CHAPTER 9

CONCLUSIONS AND SUGGESTIONS

In this study, the inverse spinel lithium nickel vanadate, $LiNiVO_4$ and manganese doped lithium nickel vanadate, $LiNi_{1-x}Mn_xVO_4$, with x = 0.25 have been successfully synthesized by the sol-gel and polymer precursor techniques. The product obtained can be easily synthesized at low temperatures in air with incorporation of citric acid as the chelating agent. Both methods manifested the production of the nano-sized particles. In this work, the improvement in the redox process can be obtained at high temperatures for the undoped system. As for the doped system, better reversibility can be achieved at product calcined at lower temperature which suggests improved kinetics of Li^+ intercalation in the cell system. From the work done in this thesis, the following conclusions can be made:

The pure phase inverse spinel is successful prepared by sol-gel and polymer precursor method. The preparation procedure was rather practical than the conventional solid state reaction proposed as the synthesize process does not require long heating time at high temperature. The preparation of co-doped inverse spinel by using manganese was also prepared by sol-gel and polymer precursor method. The dopant material was added to reduce the amount of nickel in the stoichiometric compound. Acetates and ammonium metavanadate were used as raw materials in this work as very useful as they are soluble in water.

The precursors obtained were examined by TGA. TGA results suggest that the desired compounds can be expected after sintering the precursor at the minimum temperature of around 500 ^{o}C for the compound prepared by both sol-gel and polymer precursor methods and at around 750 ^{o}C for the doped compound by the sol-gel method and polymer precursor method. The weight losses indicate that the proposed reactions for the production of the doped and undoped system are:-

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

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

The synthesis using acetates as starting materials leads to the formation of single phase of inverse spinel structure as acquired in the XRD analysis. The objectives mentioned in Chapter 1, the single phase of inverse spinel $LiNiVO_4$ cathode was obtained at temperature as low as 600 °C in 3 hours by sol-gel method and at temperature as low as 500 ^{o}C in 3 hours for $LiNiVO_4$ prepared by polymer precursor method with no trace of NiO impurities. As for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ by sol-gel and polymer precursor method, such compound was successful calcined at temperature as low as 500 °C in 3 hours for single phase of inverse spinel $LiNiVO_4$ product.

The diffractograms of the four cathode systems suggest that the products in this work are all have the same cubic structure system. The presence of stronger peak of [220] than weak [111] peak clearly indicates the sintered powder has inverse spinel structure. The crystallinity nature of [220] peak over the strongest peak at [311] plane ($I_{[220]}/\ I_{[311]}$)

in the XRD pattern were observed. The closest ratio of atomic ratio of Ni: V for the undoped samples is 1 : 1.0297 at firing temperature of 800 °C and for the doped samples is 2.8227 : 1 at 600 °C which is closest to 3:1 atomic ratio of Ni:Mn. The lattice parameters for all system in this work obtained by XRD analysis were in good agreement to the JCPDS data.

The particle morphology studies of the prepared cathodes depict increasing particle growth upon increasing firing temperature. The SEM micrograph for the lower sintering temperature of each product unveils the sticky and fluffy-looked surface morphology. As the temperature rose up, the particle size becomes more clustered and the particle edges were clearly visible. The porous micrograph was obtained for the $LiNiVO_4$ prepared by polymer precursor method shows fragile-look particle morphology upon lower sintering temperature. The particle growth and more densified particle were observed as the temperature increases. The particle clusters have smoother surface upon highest sintering temperature.

The flakey-looking surface with large voids microstructure was obtained for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ by sol-gel method. The formation of larger particles was noticed having clearer particle cluster upon increasing temperature. The surface morphology of the $LiNi_{0.75}Mn_{0.25}VO_4$ by polymer precursor method displays almost similar behavior as other systems prepared in this work with developed particle as the firing temperature increases. The polyhedral morphology with smaller voids was observed at the maximum firing temperature.

The particle size from TEM analysis for the undoped samples is 44 nm (sol-gel system) and 33 nm (polymer precursor system). The size for the doped sample by sol-gel method has 24 nm while around 18 nm of particle size obtained for doped sample by polymer precursor method. From the image captured by TEM analyzer, the acquired particle size in all systems in this work supports the calculated crystallite size obtained from the XRD results.

The product prepared by polymer precursor method exhibits smaller particles size than sol-gel method. The addition of doped material, Mn in the compound during the synthesis has led to even smaller particle size. Doping of manganese helps to inhibit the particle growth having the smallest crystal size with help of PEG gelling agent. The crystallite size was calculated by the Scherrer equation (Equation 3.2) for the average crystal size. The obtained values for the undoped $LiNiVO_4$ by sol-gel method and $LiNiVO_4$ by polymer precursor method were around 42 nm to 68 nm and 33 nm to 48 nm, respectively. The calculated crystallite size for the doped $LiNi_{0.75}Mn_{0.25}VO_4$ for sol-gel system was found to be in the range of 23 nm to 35 nm while smaller range of average crystal size was obtained at 19 nm to 39 nm for $LiNi_{0.75}Mn_{0.25}VO_4$ by polymer precursor method. In addition, the particle size obtained through calculation using XRD data supports the nanosize of the product from the TEM analysis. This is evidence for the fulfillment of objective number two stated in subsection 1.3 of Chapter 1.

The atomic ratio from elemental studies by the EDAX analysis in this work is in good agreement to the proposed stoichiometric amount. The ratio of 1:1 mole of metal cations of Ni to V of single phase product satisfies the value of prepared composition. Moreover, the calculated ionic number does not change as the result obeys stoichiometrically by the EDAX measurement suggesting no additional gas preferred during the firing process. The ratio of distribution in the EDAX studies shows the $LiNiVO_4$ synthesized at 800 ^oC sintering temperature has a ratio closest to 1:1 of Ni:V.

As for the doped system $LiNi_{0.75}Mn_{0.25}VO_4$, the EDAX results show product fired at 600 ^{o}C is the closest ratio of 3:1 of Ni:Mn.

The cyclic voltammetry shows that the cathodic and anodic peaks of the undoped sample were well defined at higher temperature. In addition, smaller value of potential separation of the $LiNiVO_4$ also suggests better reversibility for the higher firing temperature of the treated sample. The voltage difference of the anodic and cathodic peak for $LiNi_{0.75}Mn_{0.25}VO_4$ system has experienced a slight increase for sample treated at lower temperature but the area under peak was increases upon few cycling. Therefore, the better capacity can be retained as compared with the sample fired at higher temperature.

Suggestion for Further Work

For further work, studies should be focused on the electrochemical impedance spectroscopy (EIS) analysis which can be carried out to investigate electrical conductivity of the cathode. Therefore, the diffusion coefficient can be calculated to give detailed information on the kinetics of lithium ion transfer in the cathode. The electrochemical performance of the inverse spinel cathode can be improved by selection of suitable coating materials to prevent the dissolution of the cathode into the electrolyte. The study of electronic properties of the cathode may be useful to determine the local atomic occupancy of 3d transition metal oxides in the inverse spinel host lattice structure by x-ray photoelectron spectroscopy (XPS) analysis. The charge-discharge profile can be analysed to study the discharge behaviour of the Li^+ intercalation cathode.