CHAPTER – V
SUMMARY AND CONCLUSIONS

The salient features of this work are:

(i) Optimisation of a sol gel technique for the synthesis of the substituted spinels.

(ii) The synthesis temperature and the duration of heat treatment are lower compared to previous reports.

(iii) Single phase vanadium substituted spinel has been obtained for the first time.

(iv) Development of a simple synthesis procedure for tin based composite oxide anodes.

(v) Results on cell studies using the tin based composite oxide anodes and substituted spinel cathodes are reported for the first time.

(vi) Results on cell studies using tin oxide anodes and substituted spinel cathodes are reported for the first time.

Ni, Co, Zn, Cu and V substituted LiMn$_2$O$_4$ powders were synthesized by a novel sol gel technique using the acetate/nitrate precursors, acrylamide and ammonium persulphate. They were then preheated at 300°C in air, followed by a final heat treatment in air at temperatures in the range 550°C to 750°C for durations ranging from 8 to 16 hours depending on the substituent.

TG/DTA studies were used to deduce the decomposition kinetics of the preheated samples for the Nickel substituted spinels. Using the above information the synthesis temperature was fixed.
EDS measurements indicated that the actual ratios of Mn to Ni in the compositions are consistent with the normal composition.

BET measurements carried out on the samples indicated that the surface area varies in the range of 2.75 to 1.0 $\text{m}^2/\text{g}$ as the nickel content increases.

The powder XRD patterns of LiMn$_{2-x}$Ni$_x$O$_4$ (with $x = 0.1 - 0.5$) indicate the formation of single phase material belonging to the cubic structure. This indicates that the Ni ions substitute the Mn sites homogeneously. The lattice constant decreases as the concentration of Ni increases.

XPS studies indicated that the Mn$2p_{3/2}$ component peak is intermediate between those of $\alpha$-Mn$_2$O$_3$ and MnO$_2$ and larger than MnO. The Ni$2p_{3/2}$ spectra are typical of Ni$^{2+}$ compounds, suggesting that Ni substitutes Mn in the divalent state. The BE peak for Li 1s is located at values closer to Li$_2$O. All oxygen 1s spectra exhibit complex profiles formed by a major component attributable to Mn(M)-O-Mn(M).

FTIR spectra of the samples with different substitutions of nickel, indicate that as the nickel substitution increases from $x = 0.1$ to 0.5 in LiMn$_2$O$_4$, the absorption band shifts towards higher frequency side, indicating the partial substitution of octahedral Mn with the Ni ions.

Electrochemical studies indicated the reversible nature of the cathode material when cycled between 3V and 5V. The positions and reversibilities of the anodic and cathodic peaks imply that Li is intercalated into an octahedral site of the MnO$_6$ framework.
Cells were fabricated with the nickel substituted spinel \((\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4)\) as cathode, mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with LiPF\(_6\) as electrolyte and lithium as the anode. The discharge capacity of the cell was 100 mAh/g at first discharge, the discharge loss was very small and the cells retained their capacity even beyond 100 cycles.

Impedance measurements were conducted after the first and second charge and discharge cycles in the frequency range 10 KHz – 10 mHz. A single semicircle was observed for both charge and discharge cycles. The resistance of the \(\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4\) on Al mesh was less than 40 ohms even after the first and second discharge and charge cycles. This indicates good cycleability.

TG/DTA studies were used to deduce the decomposition kinetics of the preheated samples for the cobalt substituted spinels. Using the information the synthesis temperature was fixed.

The powder XRD patterns of \(\text{LiMn}_{2-x}\text{Co}_x\text{O}_4\) (with \(x = 0.1 - 0.5\)) indicate the formation of single phase material belonging to the cubic structure. This indicates that the Co ions substitute the Mn sites homogeneously. The lattice constant decreases as the concentration of Co increases.

EDS measurements indicated that the actual ratios of Mn to Co in the compositions are consistent with the normal composition.

BET measurements on the samples indicated that the surface area changes from 2.0 to 1.2 m\(^2\)/g as the cobalt content increases.
XPS studies indicated that the Mn2p3/2 component peak is intermediate between those of α-Mn2O3 and MnO2 and larger than MnO. The Co2p3/2 are closer to Co3O4, indicating that Co enters the 'Mn' lattice in the tervalent state.

FTIR spectra of the samples with different substitutions of Co, indicate bands due to CoO6 vibrations at 400-650 cm⁻¹. Infrared bands located in the high frequency region are due to Co-O stretching. As cobalt substitution increases from x = 0.1 to 0.5, the absorption bands shift to high frequency side indicating partial substitution of octahedral Mn with Co ions.

Electrochemical studies indicated the reversibility of the cathode material and a two step redox nature of the specimen which corresponds to lithium intercalation/de-intercalation into the LiMn2O4 spinel host matrix. The cyclic voltammograms were recorded in the range 3.0 to 4.2 vs Li/Li⁺.

Cells were fabricated with the cobalt substituted spinel (LiMn1.5Co0.5O4) as cathode, mixed solvent of EC, DMC with LiPF6 as electrolyte and lithium as the anode. The discharge capacity of the cell was 70 mAhg⁻¹ after the first discharge, the discharge loss was only 1.5% of the initial capacity even beyond 100 cycles.

Electrochemical impedance spectroscopy was used to investigate the interfacial resistance in the electrode. The impedance plot shows the interfacial resistance of the electrode below 90Ω after 50 cycles.

TG/DTA studies were used to deduce the decomposition kinetics and for fixing the synthesis temperature for the zinc substituted spinels.
The powder XRD patterns of LiMn$_{2-x}$Zn$_x$O$_4$ (with $x = 0.1 - 0.5$) indicate the formation of single phase material belonging to the cubic structure. This indicates that the Zn$^{2+}$ ions substitute the Mn sites homogeneously. The lattice constant decreases slightly as the concentration of Zn increases.

EDS measurements indicated that the actual ratios of Mn to Zn in the compositions are consistent with the normal composition.

BET measurements on the samples indicated that the surface area decreases from 2.02 to 1.10 m$^2$/g as the zinc content increases.

FTIR spectra of the samples with different substitutions of Zn, indicate bands due to Mn-O and Zn-O stretching vibrations in the region 400 to 800 cm$^{-1}$. Bands at 3456.3 cm$^{-1}$ and 1122.0 cm$^{-1}$ are due to absorbed water. At around 629.7 cm$^{-1}$ a strong absorption peak is observed, due to the vibrations of the LiMn$_2$O$_4$ spinel. As Zn substitution increases, this absorption band shifts to a higher frequency side indicating the strong binding of octahedral Mn-O with the Zn substitution. The number of stretching frequencies decrease as the concentration of Zn decreases, indicates, that the increase in metal content blocks the bands.

Cells were fabricated with the zinc substituted spinel (LiMn$_{1.5}$Zn$_{0.5}$O$_4$) as cathode, mixed solvent of EC, DMC with LiPF$_6$ as electrolyte and lithium as the anode. The discharge of the cell was $-120$ mAh g$^{-1}$ after the first discharge, the discharge loss was very negligible upto 80 cycles, beyond which there is a decrease in capacity.
Impedance measurements were conducted after the first and second charge and discharge cycles. A single semicircle was observed during the first and second charge and discharge cycles. The resistance of the LiZn$_{0.5}$Mn$_{1.5}$O$_4$ on Al mesh was around 20 ohms even after the second discharge and charge cycles.

The TG/DTA results were used to deduce decomposition kinetics and the synthesis temperature of the copper substituted spinels.

EDS measurements indicated that the actual ratios of Mn to Cu in the compositions are consistent with the normal composition.

BET measurements on the samples indicated that the surface area decreases from 1.90 to 1.20 m$^2$/g as the copper content increases.

X-ray diffraction studies on the copper substituted spinels indicates the formation of single phase material after heating at high temperature. The lattice parameter of the cubic spinel phase was found to decrease as the concentration of copper increased from $x = 0.1$ to $x = 0.5$.

FTIR spectra of the samples with different composition indicated bands due to absorbed water. The stretching vibrations due to Li-O and Mn-O were also observed. On increasing the substitution of copper, the peak shifts to the higher frequencies indicating the substitution of copper ions in the spinel lattice.

Electrochemical studies indicated that the cells could be cycled in the potential range 3.3 – 5.1V. As the copper content increases, the peaks which are located at 4.05 and 4.16V in the cyclic voltammograms of LiMn$_2$O$_4$
(attributed to a two-step extraction of lithium from the tetrahedral 8a site) shifts to higher voltage.

Cells were fabricated with the copper substituted spinel (LiMn$_{1.5}$Cu$_{0.5}$O$_4$) as cathode, mixed solvent of EC, DMC with LiPF$_6$ as electrolyte and lithium as the anode. The discharge capacity decreased from 105 mAh g$^{-1}$ to 60 mAh g$^{-1}$ as the Cu concentration increases. The cells could be cycled up to 60 cycles beyond which capacity fading occurs.

Impedance measurements were made after the first and second discharge and charge cycles which indicated two semicircles which may be attributed to Li$^+$ ion migration through active materials, coupled with film capacitance on high frequency side and the low frequency semicircle may be due to interfacial resistance between cathode and electrolyte.

The TG/DTA results were used to deduce the decomposition kinetics and the synthesis temperature of the vanadium substituted spinels.

EDS measurements indicated that the actual ratios of Mn to V in the compositions are consistent with the normal composition.

BET measurements indicated that the surface area of the material decreases as the concentration of the substitution increases from $x = 0.1$ to 0.5. The surface area of the samples decreases from 2.10 to 0.10 m$^2$/g as the vanadium content increases.

XRD studies made on the materials of the compositions from $x = 0.1$ to 0.5 indicates that vanadium ions substitute the Mn$^{3+}$ ions. As the concentration of the vanadium incorporation in the Mn site increases, the peaks were
observed to shift to higher angle side. The lattice parameter ‘a’ of the cubic spinel slightly decreases as the concentration of vanadium increases indicating the topotactic reaction mechanism associated with vanadium doping.

FTIR studies made on the vanadium substituted spinels of different compositions indicated a strong absorption peak around 900 cm⁻¹ due to the stretching of VO₄, another stretching vibration was observed around 490 cm⁻¹ due to Li-O. As vanadium substitution increases, the absorption bands shifts towards the higher frequency side indicating the partial substitution of octahedral Mn with the vanadium.

Cells were fabricated with the vanadium substituted spinel (LiMn₁.₅V₀.₅O₄) as cathode, mixed solvent of EC, DMC with LiPF₆ as electrolyte and lithium as the anode. The discharge capacity decreases from 140 mAh g⁻¹ to 90 mAh g⁻¹ as the vanadium concentration increased from x = 0.1 to 0.5. The cells were stable upto 60 cycles, beyond which capacity fading occurs due to electrolyte oxidation at high voltages.

Impedance measurements were made after the first and second discharge cycles, which indicated a single semicircle. The resistance of the electrode was less than 20 ohms.

The development of tin based composite oxide (TCO) as an alternative anode to lithium and high capacity carbonaceous materials is of recent origin. These amorphous tin based composite oxides provide a very high reversible
gravimetric capacity of > 600 mAh g\(^{-1}\). In view of the above fact TCO was synthesized in the laboratory by the sol gel route.

XRD studies on the TCO material synthesized in an argon atmosphere exhibited amorphous structure. Heat treatment in a mixed argon-oxygen atmosphere lead to the formation of crystalline material. All the lines for SnO\(_2\) (cassiterite) in addition to those of tin (IV) pyro-phosphate are observed.

XPS measurements on TCO before and after lithiation indicated that the electron binding energy of Sn 3d\(_{5/2}\) shifts about 1.4 eV to lower energy, indicating a valency state change of Sn.

The lithium storage capacity of TCO was investigated by electrochemical insertion of Li ions into TCO with Li-metal electrode as anode and TCO as cathode. EC, DMC and LiPF\(_6\) was used as electrolyte. In the first cycle, the Li-ion storage capacity reached 1030 mAh/g. Subsequent Li-release processes up to 1.2V yielded a coloumbic capacity of 650 mAh g\(^{-1}\) accompanied by a 37% loss of the initial discharge efficiency which remained constant without causing a significant increase in electrode resistance. The reversible Li-ion storage capacity was 600 mAh g\(^{-1}\), which is comparable to best hydrogen-storage alloys.

The charge-discharge cycleability for the cells with TCO as anode, substituted spinels as cathodes and EC:PC and LiPF\(_6\) as electrolyte. The discharge capacity decrease was constant even beyond 60 cycles. The discharge capacity was nearly twice with that obtained with lithium anode.

The cells retained their capacity even beyond 100 cycles.
Tin oxide was also used as anode and the substituted spinels were used as cathodes. For this purpose, SnO₂ was prepared by precipitation technique. Aqueous solutions of SnCl₂ was the precursor and 0.035M acetic acid was added to stabilize it. Aqueous NH₄OH was slowly added and Sn(OH)₂ was formed. After calcinations SnO₂ is obtained.

XRD studies indicated single phase peaks corresponding to cassiterite phase.

The electrochemical behaviour of the electrode was studied by using SnO₂ pellet as working electrode and lithium anode separated by polypropylene wetted with 1M LiPF₆ in EC, DMC. The first cycle shows a large peak with a maximum at about 0.7V vs Li, this peak is absent in the subsequent cycles and the electrode shows reversible behaviour. Total reversible capacity in the range of 400 mAh g⁻¹ were obtained at a discharge current density of 0.3 mA cm⁻². At higher discharge current densities a capacity as high as 300mAh g⁻¹ was obtained.

After Cycling experiments, XRD pattern on the SnO₂ electrodes indicated only a weak (211) reflection of the cassiterite phase. The other reflections observed on the cycled samples can be indexed according to the pattern of metallic Sn.

Cell studies were carried out using SnO₂ as anode; EC, DMC in LiPF₆ as electrolyte and substituted spinels as cathodes. An average capacity of 100mAh g⁻¹ is observed for all the substituted spinel cathode based cells upto 80 cycles, beyond which the capacity decreases.
The results of the present work indicate that the simple sol-gel acrylamide route can be employed for obtaining single phase material. Cells based on the spinel cathodes have exhibited performance comparable to earlier reports. Cells with TCO anodes have yielded higher capacities than with lithium and tin oxide anodes. A proper choice of the anode and suitable cathode can be made depending upon the application desired. Further work should be carried out to improve the cycle life of the cells.