The enormous growth in portable electronic devices such as cellular phones, laptop computers, etc., has motivated interest in compact, light weight batteries with high energy densities. Lithium ion batteries are used in the above applications, since they provide higher energy density compared to other available rechargeable batteries such as lead acid, nickel- cadmium, nickel- metal hydride batteries, etc. In recent years, the rechargeable battery market has further expanded and tends to increase exponentially. Hence, the lithium battery technology is receiving most attention. Ever growing demand for batteries leads the industry and government to make huge investment in battery research and development. Lithium battery research not only involves enhancement of cyclability, high energy density but also seriously considers the safety, environmental friendliness, cost issues, etc. Hence, a wide range of materials (anode, cathode, electrolytes, etc) have been developed and investigated to improve the lithium battery technology.

In lithium ion batteries, chemical energy stored in the positive electrode is released and converted into electrical energy through an intercalation process. Lithium transition metal oxides have been used as promising positive electrode (cathode) materials, since they show large stability region with respect to lithium content than other class of intercalation compounds. The intercalation process of lithium ions are accompanied by redox of transition metal ions. Therefore, much research has been focused on the understanding of lithium intercalation / de-intercalation mechanism, and modifying materials to suppress the structural change of lithium transition metal oxides during the intercalation / de-intercalation process to achieve better battery performance. Layered LiCoO$_2$, LiNiO$_2$ and LiMnO$_2$, spinel LiMn$_2$O$_4$, \ldots
inverse spinel LiNiVO$_4$, LiCoVO$_4$ and olivine LiFePO$_4$ are the most used and studied cathode materials in the last two decades. Recently, it has been found that the nanocrystalline cathode materials exhibit high storage capacity, voltage and charging / discharging rates due to much shorter diffusion paths for Li$^+$ diffusion and the smaller dimensional change during intercalation and de-intercalation process. Synthesis process plays major role in the development of nanocrystalline cathode materials with desired physiochemical properties. Wet chemical processes such as polyol, sol-gel, combustion etc., are used for this purpose.

Due to the less structural stability, high capacity fading, while charging/discharging, less energy density in the layered and spinal structured cathode materials and so, there is a need for further development, in order to achieve an improved electrochemical performance of materials. In 1997, J.B. Goodenough et al., first discovered the electrochemically active lithium iron phosphate (LiFePO$_4$) olivine compound. The lithium iron phosphate is found to have good electrochemical properties compared to layer and spinel structure materials with potentially low cost, high natural abundance of raw materials and environmentally friendliness. However, lithium iron phosphate cathode material has several disadvantages, which impede its industrial applications. Recently, researchers have developed other olivine materials [LiMPO$_4$: M= Mn, Co &Ni] using various preparative methods. But, they obtained an acceptable electrochemical properties due to the some intensive drawbacks like (i) very low electronic conductivity in its pure form, of the order of $10^{-9}$ S cm$^{-1}$, (ii) slow lithium ion diffusion in the solid phase due to high defects formation in lithium ion diffusion path, and (iii) Jahn-Teller distortion. These drawbacks can be overcome by various strategies,
including carbon coating, conductive additives, partial substitution, alien cation doping, and synthesizing various shapes of nanosize crystallites (like spheres, rods etc.), using various synthesis methods. The advantages and properties of olivine structured materials motivated me to develop the shape controlled pure and carbon coated \([\text{LiMPO}_4: \text{M}=\text{Mn, Co & Ni}]\) nanocrystalline cathode materials for improving the storage capacity and cycleability of lithium ion batteries.

In the present work, pure and carbon coated lithium transition metal phosphate \([\text{LiMPO}_4: \text{M}=\text{Mn, Co & Ni}]\) systems were chosen to develop in different shapes such as nanorods, nanospheres using polyol and resin coating processes. Further, all prepared materials are characterized by powder X – ray diffraction (XRD), Fourier transform infrared radiation (FTIR), Raman spectroscopy (RS), scanning electron microscopy (SEM), transmission electron microscopy and energy dispersive X-ray spectroscopy (TEM-EDS). The best property compounds were chosen as a cathode material for the fabrication of CR2032 coin cell type of lithium ion batteries.

The thesis entitled “Synthesis and characterization of pure and carbon coated \(\text{LiMPO}_4 (\text{M}=\text{Mn, Co & Ni})\) nanomaterials for lithium ion battery applications” contains seven chapters.

**First chapter** of the thesis briefly discusses the importance of lithium ion batteries among the available batteries, based on their energy density and also briefly classifies the types of batteries with examples, based on the reversibility of the electrode reaction. It also briefly discusses the major components of battery and highlights the existing problems involved in the commercial cathode materials with respect to safety, environmental concern and fulfillment of growing energy demands for the recent portable electronic device applications. Finally, it proposes the possible remedies to overcome the above mentioned problems by preparing the
nanostructured materials and introducing the surface modified olivine structured lithium based transition metal phosphates.

**Second chapter** briefly discusses the available wet chemical methods like polyol, sol-gel, combustion, thermo-mechanical, hydro-thermal, co-precipitation, etc., along with their respective merits and demerits for the preparation of nanocrystalline materials. It also briefly discusses the characterization techniques used in the present investigation like powder X-ray diffraction (XRD), Fourier transform infrared radiation (FTIR), Raman spectrometer, scanning electron microscope- Energy dispersion spectroscopy (SEM-EDS), High-resolution transmission electron microscopy (HRTEM), Raman Spectroscopy. Also, briefly explains the transport studies like dc & ac conductivity, dielectric and modulus and transport number studies respectively, through impedance and Wagner polarization measurements. Finally, describing the fabrication and electrochemical characterization of CR2032 coin cells using newly developed cathode materials.

**Third chapter** discusses the preparation of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles using PVP assisted polyol and resin coating processes.

- Pure LiMPO₄ (M= Mn, Co & Ni) nanoparticles were prepared by polyvinylpyrrolidone (PVP) assisted polyol process. All precursor materials are mixed with the ethylene glycol (polyol) and heated under distillation condition up to 465 K for 3 h. The precipitation in the bottom of the flask was washed with acetone and heated up to 873 K to get the pure crystalline nanomaterials. At this temperature, ethylene glycol will convert in to the glycolic acid, which has high chelating agent property due its hydroxyl and carboxyl functional groups. In this reaction, PVP acts as a stabilizer to obtain the different shaped nanoparticles.
The novel resin coating process was used for the thin and uniform carbon coating upon the nanoparticle surface to increase the electrical conductivity of the materials. In this process, synthesized pure LiMPO₄ (M= Mn, Co & Ni) nanoparticles were added into the solution of EG (ethylene glycol)+ PAA (Poly acrylic acid) and heated up to 353 K under constant stirring for 1h. After formation of high density resin, nanoparticles were again heated up to 623 K for 1h to get the thin carbon coating over the surface of the LiMnPO₄ nanorods. At 623 K, hydrogen and oxygen compounds will evaporate, and the remaining carbon will form a thin layer upon the LiMPO₄ (M= Mn, Co & Ni) nanoparticles.

**Fourth chapter** discusses the characterization of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles.

Phase purity and structure of both pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles were examined by the XRD and FTIR. FTIR confirmed the presence of the carbon in the LiMPO₄ (M= Mn, Co & Ni) nanoparticle samples by showing the C=C symmetrical stretching band. Further, Raman spectral results show the amorphous nature of the carbon coating in the LiMPO₄ (M= Mn, Co & Ni) nanoparticle samples. SEM images of LiMPO₄ (M= Mn, Co & Ni) nanoparticles gives the shape and size of the nanoparticles. Finally, HRTEM confirmed the thickness and uniformity of the carbon coating upon LiMPO₄ (M= Mn, Co & Ni) nanoparticles.

**Fifth chapter** discusses the impedance and ac conductivity studies of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles.
The Impedance plots were plotted for the both pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles using the measured impedance data by the Alpha frequency analyzer (NOVOCONTROL, Germany) from room temperature to 773 K. The resistance of samples was obtained by analyzing measured impedance data using winfit software. Also, this chapter discuss the frequency dependent and independent conductivity, dielectric constant and modulus of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles with respect to temperature. Finally, this chapter includes the transport number studies of both pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles using Wagner polarization method to estimate the electronic conductivity enhancement.

Sixth chapter discusses the fabrication and electrochemical characterization of the CR2032 coin cells using the synthesized pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticle samples.

CR 2032 coin cells are fabricated by using synthesized both pure ad carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles. For fabricating coin cells, the cathode is made with composition of 80% of active material + 15% Super P carbon + 5% PVDF and anode is the lithium metal. The electrolytes used for pure and carbon coated LiMnPO₄/Li coin cells is 1M LiPF₆ in EC: DMC: EMC (1:1:1) but, for LiCoPO₄/Li and LiNiPO₄/Li cells, the electrolyte used 1M LiPF₆ in EC: DMC (LP30, Merck chemicals) due to high reduction potentials.

The discharge capacities and cycleability of the fabricated batteries are examined by measuring the cycleability, discharge characteristics using the battery cycle tester (BCT).
Seventh chapter discusses the summary of the present investigation and the future work

Pure and carbon coated LiMPO$_4$ (M= Mn, Co & Ni) nanoparticles were synthesized using PVP assisted polyol and resin coating processes and characterized by XRD, FTIR, SEM, TEM-EDS, Raman & Impedance spectroscopy. Finally, fabrication of CR2032 coin cells were made using the newly developed samples and characterized using battery cycle tester.

It is concluded that the carbon coated lithium transition metal phosphates [LiMPO$_4$: M= Mn, Co & Ni] are the important materials as cathodes for high voltage and high energy density Li-ion batteries.