CHAPTER 2

LITERATURE REVIEW

2.1 Development of lithium ion batteries

The year 1991 marks the beginning of lithium ion battery technology (Ozhuku and Brodd, 2007). Lithium is the lightest metal and is also one of the metals with highest reduction potential. These criteria contribute to theoretical capacity of 3860 Ah/kg. This value is high compared to zinc and lead which is 820 Ah/kg and 260 Ah/kg respectively (Vincent, 2000). Lithium ion batteries become best choice for the fuel cell–battery hybrid devices among other battery systems such as nickel-cadmium, nickel-metal hydride and zinc air. This is due to the high energy density and good cycling performance of lithium ion batteries (Prakash *et al*., 2009).

2.2 Cathode materials for lithium ion batteries

Being an important component in batteries, cathode materials play a significant role in the electrochemical performance of a battery. The following requirements are key factors for successful cathode materials (Whittingham, 2004):

(a) Contains transition metals that are readily reduced / oxidized;

(b) The material should able to react with lithium reversibly and does not change the host structure when lithium is inserted;

(c) The material is able to react with lithium providing high capacity and high voltage in order to get high energy storage;

(d) Able to react with lithium very rapidly for high power density;

(e) Good electronic conductor enabling easy movement of electrons during chemical reaction;

(f) Stable structure during charge and discharge processes;

(g) Low cost and environmentally friendly.

$LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ are some of the examples of cathode materials used in lithium ion batteries (Ritchie *et al*., 1999).

Lithium Cobalt Oxide

Lithium Cobalt Oxide ($LiCoO_2$) has theoretical capacity of 274 mAh g^{-1} and energy density of 1070 Wh kg^{-1}(Burukhin *et al*., 2002). There are two types of $LiCoO_2$, low temperature $LiCoO_2$ (LT- $LiCoO_2$) and high temperature $LiCoO_2$ (HT- $LiCoO_2$) (Kang *et al*., 1999; Yoon and Kim., 1999; Levasseur *et al*., 2000). LT- $LiCoO_2$ has spinel structure with space group $Fd\bar{3}m$ and HT- $LiCoO_2$ exhibits rhombohedral structure with space group $R\bar{3}m$ (Santiago *et al*., 2003; Antolini, 2004; Brylev *et al*., 2003). Fig 2.1 depicts the structure of $LiCoO_2$.

Kang *et al* (1999) synthesized LT- $LiCoO_2$ and HT- $LiCoO_2$ using citrate sol gel method. XRD from this work is shown in Fig 2.2. The diffractogram of HT- $LiCoO_2$ exhibits (003), (101), (006), (012), (015), (107), (018), (110) and (113) peaks while the LT- $LiCoO_2$ exhibits (111), (311), (222), (400), (331), (333), (440) and (531) reflection peaks.

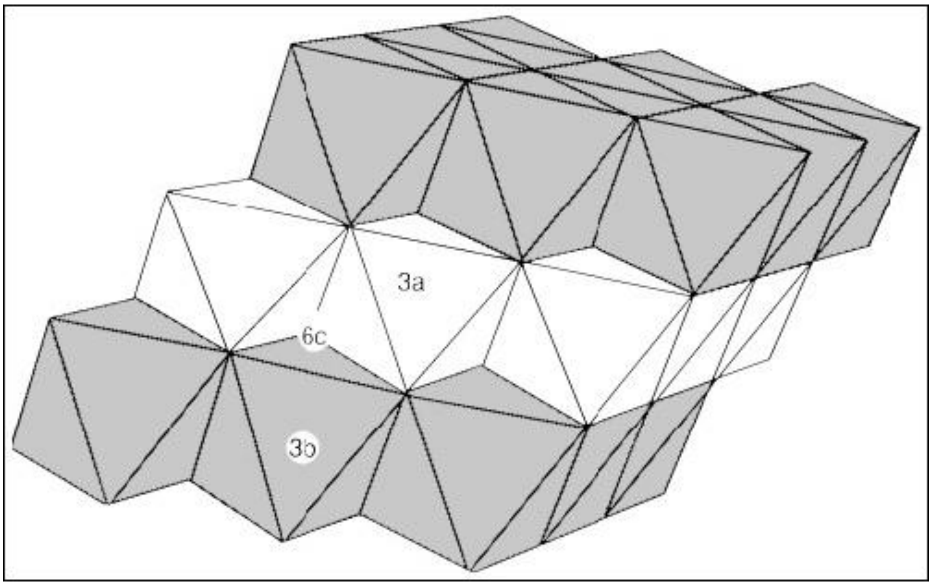

Fig 2.1: Structure of $LiCoO_2$ (alcantara *et al*., 1997)

In practise, due to structural instability during deliathiation, only half of the theoretical capacity is achieved (Needham *et al*., 2007). Cobalt has been substituted with other transition metals metallic elements in order to get better cycling performance and reduce toxicity (Sathiyamoorthi *et al*., 2008). Aluminium has been used to substitute cobalt (Amdouni *et al*., 2003; Myung *et al*., 2001). $LiTi_{0.01}Co_{0.99}O_2$ delivers an initial charge capacity of 157 mAh g^{-1} and initial discharge capacity 148 mAh g^{-1}. The initial discharge capacity is increased with the doping of titanium in $LiCoO_2$. The capacity retained at 135 mAh g^{-1} after 10 cycles. Further increase of dopant content did not improve the capacity (Gopukumar *et al*., 2003).

Sathiyamoorthi *et a*l (2008) prepared $LiCo_{0.8}$ $M_{0.2}O_2$ (M= Mg, Ca and Ba). Only $LiCo_{0.8}$ $Mg_{0.2}O_2$ exhibited slight increase in initial discharge capacity of 196 mAh g^{-1}compared to 191.6 mAh g^{-1} for $LiCoO_2$. Discharge capacity of $LiCoO_2$ reduced to 77.5 mAh g^{-1} after 25 cycles with capacity loss about 22.5 %. $LiCo_{0.8}$ $Mg_{0.2}O_2$ retained 97.6 % of its capacity at 25th cycle which gives the value of 191.3 mAh g^{-1}. $LiCo_{0.8}$ $Ca_{0.2}O_2$ and $LiCo_{0.8}$ $Ba_{0.2}O_2$ delivered discharge capacity of 178.5 mAh g^{-1} and 164 mAh g^{-1}

respectively. The capacity loss of both samples is around 2.7 % and 3.5 %. Hence Ga and Ba doping helped reduce capacity loss although initial discharge capacity is lower than $LiCoO_2$ being 183.5 mAh g^{-1} and 170 mAh g^{-1} respectively.

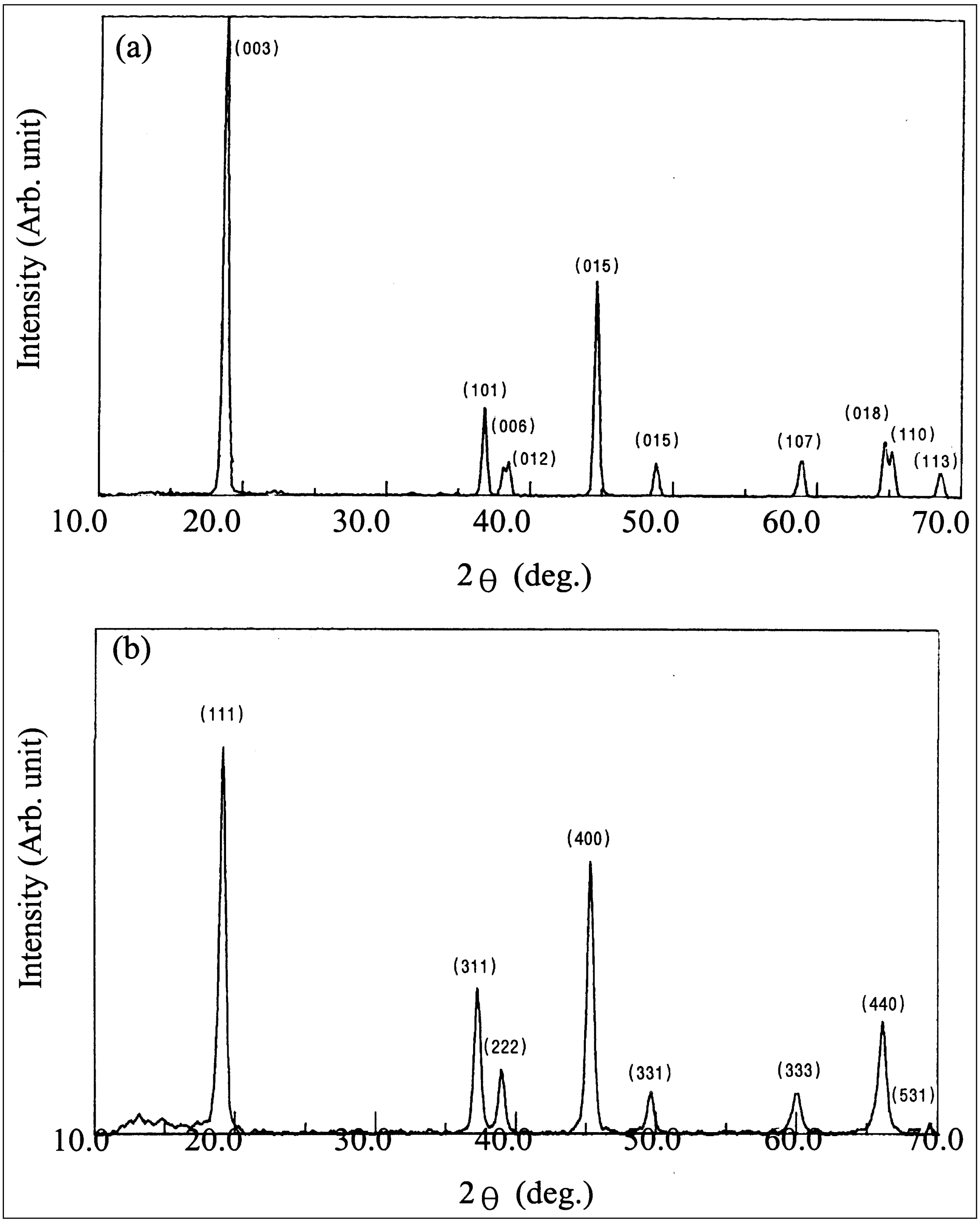

Fig 2.2: XRD of (a) HT- $LiCoO_2$ (b) LT- $LiCoO_2$ (Kang *et al.*, 1999)

Galium has been substituted in $LiCoO_2$ (Tong *et al.*, 2006). Both $LiCoO_2$ and Ga doped

$LiCoO_2$ deliver nearly similar first discharge capacity of ~160 mAh g^{-1} at 2.8 V cut-off. After 50 cycles, the discharge capacity of $LiCoO_2$ only retains 43.7 % of its initial capacity. $LiCo_{0.975}Ga_{0.025}O_2$ retains 87.9 % of its initial capacity at the end of 50th cycle.

Manganese doped $LiCoO_2$ has been studied by Suresh *et al.*, (2005a). Charge – discharge cycling shows that $LiCo_{0.8}Mn_{0.2}O_2$ exhibits the best cycling stability. Initial discharge capacity of 143 mAh g^{-1} was obtained by $LiCo_{0.8}Mn_{0.2}O_2$ while $LiCoO_2$ delivers 125 mAh g^{-1}. The capacity stabilized at 138 mAh g^{-1} from 4th cycle until 25th cycle for $LiCo_{0.8}Mn_{0.2}O_2$. $LiCoO_2$ only delivers about 120 mAh g^{-1} at 25th cycle.

Table 2.1: Summary of $LiCoO_2$ and its derivatives

Material	**Initial Capacity ($mAhg^{-1}$)**	**Capacity /Cycle ($mAhg^{-1}$)**	**Reference**
$LiCoO_2$	134.0	128.0 (10^{th} cycle)	Gopukumar *et al.*, 2003
$LiTi_{0.01}Co_{0.99}O_2$	148.0	135.0 (10^{th} cycle)	Gopukumar *et al.*, 2003
$LiCoO_2$	191.6	77.5 (25^{th} cycle)	Sathiyamoorthi *et al.*, 2008
$LiCo_{0.8}Mg_{0.2}O_2$	196.0	91.3 (25^{th} cycle)	Sathiyamoorthi *et al.*, 2008
$LiCo_{0.8}$ $Ca_{0.2}O_2$	183.5	78.5 (25^{th} cycle)	Sathiyamoorthi *et al.*, 2008
$LiCo_{0.8}Ba_{0.2}O_2$	170.0	64.0 (25^{th} cycle)	Sathiyamoorthi *et al.*, 2008
$LiCoO_2$	160.0	69.9 (50^{th} cycle)	Tong *et al.*, 2006
$LiCo_{0.975}Ga_{0.025}O_2$	160.0	140.6 (50^{th} cycle)	Tong *et al.*, 2006
$LiCoO_2$	125.0	120.0 (25^{th} cycle)	Suresh *et al.*, 2005
$LiCo_{0.8}Mn_{0.2}O_2$	143.0	138.0 (25^{th} cycle)	Suresh *et al.*, 2005

Lithium Nickel Oxide

Lithium Nickel Oxide ($LiNiO_2$) is another cathode material for lithium ion batteries. It has high discharge capacity and is cheaper compared to $LiCoO_2$ (Sun *et al*., 2006; Choi *et al*, 1998). $LiNiO_2$ has rhombohedral structure with space group of R3m (Chang and Kumta., 2005; Kalyani and Kalaiselvi., 2005). The stucture of $LiNiO_2$ is presented by Fig 2.3. Fig 2.4 indicates XRD pattern of $LiNiO_2$.

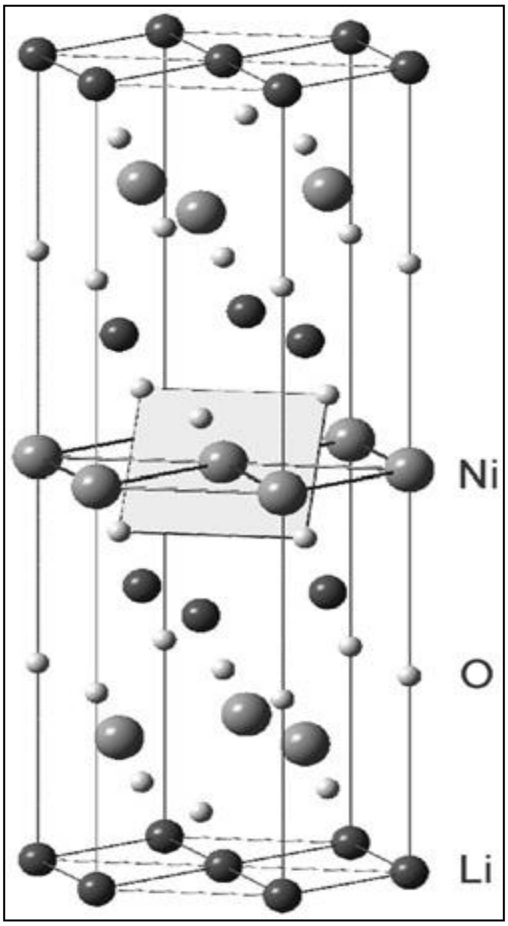

Fig 2.3: Structure of $LiNiO_2$ (Cao *et al*., 2009)

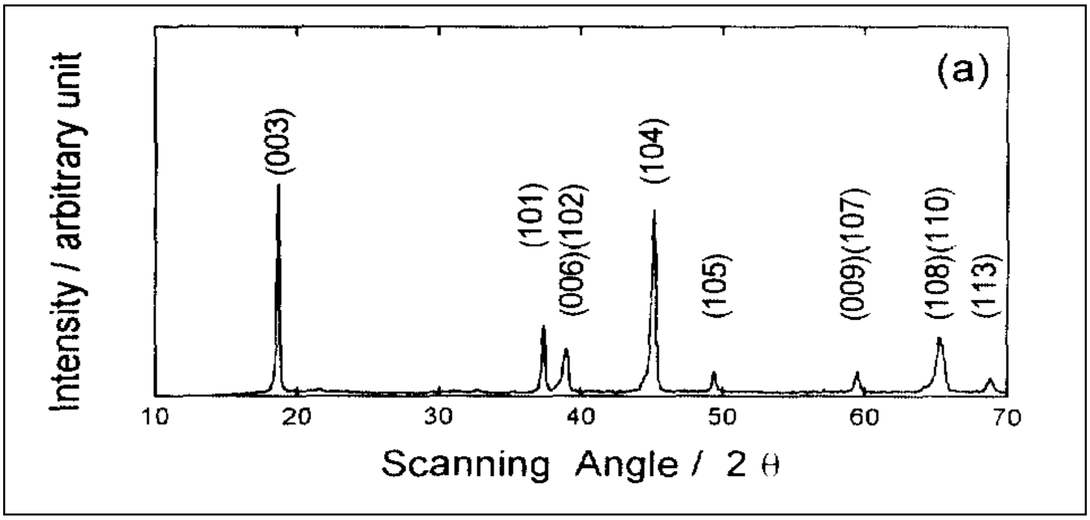

Fig 2.4: XRD of $LiNiO_2$ (Choi *et al.*, 1998)

$Li_{1-x}Ni_{1+x}O_2$ (x>0) results in presence of Ni^{2+} in the lithium sites that reduces lithium diffusion. Unstable ideal stoichiometry of $LiNiO_2$ affects the electrochemical performances (Yamada *et al.*, 1995; Delmas *et al.*, 1999; Molenda *et al.*, 2002; Kalyani and Kalaiselvi., 2005; Arai *et al.*, 1997).

$LiNiO_2$ has been substituted with titanium using direct molten salt synthesis (Ha *et al.*, 2006). $LiNi_{0.975}Ti_{0.025}O_2$ showed better capacity retention compared to $LiNiO_2$. However $LiNi_{0.95}Ti_{0.05}O_2$ and $LiNi_{0.9}Ti_{0.1}O_2$ exhibit less capacity retention compared to $LiNi_{0.975}Ti_{0.025}O_2$ and $LiNiO_2$. This is because titanium is electrochemically inactive and delivers less capacity as the titanium content increases in $LiNiO_2$. Initial capacity of $LiNi_{0.975}Ti_{0.025}O_2$ is 171 mAh g^{-1} and is retained 164 mAh g^{-1} on the 30th cycle.

Song *et al.* (2009) reported on $LiNiO_2$, $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.975}Al_{0.025}O_2$, $LiNi_{0.995}Ti_{0.005}O_2$ and $LiNi_{0.990}Al_{0.005}Ti_{0.005}O_2$. $LiNi_{0.990}Al_{0.005}Ti_{0.005}O_2$ exhibits high initial discharge capacity of 196.3 mAh g^{-1} compared to other compositions. $LiNiO_2$, $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.975}Al_{0.025}O_2$ and $LiNi_{0.995}Ti_{0.005}O_2$ deliver initial discharge capacity of 161.8 mAh g^{-1}, 174.4 mAh g^{-1}, 170.5 mAh g^{-1} and 172.9 mAh g^{-1}

respectively. However at the end of 20th cycle, $LiNiO_2$ delivered high discharge capacity of 143.5 mAh g^{-1} while $LiNi_{0.975}Ga_{0.025}O_2$, $LiNi_{0.975}Al_{0.025}O_2$, $LiNi_{0.995}Ti_{0.005}O_2$ and $LiNi_{0.990}Al_{0.005}Ti_{0.005}O_2$ exhibited 117.4 mAh g^{-1}, 90.5 mAh g^{-1}, 85.5 mAh g^{-1} and 113.8 mAh g^{-1} respectively.

$LiNiO_2$ has been doped with non-transition elements such as gallium and magnesium (Yu *et al.*, 2000). Simultaneous doping of these elements in the $LiNiO_2$ improved cycling performance. $LiGa_{0.02}Mg_{0.03}Ni_{0.95}O_2$ exhibited discharge capacity of 135 mAh g^{-1}. This value is almost constant during 20 cycles and the capacity loss is only about 1.5 %. While $LiNiO_2$ losses its capacity about 12.2 % after 20 cycles.

The properties of Al and Mg doped $LiNiO_2$ have been studied by Kim *et al.*, (2006). $LiNi_{0.9}Al_{0.05}Mg_{0.05}O_2$ delivered high initial discharge capacity of 173 mAh $g^{-1}$and stabilizes around ~180 mAh g^{-1} at 40th cycle. The capacity fading can be observed when aluminium content increased to 0.10 because aluminium is electrochemically inactive. These results suggest that ratio of 5 % aluminium and magnesium substitution to nickel improved the structure stability and raises the capacity.

Table 2.2: Summary of $LiNiO_2$ and its derivatives

Material	**Initial Capacity ($mAhg^{-1}$)**	**Capacity /Cycle ($mAhg^{-1}$)**	**Reference**
$LiNiO_2$	161.8	143.5 (20th cycle)	Song *et al.*, 2009
$LiNi_{0.975}Ga_{0.025}O_2$	174.4	117.4 (20th cycle)	Song *et al.*, 2009
$LiNi_{0.975}Al_{0.025}O_2$	170.5	90.5 (20th cycle)	Song *et al.*, 2009
$LiNi_{0.995}Ti_{0.005}O_2$	172.9	85.5 (20th cycle)	Song *et al.*, 2009

$LiNi_{0.990}Al_{0.005}Ti_{0.005}O_2$	196.3	113.8 (20th cycle)	Song *et al*., 2009
$LiNi_{0.975}Ti_{0.025}O_2$	171.0	164.0 (30th cycle)	Ha *et al*., 2006
$LiGa_{0.02}Mg_{0.03}Ni_{0.95}O_2$	135.0	133.0 (20th cycle)	Yu *et al*., 2000
$LiNi_{0.9}Al_{0.05}Mg_{0.05}O_2$	173.0	180.0 (40th cycle)	Kim *et al*., 2006

Lithium Manganese Oxide

Lithium manganese oxide ($LiMn_2O_4$) is low cost, has high reduction potential and is nontoxic (Hon *et al*., 2002; Vivekanandhan *et al*., 2006; Fey *et al*., 2006a; Ouyang *et al*., 2009). Fig 2.5 shows the structure of $LiMn_2O_4$. $LiMn_2O_4$ has spinel structure with Fd3m space group. Its diffractogram shows (111), (311) and (400) reflections (Myung *et al*., 2000). These peaks correspond to the lithium ions at tetrahedral 8a sites and manganese ions at 16 d sites (Yi *et al*., 2009). Fig 2.6 displays the XRD pattern of $LiMn_2O_4$ as reported in literature (Wu *et al*., 2006).

Among the problems preventing this material for commercialization are Jahn –Teller distortion and dissolution of Mn ion in the electrolyte during cycling (Li *et al*., 2007). $LiMn_2O_4$ undergoes phase change from cubic to tetragonal during Jahn Teller distortion. As a result, anisotropic volume change occurs, which causes capacity fading (Horn *et al*., 1999; Verhoeven *et al*., 2000; Yamada *et al*., 1999; Li *et al*., 2009; Chung *et al*., 2004).

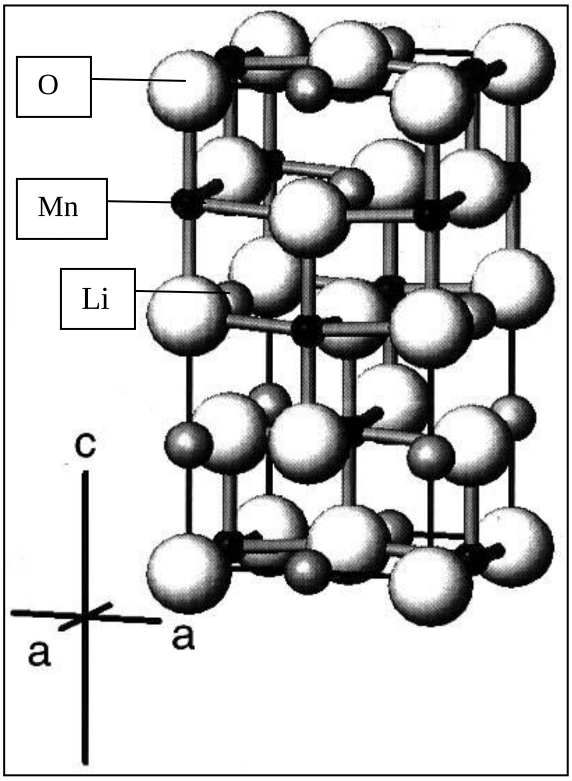

Fig 2.5: Structure of $LiMn_2O_4$ (Sugiyama *et al*., 2001)

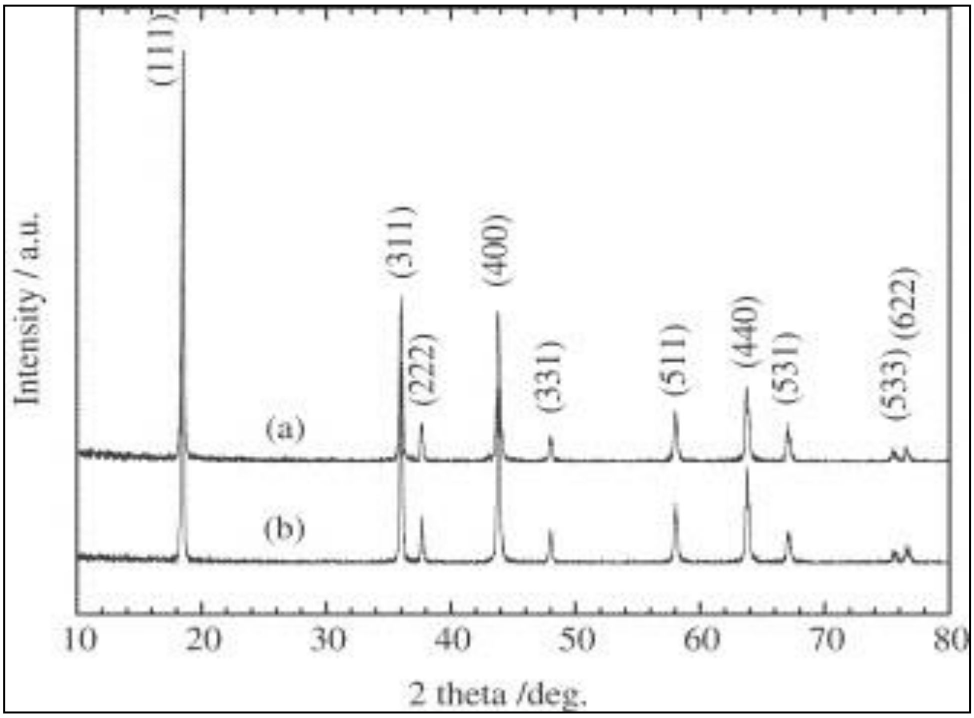

Fig 2.6: XRD of $LiMn_2O_4$ (a) spray drying method (b) solid state reaction (Wu *et al*., 2006)

According Tsang and Manthiram., (1996) controlled particle size of $LiMn_2O_4$ is one of the ways to overcome this problem. Partial substitution of manganese ions with other metal cations can reduce Jahn-Teller distortion and stabilize the cubic structure and overcome capacity fading (Lee *et al*., 2000; Deng *et al*., 2004). Examples include $LiM_xMn_{2-x}O_4$ (M = Co and Al, $0 \leq x \leq 0.3$) (Bakenov and Taniguchi., 2005), $LiM_{0.05}Mn_{1.95}O_4$ (M = Al, Co and Zn) (He *et al*., 2006), $LiMn_2O_4$ substituted with selenium (Yoon *et al*., 2002), chromium (Wang and Lu., 2003), aluminium (Julien *et al*., 2002), magnesium (Subramania *et al*., 2005) and etc.

Subramania *et al*., (2005) have studied $LiMg_yMn_{2-y}O_4$ ($0 \leq y \leq 0.2$) and obtained an initial discharge capacities for $LiMn_2O_4$, $LiMg_{0.05}Mn_{1.95}O_4$, $LiMg_{0.1}Mn_{1.9}O_4$, $LiMg_{0.15}Mn_{1.85}O_4$ and $LiMg_{0.2}Mn_{1.8}O_4$ as 137 mAh g^{-1}, 132 mAh g^{-1}, 118 mAh g^{-1}, 100 mAh g^{-1} and 90 mAh g^{-1} respectively. After 25 cycles, 75 % of capacity remained in $LiMn_2O_4$. $LiMg_{0.05}Mn_{1.95}O_4$ and $LiMg_{0.1}Mn_{1.9}O_4$ loss about 12 % and 2.33 % of its capacity respectively. $LiMg_{0.15}Mn_{1.85}O_4$ and $LiMg_{0.2}Mn_{1.8}O_4$ retained 93 % and 90.5 % of the first discharge capacity respectively. It can be confirmed that the composition of $LiMg_{0.1}Mn_{1.9}O_4$ showed better cycling performance.

The structural and electrochemical properties of chromium substituted $LiMn_2O_4$ was studied by Su *et al*., (2004). Initial discharge capacity of $LiMn_2O_4$ was 118.9 mAh g^{-1} which decreased to 87.5 mAh g^{-1} after 30 cycles. $LiCr_yMn_{2-y}O_4$ at y = 0.03 and 0.05 delivered discharge capacity of 123.1 mAh g^{-1} and 121.6 mAh g^{-1} respectively. $LiCr_{0.03}Mn_{1.97}O_4$ loses its capacity about 14.4 % to 105.3 mAh g^{-1} while $LiCr_{0.05}Mn_{1.95}O_4$ only lost about 12.2 % at 30th cycle. These results are stating that the doping of chromium improved the structural stability during lithium intercalation.

Electrochemical studies have been performed on $LiM_{0.05}Mn_{1.95}O_4$ with M = B, Al, Co and Ni (Lee *et al.*, 2000). Initial discharge capacity of $LiMn_2O_4$, $LiB_{0.05}Mn_{1.95}O_4$, $LiAl_{0.05}Mn_{1.95}O_4$ $LiCo_{0.05}Mn_{1.95}O_4$ and $LiNi_{0.05}Mn_{1.95}O_4$ is 136 mAh g^{-1}, 95 mAh g^{-1}, 133 mAh g^{-1}, 122 mAh g^{-1} and 125 mAh g^{-1} respectively. After 100 cycles, the capacity loss of the materials stated earlier is 16 %, 44 %, 5 %, 8 % and 2 % respectively. From the results, it can be explained that the substitution improved the capacity retention except for Boron-substituted sample. Structural instability was the reason for this fading.

$LiMn_2O_4$ was doped with aluminium, cobalt and zinc (He *et al.*, 2006). Undoped sample exhibits initial capacity of 119 mAh g^{-1}. $LiAl_{0.05}Mn_{1.95}O_4$ delivers initial capacity of 110 mAh g^{-1} while $LiCo_{0.05}Mn_{1.95}O_4$ exhibits around 106 mAh g^{-1}. Lowest initial discharge capacity of 96 mAh g^{-1} was exhibited by $LiZn_{0.05}Mn_{1.95}O_4$. However capacity of $LiMn_2O_4$ decreased to 25 mAh g^{-1}after 30 cycles. Capacity loss of $LiAl_{0.05}Mn_{1.95}O_4$, $LiCo_{0.05}Mn_{1.95}O_4$ and $LiZn_{0.05}Mn_{1.95}O_4$ were reported as 11 %, 3 % and 6 % respectively at the end of 30 cycles. Co doped $LiMn_2O_4$ exhibits better cycling performance. Structural distortion was reduced by the substitution.

Table 2.3: Summary of $LiMn_2O_4$ and its derivatives

Material	**Initial Capacity ($mAhg^{-1}$)**	**Capacity /Cycle ($mAhg^{-1}$)**	**Reference**
$LiMn_2O_4$	137.0	102.8 (25th cycle)	Subramania *et al.*, 2005
$LiMg_{0.05}Mn_{1.95}O_4$	132.0	116.2 (25th cycle)	Subramania *et al.*,2005
$LiMg_{0.1}Mn_{1.9}O_4$	118.0	115.3 (25th cycle)	Subramania *et al.*, 2005
$LiMg_{0.15}Mn_{1.85}O_4$	100.0	90.0 (25th cycle)	Subramania *et al.*, 2005

LiMg$_{0.2}$Mn$_{1.8}$O$_4$	90.0	81.5 (25th cycle)	Subramania *et al.*, 2005
LiMn$_2$O$_4$	118.9	87.5 (30th cycle)	Su *et al.*, 2004
LiCr$_{0.03}$Mn$_{1.97}$O$_4$	123.1	105.3 (30th cycle)	Su *et al.*, 2004
LiCr$_{0.05}$Mn$_{1.95}$O$_4$	121.6	106.8 (30th cycle)	Su *et al.*, 2004
LiMn$_2$O$_4$	136 .0	114.2 (100th cycle)	Lee *et al.*, 2000
LiB$_{0.05}$Mn$_{1.95}$O$_4$	95.0	53.2 (100th cycle)	Lee *et al.*, 2000
LiAl$_{0.05}$Mn$_{1.95}$O$_4$	133.0	126.4 (100th cycle)	Lee *et al.*, 2000
LiCo$_{0.05}$Mn$_{1.95}$O$_4$	122.0	112.2 (100th cycle)	Lee *et al.*, 2000
LiNi$_{0.05}$Mn$_{1.95}$O$_4$	125.0	122.5 (100th cycle)	Lee *et al.*, 2000
LiMn$_2$O$_4$	119.0	25.0 (30th cycle)	He *et al.*, 2006
LiAl$_{0.05}$Mn$_{1.95}$O$_4$	110.0	97.9 (30th cycle)	He *et al.*, 2006
LiCo$_{0.05}$Mn$_{1.95}$O$_4$	106.0	102.8 (30th cycle)	He *et al.*, 2006
LiZn$_{0.05}$Mn$_{1.95}$O$_4$	96.0	90.2 (30th cycle)	He *et al.*, 2006

Olivines (LiMPO$_4$ M = Fe, Co)

Olivine type lithium iron phospate (LiFePO$_4$) is one of the cathode materials getting attention worldwide because of its high theoretical specific capacity of 170 mAh g^{-1} and operates at flat voltage of 3.4 V versus lithium (Luo *et al.*, 2008; Li *et al.*, 2007; Kwon *et al.*, 2004). The flat discharge voltage of LiFePO$_4$ enables safety usage for organic electrolytes (Kim *et al.*, 2007b). Apart from that, it is also inexpensive, less toxic and exhibits better thermal stability compared to $LiNiO_2$, $LiCoO_2$ and $LiMn_2O_4$ (Bauer *et al*., 2005; Chang *et al*., 2006; Chen *et al*., 2008). The structure of $LiFePO_4$ is as depicted in Fig 2.7.

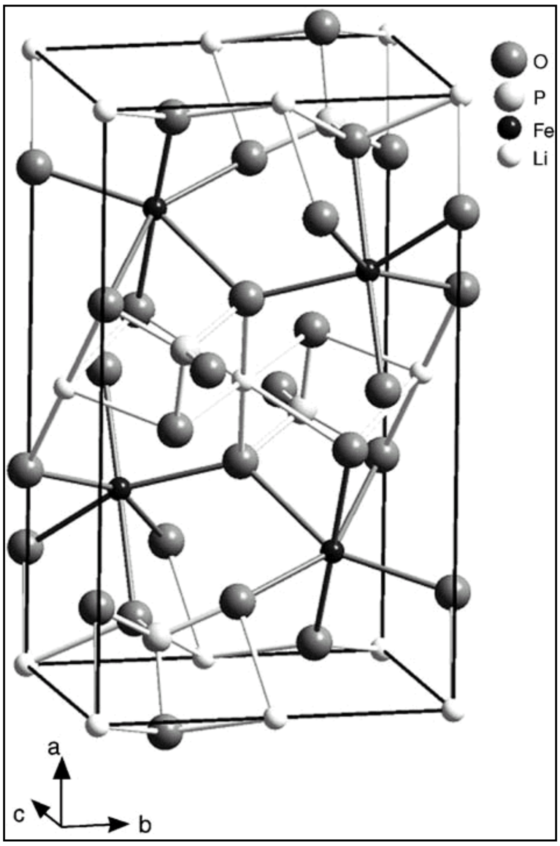

Fig 2.7: Structure of $LiFePO_4$ (Nyten *et al*., 2006)

However poor electronic conductivity and low lithium diffusion have limited its application (Lee and Teja., 2005; Ojczyk *et al*., 2007; Zheng *et al*., 2008a; Gao *et al*., 2009; Konarova *et al*., 2009). Slow diffusion of lithium ions at the interface of $LiFePO_4$ can be improved by particle size reduction (Lee *et al*., 2005; Yang *et al*., 2005). Many efforts have been taken towards increasing the conductivity such as carbon coating (Shin *et al*., 2006; Kuwahara *et al*., 2008; Prosini *et al*., 2001; Chung and Kim., 2004; Belharouak *et al*., 2005) and doping (Wang *et al*., 2005; Liu *et al*., 2006; Shin *et al*., 2008; Sun *et al*., 2009; Ou *et al*., 2008).

$LiCoPO_4$ is another interesting cathode material in olive type structure group (Kishore *et al*., 2005; Bramnik *et al*., 2005; Wolfenstine, 2006; Huang *et al*., 2005). High theoretical capacity of $LiCoPO_4$ about 167 mAh g^{-1} is considered as one of the main factors to be applied in lithium ion batteries (Rabanal *et al*., 2006; Wolfenstine *et al*., 2007; Li *et al*., 2009). It has higher energy density ~ 800 Wh kg^{-1} compared to $LiCoO_2$ which shows ~ 540 Wh kg^{-1}(Martin *et al*., 2008; Han *et al*., 2009; Wolfenstine *et al*., 2005). However $LiCoPO_4$ undergoes partial decomposition beyond 4.3 V (Martin *et al*., 2008) and poor lithium ion diffusion (Grigoronova *et al*., 2005; Han *et al*., 2009). This problem can be overcome by doping (Kishore *et al*., 2005; Li *et al*., 2009) and reduced particle size (Rabanal *et al*., 2006).

Lithium Nickel Vanadate

Lithium nickel vanadate also known as lithium nickel vanadium oxide ($LiNiVO_4$) is getting attention as a potential candidate for cathode material with its high voltage of 4.8 V versus Li^+ (Prabaharan *et al*., 1997; Fey *et al*, 1997). High voltage of cathode materials promise great energy density in batteries which is an important aspect in rechargeable batteries among other aspects such as long cycling, safety, stable charge-discharge etc (Lu *et al*., 1999; Liu *et al*., 2002). An inverse spinel structure of $LiNiVO_4$ is found to be another attractive factor compared to spinels. The structure of $LiNiVO_4$ is shown in Fig 2.8.

In inverse spinels Li and Ni atoms occupy the octahedrally coordinated interstices equally and randomly and the V atoms occupy the tetrahedrally coordinated interstices (Liu *et al*., 2002; Bhuvaneswari *et al*., 2005; Kalyani *et al*., 2002). On comparison to normal spinels such as $LiMn_2O_4$, Li and Ni atoms in $LiNiVO_4$ replace the two Mn atoms and the V atoms replace the Li atom in $LiMn_2O_4$ (Liu *et al*., 2002; Raveendranath *et al*., 2006).

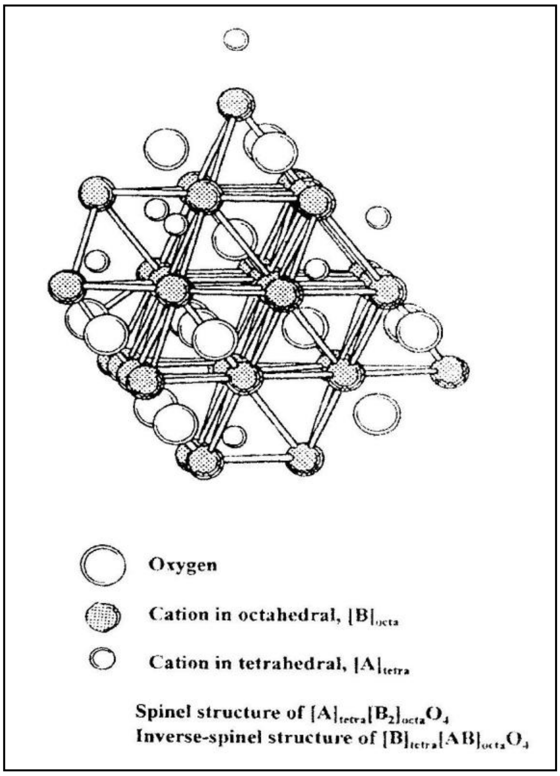

Fig 2.8: Structure of $LiNiVO_4$ (Fey *et al*., 1999)

Deep interest in this inverse spinel $LiNiVO_4$ enables research on various types of synthesis methods as it is main point to produce good physical and electrochemical properties (Kalyani *et al*., 2002).

$LiNiVO_4$ has been prepared by the solution precipitation method by Fey *et al*., (1999). pH value was adjusted during preparation by adding diluted nitric acid or ammonium hydroxide solution. XRD confirmed that only the product obtained at pH=3 gave pure $LiNiVO_4$ as confirmed by JCPDS data. The samples at pH=7 and pH=11 contain NiO impurities as stated in Fig 2.9.

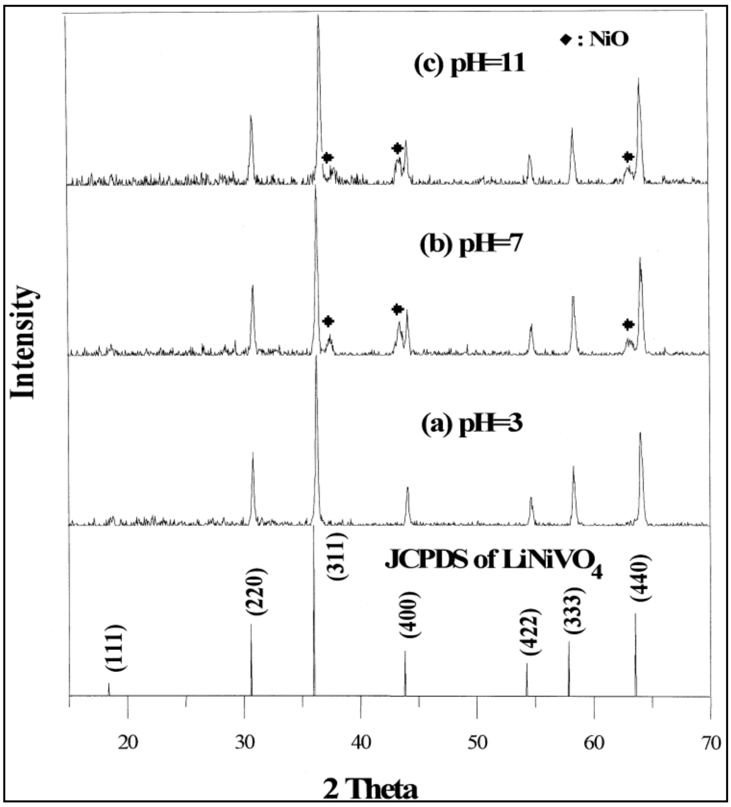

Fig. 2.9: XRD patterns of $LiNiVO_4$ at different pH (Fey *et al*., 1999)

Initial discharge capacity of $LiNiVO_4$ with pH=3, pH=7 and pH=11 is 24 mAh g^{-1}, 19 mAh g^{-1} and 23 mAh g^{-1} respectively. The values decrease to 22 mAh g^{-1}, 18 mAh g^{-1} and 16 mAh g^{-1} at second cycle. The sample of pH=3 exhibits better cycling performance.

Soft chemistry approach to prepare $LiNiVO_4$ has been carried out by Kalyani *et al*., (2002). Starch was added as carbonaceous fuel in this method. Impurities such as NiO and Li_3VO_4 were found to be absent for all the samples sintered from 400°C to 800°C. First discharge capacity of 90 mAh g^{-1} decreased to nearly 20 mAh g^{-1} at the end of fifth cycle as displayed by the Fig 2.10. Oxidation of electrolyte at high voltage is considered as one of the reasons for this capacity fading.

Glycerol assisted gel combustion was used to synthesis $LiNiVO_4$ (Vivekanandhan *et al*., 2004). Product obtained at 450°C for 12 hours was free from impurities and showed crystallite size of 39 nm. Cycling studies was not reported in this work.

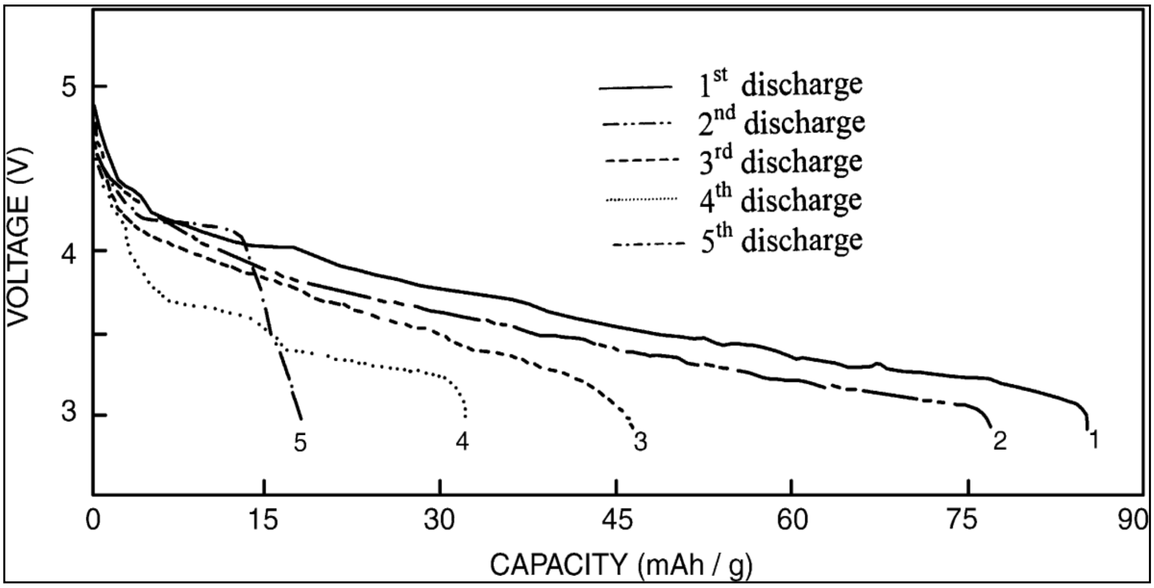

Fig. 2.10: Voltage versus discharge capacity (Kalyani *et al*., 2002)

Lu *et al*.(1999) synthesized $LiNiVO_4$ using solid state reaction. Impurities such as $LiVO_3$, $LiVO_3 \cdot 0.5H_2O$ and NiO were present at quenching temperatures of 500°C and 600°C. NiO was still present at the quenching temperatures of 700°C, 800°C and 1000°C. Calcination at 700°C for 6 hours diminished the impurity completely. Higher calcination temperature of 800°C required only 4 hours for the formation of pure $LiNiVO_4$. Microstructured $LiNiVO_4$ was obtained after calcination at low temperature. Electrochemical studies were not included in this work.

Lai *et al* (2001) obtained $LiNiVO_4$ by solid state reaction and complex-precipitate gel method. Both samples were cycled in the range of 3.0 – 4.8 V under the current drain of 0.2 mA/cm^2. Fig 2.11 presents the curve of specific capacity as reported. Eventhough the first discharge capacity of $LiNiVO_4$ by solid state reaction is around 59.8 mAh g^{-1}

and by complex-precipitate gel method is nearly 47.0 mAh g^{-1}, the capacity loss is high after the first cycle.

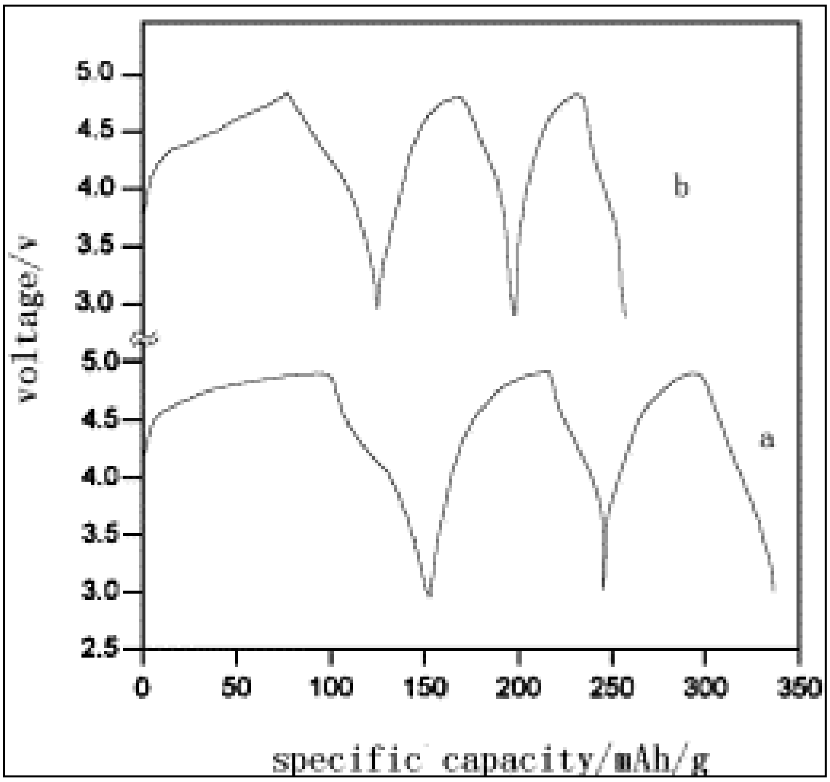

Fig 2.11: Specific capacity of (a) complex-precipitate gel method (b) solid state reaction (Lai *et al.*, 2001)

2.3 Sol gel method

The sol gel method is proven as an effective method to produce electrode materials compared to traditional solid state reaction in terms of (Fu *et al.*, 2005):

(a) Homogeneity

(b) Lower synthesis temperature

(c) Shorter sintering time

(d) Better crystallinity

(e) Uniform particle distribution

(f) Smaller particle size

Based on these properties, sol gel method is used widely to synthesise electrode materials for lithium ion batteries (Khomane *et al*., 2008; Liu *et al*., 2004; Yi *et al*., 2006 and Sun, 1997). Spinel $Li_{1.03}Mn_2O_4$ was prepared by sol gel method using glycolic acid as chelating agent by at lower temperature and shorter synthesis time (Sun, 1997). Better electrochemical performance was exhibited using $LiMn_2O_4$ prepared by the sol gel method (Yi *et al*., 2006).

2.4 Coating of cathode materials

Cathode materials were further improved by coating with oxides. The coatings avoid direct contact of active material with electrolyte (Li *et al*., 2006). A lot of research were carried out on ZnO coated $Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ (Suresh *et al*., 2005), TiO_2 coated $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (Zheng *et al*., 2008), La_2O_3 coated $LiNi_{0.8}Co_{0.2}O_2$ (Fey *et al*., 2005), TiO_2 coated $LiMn_2O_4$ (Yu *et al*., 2006), ZnO coated $LiNi_{0.5}Mn_{1.5}O_4$ (Sun *et al*., 2003), CeO_2 coated $LiMn_2O_4$ (Ha *et al*., 2007), ZnO coated $LiCoO_2$ (Fang *et al*., 2004), Co_3O_4 coated $LiCoO_2$ (Fey *et al*., 2005), Al_2O_3 coated $LiCoO_2$ (Liu *et al*., 2002) and etc.

$Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ was coated with ZnO to improve the electrochemical performance (Suresh *et al*., 2005). Even though initial discharge capacity of bare and ZnO coated $Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ was about 215 mAh g^{-1}, the discharge capacity of bare $Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ decreased about 25% at 50th cycle. Discharge capacity of ZnO coated

$Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ still maintained at 210 mAh g^{-1} at the end of 50th cycle. ZnO coating stabilized the capacity of $Li_{0.9}Mn_{0.9}Ni_{0.1}O_2$ as reported by Suresh and co-workers.

Cycle efficiency of $LiNi_{0.8}Co_{0.2}O_2$ was improved when coated with La_2O_3. Initial charge and discharge capacity of pristine $LiNi_{0.8}Co_{0.2}O_2$ was found to be 203 mAh g^{-1} and 185 mAh g^{-1} respectively. The values were higher for 1.0 wt. % La_2O_3 coated $LiNi_{0.8}Co_{0.2}O_2$ which reached charge capacity of 206 mAh g^{-1} and discharge capacity of 199 mAh g^{-1}. The initial cycle efficiency was also higher at about 96.6 % for coated $LiNi_{0.8}Co_{0.2}O_2$ compared to 91.1 % for pristine. According to Fey and co-workers (2005) $LiNi_{0.8}Co_{0.2}O_2$. La_2O_3 coating protects the active material from HF attack and improved the capacity (Fey *et al*., 2005).

Pristine $LiMn_2O_4$ exhibited high initial discharge capacity of 107 mAh g^{-1} at 0.5 C and decreased to 98 mAh g^{-1} at 40th cycle. While 2 % CeO_2 coated $LiMn_2O_4$ released 101 mAh g^{-1} at initial discharge capacity and 97 mAh g^{-1} at 40th cycle. Capacity retention of pristine sample is only 92 % compared to 96 % for coated sample. This shows that the CeO_2 coating is able to improve capacity retention (Ha *et al*., 2007).

ZnO was coated on $LiCoO_2$ to prevent surface reaction which occurs at high cutoff voltage and results in capacity fading. 0.2 wt. % ZnO coated $LiCoO_2$ showed capacity loss of 10.4 % after 30 cycles. Capacity loss of pristine $LiCoO_2$ was about 30.6 % at the end of 30th cycle. Although initial capacity of coated $LiCoO_2$ is slightly lower than pristine but it has better capacity retention. The coating of ZnO reduced the capacity fading faced by $LiCoO_2$ (Fang *et al*., 2004).

Improvements on structure and cycling were studied on Al_2O_3 coated $LiCoO_2$ (Liu *et al*., 2002). Bare $LiCoO_2$ exhibited 198 mAh g^{-1} in the first cycle and capacity loss was about 40 % in the 20th cycle. Although the first discharge capacity of coated $LiCoO_2$

was only about 185 mAh g^{-1}, but the capacity tends to increase in the first four cycles. The discharge capacities of coated $LiCoO_2$ were more stable compared to bare $LiCoO_2$ because the value of 196 mAh g^{-1} at fourth cycle decreased to 190 mAh g^{-1} in the 20th cycle. Surface coated $LiCoO_2$ avoid Co^{4+} to react with electrolyte directly which causes capacity loss.

Son and co-workers (2004) coated $LiMn_2O_4$ with silver metal and found better cycling performance. 3.2 wt. % Ag showed improved charge-discharge capacity due to its low resistance and improved electron conduction between $LiMn_2O_4$ particles.

AlF_3 was coated on $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ to investigate the effects on electrochemical properties (Kim *et al.*, 2008). The initial discharge capacity of $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ and AlF_3 coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ is 183 mAh g^{-1} and 188 mAh g^{-1} respectively. At the same time coated sample exhibted excellent capacity retention about 96 % of its initial capacity while the uncoated only remain 86.5 % of its initial capacity. The results reveal that the AlF_3 coating lowered and stablized the interfacial resistance between cathode and electrolyte. It protects the core material during intercalation.

Similar coating which was carried out on $LiCoO_2$ improved the cycling performance when cycled in 3.0-4.5 V (Sun *et al.*, 2006). Both pristine and AlF_3 coated $LiCoO_2$ delivered similar initial discharge capacity of 180 mAh g^{-1}. However the capacity of pristine sample faded after 50 cycles and became 30 mAh g^{-1}. AlF_3 coated $LiCoO_2$ exhibited excellent capacity retention of 98 % and showed better cycling stability.

$Li[Co_{0.1}Ni_{0.15}Li_{0.2}Mn_{0.55}]O_2$ was applied with $Co_3(PO_4)_2$ coating (Lee *et al.*, 2008). Sintering temperature of the sample was proved as another factor that affects electrochemical performance of the battery. Samples sintered at low temperature such as 500 °C showed low capacities which caused by structural instability. At the same time, high sintering temperature of 1000 °C resulted in aggregates of samples and leads to poor Li^+ transport. However the samples coated with 2 wt. % and 3 wt. % of $Co_3(PO_4)_2$ sintered at 800 °C reveal high cycling stability.

SrF_2 was used as coating material for $LiMn_2O_4$ because of its stability in HF (Li *et al*., 2009). Increase of SrF_2 coating amount on $LiMn_2O_4$ resulted in decrease of discharge capacity. Inactive SrF_2 coating may causes capacity fading when the coating amount increased. It can be explained that difference between voltage at charge and discharge curves increases which exhibits high polarization at higher coating level. The results obtained in this work relate increase of polarization of the electrode with decrease of discharge capacity. 2.0 mol% SrF_2 coated $LiMn_2O_4$ showed better capacity retention about 86.9 % after 50 cycles compared to uncoated $LiMn_2O_4$ which only remain 79.3 % at 50th cycle.

$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was coated with TiO_2 (Wu *et al*., 2009). Bare and 0.5 wt. % TiO_2 coated samples delivered similar discharge capacity about 167.1 mAh g^{-1} and 165.7 mAh g^{-1} respectively. The first discharge capacity of 1.0 wt. % TiO_2 coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ is 171.2 mAh g^{-1} but decreased to 161.3 mAhg^{-1} when the coating amount increases to 2.0 wt. % TiO_2. The improved capacity proved that thin layer of TiO_2 enables the effective lithium intercalation that results in better electrochemical behaviour. The coating layer also prevents harmful reaction at the surface of cathode material.

ZrO_2 coating was applied on $Li(Co_{1/3}Ni_{1/3}Mn_{1/3})0_2$ (Huang *et al*., 2009). Pristine sample exhibited 168.4 mAh g^{-1} at first cycle and become 132.7 mAh g^{-1} at 100th cycle when cycled at 0.5C. 1 % ZrO_2 coated $Li(Co_{1/3}Ni_{1/3}Mn_{1/3})O_2$ showed initial discharge capacity of 166.1 mAh g^{-1} and only loss about 1 % and become 164.6 mAh g^{-1} at 100th cycle. The capacity fading of the pristine sample can be due to the change of lattice volume during cycling, cation mixing, dissolution of metal ion and electrolyte reaction at the interface of electrode as reported in this work.

$LiNi_{0.8}Co_{0.2}O_2$ has been coated with 1 wt.% of Li_2O-$2B_2O_3$ glass (Ying *et al.*, 2001). Bare sample exhibited first discharge capacity of 161 mAh g^{-1} with irreversible capacity of 47 mAh g^{-1}. About 9.3 % of capacity loss was observed at the 50th cycle. Li_2O-$2B_2O_3$ coated sample showed initial discharge capacity of 177 mAh g^{-1}. It remains capacity retention of 97.8 % after 50 cycles. Li_2O-$2B_2O_3$ is found to be good Li^+ ionic conductor which transfer Li^+ ion across the interface of the electrode. The Li_2O-$2B_2O_3$ coating layer protects the core material from corroded by the electrolyte.

Gold was used as coating layer on $LiMn_2O_4$ (Tu *et al.*, 2006). Eventhough initial discharge capacities of bare and uncoated samples are similar, the gold coated $LiMn_2O_4$ exhibits improved cycling performance. When $LiPF_6$ react with water, HF is formed. HF dissolves the manganese ions which cause the capacity fading. Thin gold layer on the surface of $LiMn_2O_4$ reduces direct contact between electrode and electrolyte. So that the dissolution of manganese ions have been reduced. This results in better electrochemical properties.

$Li_{1.03}Mn_{1.97}O_4$ was modified with SiO coating (Zheng *et al.*, 2002). Earlier few cycles of coated sample showed lower capacity than uncoated sample. From fifth cycle, the specific capacity of SiO coated $Li_{1.03}Mn_{1.97}O_4$ higher than the bare sample. The layer of SiO avoids the core material from being corroded by the electrolyte. Besides that SiO_2 is also able to trap HF which gives rise to the dissolution of Mn^{2+}. It was confirmed that SiO_2 coating improved cycling properties.

TiO_2 was coated on $LiNi_{0.8}Co_{0.2}O_2$ with the mole ratio Ti: $LiNi_{0.8}Co_{0.2}O_2$ is 0.03 (Zhang *et al.*, 2004). It was reported that bare sample lost about 49 % of its initial capacity after 100 cycles when cycled between 3.0 to 4.6 V range. Capacity of coated sample retents about 80 % of its initial capacity at the end of 100th cycle. In the bare sample, Ni^{4+} which formed at high potential could oxidize the electrolyte because Ni^{4+} has strong oxidation ability. Ti^{4+} in the coating layer which is not strong oxidizer suppresses the electroyte oxidation and improved the capacity fading of coated samples.

$LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$ was treated with ZnO with different weight percentage (Guo *et al.*, 2009). The initial charge capacity of bare sample and 0.5 wt. % ZnO coated samples similar which is about 210 mAh g^{-1}. The charge capacities of 1.5 wt. % ZnO and 3.0 wt. % ZnO coated samples are 204 mAh g^{-1} and 196 mAhg^{-1} respectively. Discharge capacity delivered by bare sample is 179 mAh g^{-1}. 0.5 wt. % ZnO coated sample exhibited discharge capacity of 175 mAh g^{-1}. This value decreases for 1.5 wt. % ZnO coating which is about 162 mAh g^{-1} and become 152 mAh g^{-1} at 3.0 wt. % ZnO. The discharge capacity decreases with increasing coating amount. Eventhough initial discharge capacity of coated samples is lower compared to uncoated sample, but it shows better improvement in long term cycling. Capacity loss of uncoated sample is about 19.6 % after 30 cycles. Capacity loss of ZnO coated samples only 6.3 %, 4.3 % and 4.6 % for 0.5 wt. % ZnO, 1.5 wt. % ZnO and 3.0 wt. % ZnO respectively. ZnO gives more stable SEI layer in order to improve electrochemical properties.

$LiMn_2O_4$ was used to coat with TiO_2 (Yu *et al.*, 2006). Uncoated sample only retained about 70 % of initial capacity after 40 cycles. Capacity loss of coated $LiMn_2O_4$ is less than 15 % at the end of 60th cycle. Initial discharge capacity of coated sample is found to be 104 mAh g^{-1} while bare sample only exhibits 96 mAh g^{-1}. These results proved that the TiO_2 coating improved the capacity retention by covering the surface of the $LiMn_2O_4$. The coating enables the structure stability during charge and discharge.

$LiNi_{0.5}Co_{0.5}VO_4$ was modified with SiO_2 to overcome side reaction at the surface (Mai *et al.*, 2003). The initial discharge capacity of bare sample was found to be 90 mAh g^{-1} while SiO_2 coated sample exhibits 100 mAh g^{-1}. Capacity retention of coated sample is about 87 % after 10 cycles. Uncoated sample showed fast decline in capacity and reached 38.7 mAh g^{-1} at the 10th cycle which shows retention only about 43 %. This improved capacity retention may be due to the SiO_2 layer on the cathode material prevents core material reacts with electrolyte.

Carbon from table sugar was applied as coating material to treat $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (Kim *et al.*, 2007). The results proved that 1 wt.% carbon coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ delivers initial capacity of 153.7 mAh g^{-1}, 150.0 mAh g^{-1}, 145.7 mAh g^{-1}, 142.6 mAh g^{-1} and 134.3 mAh g^{-1} at current rate of 0.2C, 0.5C, 1C, 2C and 5C respectively. The initial discharge capacity of uncoated sample is about 151.4 mAhg $^{-1}$, 147.0 mAh g^{-1}, 141.2 mAh g^{-1}, 137.0 mAh g^{-1} and 128.6 mAh g^{-1} at the given current rates above. From these results it can be confirmed that the capacity is improved with the carbon coating. 3 wt.% carbon coated sample exhibits initial discharge capacity of 144.6 mAh g^{-1}, 139.5 mAh g^{-1}, 132.3 mAh g^{-1}, 123.5 mAh g^{-1} and 113.2 mAh g^{-1} at current rate of 0.2C, 0.5C, 1C, 2C and 5C respectively. These values are lower compared to bare and 1 wt.% carbon coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The capacity is reduced when the carbon coating exceeds 1 wt.%. The 1 wt.% carbon coated sample exhibits better capacity due to the improved conductivity by the coating.

Active $LiCoO_2$ and inactive MgO were selected as coating materials for $LiNi_{0.8}Co_{0.2}O_2$ (Zheceva *et al.*, 2006). Initial discharge capacity delivered by $LiNi_{0.8}Co_{0.2}O_2$ is 175 mAh g^{-1}. MgO coated sample and $LiCoO_2$ coated sample exhibit initial discharge capacity of 155 mAh g^{-1} and 179 mAh g^{-1} respectively. Eventhough MgO coated $LiNi_{0.8}Co_{0.2}O_2$ delivered low initial discharge capacity than bare sample, but it has better capacity retention after 30 cycles. Capacity loss of $LiNi_{0.8}Co_{0.2}O_2$ is 22 % after 30 cycles compared to only 8 % for MgO coated $LiNi_{0.8}Co_{0.2}O_2$. $LiCoO_2$ coated $LiNi_{0.8}Co_{0.2}O_2$ shows capacity retention of 87 % after 30 cycles. This reveals that $LiCoO_2$ coated $LiNi_{0.8}Co_{0.2}O_2$ improved the cycling stability. The coating of $LiCoO_2$ on $LiNi_{0.8}Co_{0.2}O_2$ enables the structure stability and avoids the harmful reaction at the interface of electrode and electrolyte.

Summary

Literature review in this chapter opens the window to the world of cathode materials for lithium ion batteries. Different types of cathode materials with their unique properties have been explored. On the other hand, the problems faced by these cathode materials have also been introduced. This work will concentrate on inverse spinel structure of lithium nickel vanadium oxide or known as lithium nickel vanadate. It is to be noted that the review is no means by exhaustive.