CHAPTER 7

DISCUSSION

In this work, we have studied inverse spinel $LiNiVO_4$ prepared by the solution evaporation and chitosan modified solution evaporation methods. Face centered cubic structured $LiNiVO_4$ was successfully obtained by both methods. Sol gel method is a good method since it can produce homogenous samples with smaller crystallite size can be produced at lower temperatures and shorter processing time (Sun *et al.*, 1997; Lee *et al*., 1998; Peng et *al*., 1998; Piana *et al*., 2004; Yi *et al*., 2009). Due to this we have followed the sol gel method of preparation samples.

$LiNiVO_4$ has been synthesized by solid state reaction (Lu *et al*., 1999), solution precipitation method (Fey *et al*., 1999) and citric acid complex method (Liu *et al*., 2002). Lai *et al* (2001) obtained $LiNiVO_4$ by solid state reaction and complex-precipitate gel method. Soft chemistry method has been applied to prepare $LiNiVO_4$ (Kalyani *et al*., 2002). Starch was added as carbonaceous fuel in this method. Combustion method using gelatin as fuel source has been used to prepare $LiNiVO_4$. In this work, average particle size is ~ 35 nm calculated from Scherrer's equation.

Other polymer modified cathode materials include $LiCoO_2$ which has been prepared by polyacrylic acid modified sol gel method (Sun *et al*., 1999). $LiNiO_2$ has been synthesized using polyvinyl butyral polymer (Sun and Oh, 1997). $LiMnO_2$ has been prepared using polyvinyl alcohol polymer for the modification (Lu *et al*., 2001). The polymers act as a carrier for the homogenous distribution of the ions and make the crystallization easier at sintering process (Fu *et al*., 2005).

Comparison of XRD results with JCPDS data 73-1636 proves that the samples obtained from both solution evaporation and chitosan modified solution evaporation methods are inverse spinels. The peaks for the (311) and (220) planes are features of inverse spinels. Lattice parameter of pure $LiNiVO_4$ samples produced by solution evaporation method is 8.201 Å and 8.212 Å by the chitosan modified solution evaporation method. These values are in reasonable agreement with 8.217 Å (Li *et al*., 2009), 8.218 Å (Subramania *et al*., 2006), 8.217 Å (Kalyani *et al*., 2002) and 8.215 Å (JCPDS data 73-1636). To two significant figures the value is the same.

Crystallite size calculation using scherrer equation reveals that the cathode particles are smaller which synthesized using chitosan modified solution evaporation method compared to the solution evaporation method eventhough both methods show similar XRD patterns. The crystallite size calculated from the scherrer equation for $LiNiVO_4$ by solution evaporation method sintered at 700 °C is 97.2 nm and that prepared by chitosan modified solution evaporation method also sintered at 700 °C is 60.5 nm. This shows that the polymer confines the precursor into smaller volume that limits their growth size and as nanoparticles on sintering at 700 °C for 3 hours. Smaller crystallites play very important role in electrochemical performance. TEM results confirm the particles to be of nanosize and that ~80 % of the particles have diameters in the range between 11 and 50 nm. The samples sintered at 700 °C produced by the solution evaporation and chitosan modified solution evaporation method was chosen for battery fabrication.

Cyclic voltammetric studies show that the cycling stabilizes starting from 11th cycle for product obtained by solution evaporation method without polymer modification. However on the anodic run more than one peak are observed indicating that the sample may have undergone decomposition to other compounds. On the other hand, the sample from chitosan modified solution evaporation method reveals stability from the 6th cycle. There are lesser peaks on the anodic run indicating better stability.

Charge-discharge perfomance for both samples were carried at charging and discharging currents of 0.4 mA. Solution evaporation and chitosan modified solution evaporation methods deliver first discharge capacity of 10.5 mAh g^{-1} and 13.5 mAh g^{-1} respectively. The discharge capacity ends with 8.1 $mAhg^{-1}$ for sample synthesized by solution evaporation method and 12.3 $mAhg^{-1}$ for sample obtained by chitosan modified solution evaporation method. The capacity loss about 22.8 % and 8.9 % for cathode materials prepared by the solution evaporation and chitosan modified solution evaporation methods respectively. The sample from chitosan modified solution evaporation method able to retain ~ 90% of initial discharge capacity at the end of 20th cycle compared to $LiNiVO_4$ sample prepared by the solution evaporation method that retains only 78.4 %. The results clearly show that the cell utilizing $LiNiVO_4$ sample prepared by the chitosan modified solution evaporation method exhibits better electrochemical perfomance.

The improved capacity obtained from the $LiNiVO_4$ prepared by the chitosan modified solution evaporation method sample can be attributed to the factor of smaller crystallite size and material stability upon cycling. The sizes of particles become another important factor in electrochemical perfomance (Aklaloueh *et al*., 2009; Lu *et al*., 2001; Matsuda *et al*., 2004; Hwang *et al*., 2001). Diffusion of lithium ions inside the $LiNiVO_4$ electrode determines the efficiency of the intercalation processes. In smaller crystallites the lithium diffusion path is shortened, and make faster movement of lithium ions. This leads to improved cycling perfomance. Apart from that, the smaller crystallites have larger surface area which enables active charge transfer (Nieto *et al*., 2004).

The value of capacity obtained by this work is small compared with the theoretical capacity of 148 mAhg^{-1}. Such small capacity values have been reported for inverse spinel cathode materials. Pure $LiNiVO_4$ synthesized by solution precipitation method by Fey *et al* (1999) showed initial discharge capacity of 24 mAhg^{-1} but dropped to 22 mAhg^{-1} at second cycle which credits about 8.3 % of capacity loss. $LiNiVO_4$ prepared from soft chemistry have been reported by Kalyani *et al* (2002) to deliver initial discharge capacity of 90 mAh g^{-1}, which is higher than what was obtained by Fey *et al* (1999), but the capacity dropped to 20 mAhg^{-1} on the fifth cycle only. The capacity loss is about 77.7 % of its initial discharge capacity. By referring to this similar works, it can be understood that capacity fading is a serious problem encountered when inverse spinel $LiNiVO_4$ material was used as the active cathode material.

High voltage can be said to be another factor for poor cycling perfomance. Although it was found that high voltage can increase the discharge capacity, high discharge capacity comes along with poor cycling perfomance. High voltage relate well with capacity fading (Park *et al*., 2008). When transition metal oxides e.g. $LiCoO_2$, $LiMn_2O_4$, $LiNiCoO_2$, etc are charged at higher voltages, the possibility of electrolyte oxidation is very high. Electrolyte oxidation forms an insulating layer on the surface of the electrode and results in capacity loss (Guyomard *et al*., 1995). $LiNiVO_4$ cells can be charged to a high voltage of 4.8 V which offers the opportunity to oxidize the electrolyte and result in lowering the capacity with poor cycling perfomance.

To prevent the oxidized transition metal from interacting with the electrolyte and to improve the performance of the cell using inverse spinel cathode material such as $LiNiVO_4$, impurity free $LiNiVO_4$ with smaller crystallite size obtained from chitosan modified solution evaporation method was selected as bare sample to be coated with ZnO. ZnO was chosen as coating agent in this work because it is environmentally benign and inexpensive (Suresh *et al*., 2005). ZnO has been coated on $LiNi_{0.5}Mn_{1.5}O_4$ (Sun *et al*., 2003), $LiCoO_2$ (Fang *et al*., 2004), $LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$ (Guo *et al*., 2009) etc. Initial capacity of the cell using 0.2 wt. % ZnO coated $LiCoO_2$ as the active cathode material slightly lower than the initial capacity of bare $LiCoO_2$, but showed better capacity retention (Fang *et al*., 2004). Similar results were obtained from the work of Guo *et al*., (2009) where the initial discharge capacity of of the cell using ZnO coated $LiNi_{0.5}Co_{0.25}Mn_{0.25}O_2$ is lower compared with the pristine, but shows improved cycling performance.

Different amounts of ZnO were coated on this bare sample. X-ray diffractograms for all coated samples show no any peaks correspond to ZnO peaks. This confirms that the coating material does not merge into the $LiNiVO_4$ core material. This is important aspect since the coating material should not interfere with the structure of the cathode material but only covers the surface of the material. The crystallite size of 0.2 wt. % ZnO was bigger compared to bare sample. The size of crystallites are smaller than the bare sample when the coating level at 0.5 wt. % ZnO and 1.0 wt. % ZnO.

Initial discharge capacities for 0.2 wt.% ZnO and 1.0 wt.% ZnO coated samples are 13.96 mAh g^{-1} and 18.51 mAh g^{-1} respectively. 0.2 wt.% ZnO coating on $LiNiVO_4$ increased the initial discharge capacity by about 3.0 % more than that the bare sample. These results are comparable with those obtained by Fey et al (2001). In their work, $LiNiVO_4$ coated with

0.2 wt.% Al_2O_3 only increased the initial discharge capacity 5.7 % compared to the cell utilizing the uncoated $LiNiVO_4$. 0.2 wt.% ZnO coated $LiNiVO_4$ when used in batteries in

Coated sample in the work of Fey *et al* (2001) can retain 80 % cut off capacity based on first discharge capacity after 18 cycles when used in batteries. 0.2 wt.% ZnO coated $LiNiVO_4$ when used in batteries in the current work remains at 88 % of its initial discharge capacity for 20 cycles. About 82 % of cut off capacity is still maintained at the end of 20th cycle for 0.5 wt.% ZnO coated sample. However, eventhough 1.0 wt.% ZnO exhibits high initial discharge capacity, the cell can only retain 80 % cut off capacity after 5 cycles. The capacity retention of cells/batteries using of 0.2 wt.% and 0.5 wt.% of ZnO coated sample is better than that using 1.0 wt.% of ZnO in the cathode.

The cycling efficiency is another important factor to be considered. The cycling efficiency of Al_2O_3 coated sample is 64.9 % based on initial charge capacity of 57 mAh g^{-1} and discharge capacity of 37 mAh g^{-1}. In the present work, the cell utilizing 0.2 wt.% of ZnO coated sample delivers cycling efficiency of 89.9 % at first cycle. The efficiency becomes 79.9 % at the end of 20th cycle. The cell utilizing 0.5 wt.% of ZnO coated sample in the cathode shows high cycling efficiency of 98.3 % at the beginning of the charge discharge process and ends up with 87.9 % at the 20th cycle. The cell utilizing 1.0 wt.% of ZnO coated sample only achieved 68.0 % at the end 2nd cycle and 69.9 % for the following cycle. This clearly states that the efficiency is not stable when coated with large amount of ZnO.

The capacity retention and cycling efficiency of the cell were poor when the cathode contains 1.0 wt.% of ZnO coated sample. This can be explained since the coating layer on

$LiNiVO_4$ is thicker and reduces the movement of lithium ions. Since the diffusion of lithium ions is an important factor in determining the electrochemical properties of the sample and the cell in general, the excess coating layer on the surface also reduces the electronic conductivity which causes poor efficiency of the cell or batteries.

The ZnO coating layer serves as barrier to avoid direct contact between the $LiNiVO_4$ material and the electrolyte (Liu *et al*., 2002; Ying *et al*., 2001). The oxidized transition metal ions will be prevented from interacting with the electrolyte and accelerate the electrolyte decomposition. At the same time, the electrolyte is prevented from corroding the cathode material. The direct contact between electrolyte and cathode material can cause negative effects in electrochemical performance such as capacity loss, self discharge and etc.

Zhang *et al* (2004) also explained that bulk structure and interface instability affect the capacity of lithium nickel oxides. The coating layer is found to be stablizing the interfacial resistance between the cathode and the electroyte. It can be considered as important factor to protect the active material in the repetition of Li^+ intercalation (Lu *et al*., 2001).