SUMMARY

CHAPTER – VII
7.1 Summary and Conclusion

The objective of this thesis is to improve the rate capability of LiMPO₄ (M= Mn, Co & Ni) cathode materials by optimizing lithium transport and increasing the electronic conductivity. Present chapter consolidate all the experimental results observed in the present investigation of synthesis and characterization of nanocrystalline LiMPO₄ (M= Mn, Co & Ni) powders by PVP assisted polyol process and their surface modification by conductive carbon for secondary lithium batteries.

The olivine structured LiMPO₄ (M= Mn, Co & Ni) are considered as the most encouraging cathode materials because they are cheaper, less toxic, safety, good energy and power density, but some problems hinder the practical application. For example, low electronic conductivity and lithium ion diffusion coefficient leads to its lower discharge capacity and poor rate capability. In order to overcome these problems, I have systematically investigated the effect of stabilizer on microstructure, electrochemical characteristics of olivine’s and have optimized syntheses conditions. Furthermore, lithium transport in particle interior is improved by reducing the particle size without blocking 1D lithium diffusion as well as electron transport by coating with conducting carbon.

Polyvinylpyrrolidone (PVP) assisted polyol method was used for the preparation of LiMnPO₄ (M= Mn, Co & Ni) nanomaterials with improved physical properties and electrochemical properties. Further, carbon coating upon LiMnPO₄ (M= Mn, Co & Ni) nanomaterials is achieved by novel resin coating process for enhancing the electrical
conductivity of nanomaterials. XRD and FTIR results of synthesized pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) cathodes show the formation of phase and structure. SEM images give the information about the microstructures of the synthesized materials. The LiMnPO₄ sample is composed of uniform and dispersed rod like structure and also both LiNiPO₄, LiCoPO₄ samples showed sphere like structures under the SEM. HRTEM images of the prepared carbon coated LiMPO₄ (M= Mn, Co & Ni) materials show the uniformity and nanosize thickness of the carbon coating over the LiMPO₄ materials. Furthermore, Raman Spectra of all carbon coated LiMPO₄ (M= Mn, Co & Ni) materials confirm the nature of the carbon coating in the samples. The transport studies were carried out by using impedance spectroscopy. The bulk conductivity of all prepared materials is increasing with temperature. Carbon coated samples delivers high bulk conductivity than pure samples which might be due to the enhancement in electronic conductivity of materials. The activation energies of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) materials were calculated from log (σT) versus 1000/T plots. The super-impossibility of log (σ/σ₀) vs, log (ω/ω₀) at various temperatures, suggest the conductivity relaxation mechanism is temperature independent and slight deviation in a high temperature may be due to the volume of the total unit cell increasing linearly with temperature for all olivine samples. The increase in ε’ with decreasing frequency can be attributed to the contribution of charge accumulation at the interface. This leads to a net polarization of the ionic medium. Whereas at high frequencies, the periodic reversal of the field takes place so rapidly such a way that there is no charge accumulation at the interface, resulting in constant ε’ value in olivine samples. In the modulus curves, the continuous line represents the simulated M” curve, whereas the symbols correspond to
the experimental data. From these figures, it is observed that the shape of each curve is asymmetric of Non-Lorentzian type exhibiting a peak at the relaxation frequency, $f_{\text{max}}$, with a long tail extending in the region of shorter relaxation time $\tau = 1/f_{\text{max}}$ ($f_{\text{max}}$ is the relaxation frequency at $M''_{\text{max}}$ and of $M''$ vs. log $\omega$ curves) and it is also observed that there is a shift in peak frequency & variation in peak height with temperature. Finally, enhancement of electrical conductivity in carbon coated LiMPO$_4$ (M= Mn, Co & Ni) materials confirmed by the Wagner Polarization method through finding the transport number of electrons and ions. The LiMnPO$_4$/Li CR2032 coin cells fabricated by using pure LiMnPO$_4$ nanorods prepared by PVP assisted polyol method delivers higher discharge capacity of 98 mAh g$^{-1}$ at 1 C. The remaining two cells which are made up of pure LiCoPO$_4$ and LiNiPO$_4$ also delivered 144 mAh g$^{-1}$ and 72 mAh g$^{-1}$ of the discharge capacity at the rate of 0.1C, respectively. Furthermore, it is confirmed that the combination of carbon coating through resin coating technology brings further improvement in electrochemical properties of LiMPO$_4$ (M= Mn, Co & Ni) cathodes. Hence, newly developed pure and carbon coated LiMPO$_4$ (M= Mn, Co & Ni) nanomaterials by PVP assisted polyol and novel resin coating processes are suitable cathodes for the high voltage Lithium ion batteries.

7.2 Scope of the further work on surface modified cathode materials

There has been a significant research work over a decade in the area of surface modified cathode materials in order to enhance the performance of rechargeable lithium batteries due to the huge requirement of portable energy devices. Synthetic approaches (physical and chemical) towards the fabrication of surface modified nanocrystalline cathode materials received more attention to meet the requirements such as uniform and
homogeneous coating. In order to investigate the effect of surface modified cathode materials in lithium battery application, various techniques such as electrochemical impedance spectroscopy, accelerating colorimetry, atomic force microscopy, electrochemical force microscopy, etc., are can be used.