °C. An autoclave is usually utilized to handle hydrothermal state as such pressure treatment speed up the reaction between the solubility of starting reactants and lead to strong activation energy for the phase pure formation, or else the reaction can be achieved only at very high temperature [Lu *et. al,* 1999; Kanasaku *et. al,* 2000; Lianga *et. al,* 2006]. The obtained powders are dependent on the selective hydrothermal condition that can result in either crystalline or armophous [Myung *et. al,* 2002; Zhang *et. al,* 2004b; Meligrana *et. al,* 2006; Wu *et. al,* 2006; Chen *et. al,* 2007a].

Such soft reaction condition method favors in accomplishment by a number of novel materials for significant energy source applications. The development of few materials such as zeolites and microporous products that applied in gas separation and shape-selective catalyst and layered cathode materials were employed for competent secondary batteries [Walton *et. al,* 2001]. The nanosized phosphor for optical devices study was also successfully prepared by using hydrothermal process [Xue and Wang, 2010]. The other work using such method were effectively prepared crystalline ceramic powder directly from solution [Roy, 1994; Chien *et. al,* 1995; Lu and Chyl, 1996; Lu and Lo, 1997; Moon *et. al,* 1997; Lu and Lo, 1998].

To the author's knowledge, the works on preparing inverse spinel cathode material have been successfully prepared via hydrothermal technique since the year 1999 [Lu *et. al,* 1999]. The starting reactant was dissolved using propanol as the solvent instead of water

[Lu *et. al,* 1999]. The micron- sized powder was obtained as the final product after treatment at 200 °C for 2 hours. A year after, an improved crystalline inverse spinel cathode had been synthesized using the same method at 200 °C [Lu and Liou, 2000] for prolonged 6 hours and attained nano-sized powder (90 nm) with additional of small amount of ammonium carbonates. Later, the use of deionized water as the solvent was used to prevent the use of toxic medium from present work [Phuruangrat *et. al,* 2007b]. They have successfully prepared the cathode with 19-69 nm in diameter powder by 400 and 600 °C respectively for 6 hours.

However, apart from having can be directly formed from the solution, and easier to control the particle shape and size at low temperature, the hydrothermal has certain disadvantageous such as the hydrothermal slurries are potentially corrosive and such method may serve accidental explosion of high pressure chamber that cannot be prevented.

2.4.2.3 Sol-gel method

The sol gel method involves few processing steps by both chemical and physical operations that include hydrolysis, polymerization, gelation, condensation, drying and densification [Brinker and Scherer, 1990]. The technique usually begins with the metal alkoxides or salts mixing in water or in solvent (typically alcohol) at ambient or moderately elevated temperatures [Brinker and Scherer, 1990; Hench and West, 1990]. The precipitation can be prevented by controlling the pH of initial solution. This is very important measure to obtain homogeneous gel by addition of acidic or base solutions [Fu *et. al,* 2005]. On the other hand, the organic compounds with hydrophilic functional groups (hydroxides or carboxylates) in small molecules such as citric acid, oxalic acid, succinic acid, tartaric acid, acrylic acid; polymers for example poly (acrylic acid) (PAA), poly (vinyl pyrrolidone) (PVP) might be utilized to distribute the metal cation source homogeneously [Chen and He, 2001; Liu *et. al,* 2004; Fu *et. al,* 2005; Predoana *et. al,* 2007; Chen *et. al,* 2007b]. The carboxylate acid group not only acts as the chelating (complexing) agent throughout the gel solution but also as a carbon source that will improve the conductivity of the material compound [Hong *et. al,* 1997; Hwang *et. al,* 2001; Vivekanandhan *et. al,* 2005; Li *et. al,* 2007]. According to Landschoot et. al, (2004b) the complexation of citric acid will serve the formation of smaller particle; therefore will increase the surface area for better Li ion extraction/ insertion. The obtained gel precursor will be further heated to remove excess water as well as the volatile chemical components to obtain the dried decomposed powders. The pure phase of the nano crystalline product will be formed after the dried powders were fired at certain temperatures depending on the chemical nature of the precursor [Son and Kim, 2005; Zhong *et. al,* 2006].

The sol gel process contains few advantageous as the possible low temperature processing is needed throughout the process. The resultant of the powder will form smaller particle size and control in the morphology in the synthesis. The low firing temperature is also possible for such method. The final product is expected to better homogeneity and formation of the pure phase product can be easily obtained than conventional ceramic method.

The sol-gel method is actively used due to shorter time of preparation, and less energy consumed. The reported works on the sol-gel synthesis have been reviewed for preparation on the cathode materials [Liu *et. al,* 2004; Fu *et. al,* 2005]. The sol gel method [Liu *et. al,* 2001] has been applied to study the structural properties on the electronic structure of the obtained $LiNiVO_4$ with additional of glycine during the process. The same polymer source, glycine has been manifest during the preparation of pure phase $LiNiVO_4$ and $LiAl_xNi_{1-x}VO_4$ in the sol-gel combustion method [Sivashanmugam *et. al,* 2006]. Hwang and his group have discussed their work on the X-ray properties of the acidic $LiNiVO_4$ (pH= 1) synthesized by the sol gel method [Hwang *et. al,* 1998]. According to Klein (1988) and Brinker and Scherer, (1990), the sol-gel is considered promising due to many advantages over conventional solid state method such as:

i. homogeneous mixing at the atomic or molecular level
ii. good stoichiometric control
iii. low synthesis temperature
iv. short heating time
v. good crystallinity
vi. uniform particle size and small diameter, even at the nanometer level.

2.4.2.4 Polymer precursor method

The polymer precursor method is very useful to providing the nanosized $LiNiVO_4$ compound. The polymer precursor itself will act as the gelling agent where the metal ions will surrounded by polymer chains, subsequently will suppress precipitation of metal salts during evaporation process. The polymer matrix complexes between metal cations and citric acid for better dispersity [Liu *et. al,* 1996; Park *et. al,* 1997; Sun *et. al,* 1997; Hong *et. al,* 1997].

Fey have summarized the previous work on $LiNiVO_4$ synthesized by sol gel and the traditional solid state method. This is shown in Table 2.4 [Fey and Huang, 1999]. In addition, series of doping compound were reported to study the doping effect on the crystal structure [Fey *et. al*, 1997; Arrabito *et. al*, 2001].

Table 2.4 Preparation methods and reaction conditions for $LiNiVO_4$ compounds [Fey and Huang, 1999].

Starting material	Treatment
$LiVO_3$ + $NiCO_3$	500°C, 7 days
$LiVO_3$ + NiO	1000°C, 100 h
Li_2O + 2NiO + V_2O_5	800°C, 1 day to 550°C, 25 days
Li_2CO_3 + $2NiCO_3$ + V_2O_5	700°C, 12 h
Li_2CO_3 + 2NiO + V_2O_5	650°C, 18 h
$2LiOH.H_2O$ + $2Ni(NO_3)_2.6H_2O$ + V_2O_5	700°C, 6 h
$LiOH.H_2O$ + $Ni(NO_3)_2.6H_2O$ + NH_4VO_3	800°C, 12 h
$2LiNiO_2$ + V_2O_5	700°C, 2 h
Li_2CO_3 + 2NiO + V_2O_5	730°C, 12 h
$LiOH.H_2O$ + $Ni(NO_3)_2.6H_2O$ + NH_4VO_3	400°C, 192 h or 500°C, 48 h
$2LiNiO_2$ + V_2O_3	500°C, 4 h and 800°C, 6 h
$LiNO_3$ + $Ni(NO_3)_2.6H_2O$ + NH_4VO_3 + $6NH_2CH_2COOH$ (glycine)	350°C and 500°C, 6 h
$LiOH{\cdot}H_2O$ and $Ni(OH)_2$ + V_2O_3 or V_2O_5	700 °C for 2 h in air
$7LiNO_3$ (in excess) + $0.45Ni(NO_3)_2.6H_2O$ + 0.25 NH_4VO_3	200-700°C, 12 h
$LiNO_3$ + $Ni(NO_3)_2.6H_2O$ + $V(C_5H_7O_2)_3$	450°C, 12 h
$LiOH.H_2O$ + $Ni(CH_3COO)_2.4H_2O$ + NH_4VO_3	200°C, ca 15 atm for 2 h

As both $LiNiVO_4$ and $LiCoVO_4$ are poor conductor, it is essential to mix them with good electronic conductor to ensure that such electrode receive adequate electrical conductivity. Nevertheless, the mixing may serve in reducing the material's energy density [Fey and Wu, 1997; Hwang *et. al*, 2001]. Therefore, the most typical method to enhance the electrical conductivity is by using dopant, coating or an additive. Polarization problem are often not discussed in most work of such materials and not yet being solved. The Li^+ diffusion and mobility are not entirely investigated for better understanding of dopant material on the crystal structure.

2.5 Doping in inverse spinel cathode

Much effort has been applied in order to increase the performance of rechargeable batteries. Therefore, doping is one way that is commonly reported for preparing series of compound of electrode material. The mixed doped material has been introduced since such doping may enhance capacity and cycle performance of electrode. The $LiNiVO_4$ cathode are often said to have large discharged capacity loss upon continuous cycling. A number of works have been reported to improve their performance for co-doped transition metal vanadates. The mixed-doped composite does not change the structure of the inverse spinel structure but may increase the material kinetics in terms of cycle life and the capacity performance [Xie and Zhou, 2006].

Consequently, Fey and his co- worker have demonstrated the effect of doping the $LiNiVO_4$ cathode with the rare earth atom such as Ytterbium (Yb), Lanthanum (La) and Gadolinium (Gd) [Fey and Wu, 1997]. The dopant mole ratios of these materials ranged from 10^6 to 10^2. An attempt of replacing nickel by cobalt in $LiNiVO_4$ had been reported by low temperature at 800 °C for 12 hours [Fey *et. al,* 1999]. The structural analysis of such compound demonstrated inverse spinel structure. The cubic lattice constants are found to increase linearly with the stoichiometry in $LiNi_yCo_{1-y}VO_4$. Even though such compound has revealed the expected result as pristine $LiNiVO_4$ and $LiCoVO_4$, the grain size still in the range of submicron particle (0.1-1 μm). Yet, the discharge capacity demonstrated 34.8 mA h/g at 4.7 V and display large capacity fading at higher charge voltage of 4.8 V.

Landschoot's groups have studied various kinds of transition metal ions dopants for $LiCoVO_4$ such as Cu, Cr and Fe [Landschoot *et. al*, 2004b]. The preparation of the doped $LiNi_{0.5}Co_{0.5}VO_4$ nanocrystals was reported by solvothermal reaction by using isopropanol at 10-360 hours and calcination at 300 °C-600 °C for 6 hours but the electrochemical study was not reported in their work [Thongtem *et. al*, 2008]. Major challenges are often faced for the co-doped vanadate cathode materials. Those doped material were able to improve the initial capacity. However, their capacity abruptly declined after few cycles [Fey and Wu, 1997; Lai *et. al*, 2002b; Landschoot *et. al*, 2004b].

2.6 Characterization of inverse spinel

The doping using rare earth atom, Yb in $LiNiVO_4$ show an improvement by factor of three at 25 °C; an increase from 10^{-10} to 10^{-7} S/cm. On the other hand, the cobalt doping $LiNi_yCo_{1-y}VO_4$ by [Fey *et. al*, 1999] did not discussed on the capacity aspect. The $LiNiVO_4$ synthesized by combustion method using glycine as the fuel source was used as the cathode element in the Li/ $LiNiVO_4$ and C/ $LiNiVO_4$ cell systems [Prabaharan *et al*, 1997].

Improved cycleability between 3-5 V was obtained for both voltammogram. Nevertheless, the C/ $LiNiVO_4$ cell system display large capacity fading over 100 cycles. Little capacity fading was merely obtained for the Li/ $LiNiVO_4$ cell system upon cycling. The use of graphite anode in the C/ $LiNiVO_4$ cell system may serve irreversibility capacity. Still, the charge discharge data was not available in their reported work for comparison.

Table 2.5 Discharge capacity data by previous works

Method	Cell system	Discharge capacity	Reference
Solid state	Li/ $LiNiVO_4$	45 mA h/g	Fey *et. al*, 1994
Solid state	Li/ $LiNiVO_4$ in $LiBF_4$, DMC/ EC/ PC	16.3 mA h/g	Fey *et. al*, 1997
Solution precipitation	Li/ $LiNiVO_4$ in $LiPF_6$, EC/ DEC	24 mA h/g	Fey and Chen, 1999
Complex precipitate gel	Li/ $LiNiVO_4$ in $LiPF_6$, EC/ DEC	~ 55 mA h/g	Lai *et. al*, 2001
Combustion	Li/ $LiNiVO_4$ in $LiAsF_6$, EC/ DMC	90 mA h/g	Kalyani *et. al*, 2002
Combustion	C/ $LiNiVO_4$ with PvdF/ HFP polymer electrolyte	102 mA h/g	Subramania *et. al*, 2006

The actual capacities of $LiNiVO_4$ in the experiment were much smaller than the theoretical capacity of 148 mA h/g. This behavior may due to the electrolyte oxidation that has reached the maximum potential window of the electrolyte in which the electrolyte used can withstand certain voltage in the battery system. Thus, it was not a surprise that most of researchers acknowledged the electrolyte decomposition is the main cause for capacity fading in $LiNiVO_4$ cell system. There are still few reports on the capacity performance reported in the charge discharge performance of the developed cathodes for Li secondary batteries. Although the theoretical value of 148 mA h/g was not yet achieved upon removal of lithium, only capacity ranged from 16 to 102 mA h/g was attained practically. Table 2.5 summarized the reported discharge capacity on the first cycle in their respective works.

2.7 Summary

The sol-gel method and polymer precursor method offers the preparation of the cathode at low synthesis temperature, low sintering temperature and promotes the formation of smaller particle size of the obtained powders. Therefore, those techniques were implemented in this work for study of the inverse spinel $LiNiVO_4$ and Mn- doped $LiNiVO_4$. Our goal is to prepare the single phase of those products at low synthesize and firing temperature using both techniques. The additional of citric acid and polymer source would be an advantage as those materials will facilitate the formation of nanoparticle powders as the carboxylic acid serve homogeneous distribution in the chelate metal ions in the polymer matrix. The nanoparticle powder will be produced which will serve larger surface area in the calcined powders. Such nanosized powder may shorten the Li^+ ion diffusion length for faster kinetics of Li^+ ion in the crystal structure and thus improved the electrochemical properties during de/intercalation process.

The inverse spinel $LiNiVO_4$ cathode material was prepared by using few raw materials supplied by from Aldrich and Fluka. Four types of cathode systems were prepared i.e. $LiNiVO_4$, $LiNiVO_4$ + PEG, $LiNi_{1-x}Mn_xVO_4$ and $LiNi_{1-x}Mn_xVO_4$ + PEG systems. Few tests have been characterized to investigate the prepared $LiNiVO_4$ cathode material. The synthesized cathode have been characterized by x-ray diffraction (XRD), thermogravimetric/differential thermal analyzer (TGA/DTA), scanning electron microscopy (SEM), energy dispersive x-ray (EDAX), transmission electron microscopy

(TEM). All samples having single phase of $LiNiVO_4$ cathode were chosen to be further characterized after confirming with the XRD results. Subsequently, the best four samples having the smallest nano-sized particle for each system were fabricated after TEM test.

Although not all methods have been discussed in this thesis, the knowledge reviewed may be important to consider the best method that can be used to synthesize the cathode material.