CHARACTERIZATION OF PURE AND CARBON COATED LiMPO$_4$ ($M=\text{Mn, Co \& Ni}$) NANOPARTICLES
CHAPTER - IV
CHARACTERIZATION OF PURE AND CARBON COATED LiMPO₄
(M= Mn, Co & Ni) NANOPARTICLES

4.1 General introduction

4.2 Characterization of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles

4.2.1 X-ray Diffraction (XRD)

4.2.2 Fourier transform infrared spectroscopy (FTIR)

4.2.3 Raman spectroscopy

4.2.4 Scanning electron microscopy (SEM)

4.2.5 High resolution transmission electron microscope – energy dispersion X-ray spectrooscope (HRTEM-EDS)

4.3 Conclusions

References
4.1 General Introduction

In this chapter, detailed results obtained from XRD, FTIR, SEM, RS and HRTEM-EDS for all the prepared pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles are presented and discussed. The pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles were successfully prepared by PVP assisted polyol and novel resin coating processes. The structural characterizations like phase purity and structure of all the prepared materials were respectively obtained from the X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The lattice parameters and the weight percentage of the prepared material were determined by Rietveld refinement analysis using the X'pert high score plus software. Microstructure of prepared pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles was observed under the scanning electron microscopy (SEM). The amorphous nature and thickness of carbon coating over the carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles were observed by Raman spectra and high resolution transmission electron microscope (HRTEM) images. Finally, the chemical compositions of all synthesized materials were obtained by energy dispersive spectroscopy (EDS).

4.2 Characterization of pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticles

4.2.1 X-ray Diffraction (XRD)

Figures 4.1, 4.2 & 4.3 show the XRD patterns of the pure and carbon coated LiMPO₄ (M= Mn, Co & Ni) nanoparticle samples along with their respective JCPDS data. From figure 4.1a, XRD patterns of pure and carbon coated LiMnPO₄ nanorods, prepared at 873
K and the formation of the crystalline phase of pure and carbon coated LiMnPO₄ nanorod samples were confirmed by comparing with JCPDS (# 740375) data. XRD patterns of both pure and carbon coated LiMnPO₄ nanorods showed two extra peaks at 29 and 30.5, due to the crystalline Mn₂P₂O₇ phase. This peak was further analyzed by Rietveld refinement, which confirmed the presence of 98 wt.% LiMnPO₄ and 2 wt.% Mn₂P₂O₇ in the LiMnPO₄ nanorod sample. Figure 4.1b shows the Rietveld refinement results for the pure LiMnPO₄ nanorods. The crystallite size of the LiMnPO₄ nanorods was calculated using Scherrer’s formula (D = 0.9 × λ/β Cos θ) and was found to be ~63 nm. The XRD pattern of the carbon coated LiMnPO₄ nanorods did not show any extra peak for carbon phase, suggesting that the coated carbon over the LiMnPO₄ nanorods may be in an amorphous phase [1-3]. From figure 4.2, XRD patterns of pure and carbon coated lithium cobalt phosphate (LiCoPO₄) nanoparticles along with the carbon and LiCoPO₄ JCPDS data. JCPDS data confirmed the formation of structural phase. The crystallite size of the LiCoPO₄ nanoparticles was calculated using Scherrer’s formula and was found to be ~45 nm. The XRD patterns of carbon coated LiCoPO₄ nanoparticles were showing two extra peaks at 28.5 and 31.5 other than LiCoPO₄ peaks, which is indicated that presence of crystalline nature of coated carbon on LiCoPO₄ nanoparticles.
Figure 4.1: a) XRD patterns of the pure and carbon coated LiMnPO$_4$ nanorods along with JCPDS data and b) Observed XRD pattern fitted with the calculated one, using Rietveld analysis.
Figure 4.2: XRD patterns of the pure and carbon coated LiCoPO$_4$ nanoparticles along with JCPDS data
Figure 4.3: XRD patterns of the pure and carbon coated LiNiPO$_4$ nanoparticles along with JCPDS data.

From figure 4.3, XRD patterns of pure and carbon coated lithium nickel phosphate (LiNiPO$_4$) nanoparticles along with the carbon and LiNiPO$_4$ JCPDS data. JCPDS data confirmed the formation of structural phase. The crystallite size of the LiNiPO$_4$ nanorods was calculated using Scherrer’s formula and was found to be ~50 nm. Furthermore, the XRD patterns of carbon coated LiNiPO$_4$ nanoparticles were showing two extra peaks, which are due to the crystalline carbon (JCPDS#46-0943). It confirmed that the coated carbon on LiNiPO$_4$ nanoparticles was showing partially crystalline nature, which was further confirmed by the Raman Spectroscopy.
4.2.2 Fourier transforms infrared spectroscopy (FTIR)

Figures 4.4, 4.5 & 4.6 show the FTIR spectra of all pure and carbon coated LiMnPO$_4$, LiCoPO$_4$ and LiNiPO$_4$ nanoparticles respectively. From figure 4.4, the pure and carbon coated LiMnPO$_4$ nanorods FTIR spectra show bands at 900 cm$^{-1}$ and 1055 cm$^{-1}$, which are due to symmetrical and asymmetrical stretching of PO$_4^{3-}$. The IR bands between 630 and 460 cm$^{-1}$ are due to the asymmetric bending O–P–O mode. Thus, FTIR results confirmed the presence of PO$_4^{3-}$ structure in the pure and carbon coated LiMnPO$_4$ nanoparticles. The observed common peaks at 3417-3444 cm$^{-1}$ is assigned to the stretching frequency of OH (due to the adsorbed moisture). Furthermore, carbon coated LiMnPO$_4$ nanoparticle samples showed extra bands at 1712 and 1637 cm$^{-1}$, which are attributed to the symmetrical stretching of C–O and C–C respectively. IR band at 744 cm$^{-1}$ is due to P–O–C symmetric stretching and confirmed the presence of carbon over LiMnPO$_4$ nanorods in carbon coated samples [4, 5].

From figure 4.5, the FTIR spectra of the pure and carbon coated LiCoPO$_4$ nanorods show bands at 950 cm$^{-1}$ and 1070 cm$^{-1}$: which are due to symmetrical and asymmetrical stretching of PO$_4^{3-}$ respectively. The IR bands between 641 and 480 cm$^{-1}$ are due to the asymmetric bending O–P–O mode. Thus, FTIR results confirmed the presence of PO$_4^{3-}$ structure in the pure and carbon coated LiCoPO$_4$ nanoparticles. The observed broad peak from 3582-3236 cm$^{-1}$ in pure LiCoPO$_4$ sample is assigned to the stretching frequency of O-H (due to the adsorbed moisture). Furthermore, carbon coated LiCoPO$_4$ nanoparticle samples showed extra bands at 1728 and 1621 cm$^{-1}$, which are attributed to the symmetrical stretching of C-O and C-C respectively. IR band at 745 cm$^{-1}$ was due to P–
O–C symmetric stretching and confirmed the presence of carbon over LiCoPO₄ nanorods in carbon coated samples [6].

Figure 4.4: FTIR spectra of the pure and carbon coated LiMnPO₄ nanorods
Figure 4.5: FTIR spectra of the pure and carbon coated LiCoPO$_4$ nanoparticles
From figure 4.6, the pure and carbon coated LiNiPO$_4$ nanoparticles FTIR spectra show bands at 920 cm$^{-1}$ and 1045 cm$^{-1}$, which are respectively due to symmetrical and asymmetrical stretching of PO$_4^{3-}$. The IR bands between 660 and 480 cm$^{-1}$ are due to the asymmetric bending O–P–O mode. Thus, FTIR results confirmed the presence of PO$_4^{3-}$ structure in the pure and carbon coated LiCoPO$_4$ nanoparticles. Furthermore, carbon coated LNiPO$_4$ nanoparticle samples showed extra bands at 1705 and 1642 cm$^{-1}$, attributed to the symmetrical stretching of C-O and C-C respectively, broad peak from 3740-2780 cm$^{-1}$ is assigned to the stretching frequency of O-H. The IR band at 748 cm$^{-1}$
is due to P–O–C symmetric stretching and confirmed the presence of carbon over LiNiPO₄ nanoparticles in carbon coated samples [7].

4.2.3 Raman Spectroscopy

Figures 4.7, 4.8 and 4.9 show the Raman spectra of the pure and carbon coated LiMPO₄ (M=Mn, Co & Ni) nanoparticle samples. From figure 4.7, the observed bands at 953 cm⁻¹ corresponded to the symmetric A₄ mode, and the two low intensity bands at 997 and 1090 cm⁻¹ are due to the asymmetric stretching modes of the PO₄⁻³ polygon. Raman spectra of the carbon coated samples showed two bands at 1350 [D (Disordered) band of sp³] and 1592 cm⁻¹ [G (Graphene) band of sp²-type] along with PO₄⁻³ anion bands, which are due to the residual carbon [8].

**Raman spectroscopy of carbon materials:**

Single crystal graphite belongs to the D₆h symmetry group, and vibrational modes (²E₂g, ²B₂g, E₁u, and A₂u) are as shown in Figure 4.10. The two E₂g modes are Raman active and have been identified with the Raman band which obtained at 1582 cm⁻¹ and a low-frequency neutron scattering feature at 47 cm⁻¹. The E₁u (1588 cm⁻¹) and A₂u (868 cm⁻¹) are IR active and observable with IR reflectance. The B₂g modes are optically inactive, but one has been observed by neutron scattering at 127 cm⁻¹. From figures 4.7, 4.8 and 4.9, the Raman spectra of carbon coated LiMPO₄ (M= Mn, Co & Ni) shows the presence of one new band at around 1360 cm⁻¹ other than 1582 cm⁻¹ band. The reasons for the appearance of the 1360 cm⁻¹ band is quite controversial. Several workers have attributed it to a decrease in symmetry near microcrystallite edges, reducing the symmetry from D₆h to C₃v (Vibrational modes: ²A₁ and ²E) or C₆. New vibration modes of the lattice may then become active, such as an A₁ mode. A related mechanism is breakdown of the k = 0
selection rule for optical phonons near crystallite edges. Such breakdown permits phonons other than 1582 and 47 cm\(^{-1}\) to become active and the spectra reflect the density of phonon states in the lattice. A very different explanation for the 1360 cm\(^{-1}\) mode is the existence of specific vibrations at the edges. All reports concur that the 1360 cm\(^{-1}\) mode is related to structural disorder and it will be referred to as the D band hereafter [9-13].

From figure 4.8, the observed bands at 947 cm\(^{-1}\) corresponded to the symmetric A\(_g\) mode, and the two low intensity bands at 1006 and 10410 cm\(^{-1}\) are due to the asymmetric stretching modes of the PO\(_4^{3-}\) polygon. Raman spectra of the carbon coated samples showed two bands at 1311 and 1598 cm\(^{-1}\) (D and G bands) along with PO\(_4^{3-}\) anion bands, which are due to the residual carbon. From figure 4.9, Raman spectra of the carbon coated LiNiPO\(_4\) sample showed band at 944 cm\(^{-1}\) corresponded to the symmetric A\(_g\) mode of the PO\(_4^{3-}\) polygon. Also, observed two bands at 1313 and 1593 cm\(^{-1}\) (D and G bands) along with PO\(_4^{3-}\) anion bands, which were due to the residual carbon. The relative peak heights and widths of carbon bands change substantially with the reaction temperature and the nature of the precursor materials. The variation of the width and intensity of the D and G bands are related to the growth and size of different carbon phases, the presence of functional groups and impurities. Hence, the Raman spectral results of carbon coated LiMPO\(_4\) (M= Mn, Co & Ni) samples confirmed the presence of carbon. From figures 4.7, 4.8 &4.9, the high sp\(^3/\)sp\(^2\) value is correlating to a high amorphous nature which may help to enhance the electrochemical performance of LiMPO\(_4\) (M= Mn, Co & Ni) materials.
Figure 4.7: Raman spectra for the pure and carbon coated LiMnPO₄ nanorods
Figure 4.8: Raman spectra of the pure and carbon coated LiCoPO₄ nanoparticles
Figure 4.9: Raman spectra of the carbon coated LiNiPO$_4$ nanoparticles
Figure 4.10: Vibrational modes of Single crystalline graphite

(Reprinted with permission from [6], Y. Wang et.al, Chem. mater. 1990, 2, 557-563.

Copyright (1990) American Chemical Society)
4.2.4 Scanning Electron Microscopy (SEM)

Figures 4.11, 4.12, 4.13, 4.14, 4.15 & 4.16 show the SEM images obtained at different magnifications of the pure and carbon coated LiMPO$_4$ (M=Mn, Co & Ni) nanoparticle samples. From figure 4.11, the SEM images of pure LiMnPO$_4$ nanorods with high agglomeration. Figure 4.12 shows SEM images the carbon coated LiMnPO$_4$ nanorods taken at different magnifications. From figure 4.12a, the width of the carbon coated LiMnPO$_4$ nanorods was found to be 250 nm. From figure 4.13, the SEM images of the pure LiCoPO$_4$ nanoparticles at different magnifications are observed. The agglomerated spherical shape LiCoPO$_4$ particle size was found to be ~120 nm. Figure 4.14 shows the SEM images of the carbon coated LiCoPO$_4$ nanoparticles. From figures 4.14, the SEM images of the carbon coated LiCoPO$_4$ nanoparticles show highly agglomeration and the average size of the particles is found to be ~ 90 nm.

From figure 4.15, the SEM images of pure LiNiPO$_4$ nanoparticles with high agglomeration were observed. The particle size of pure LiNiPO$_4$ nanoparticles is found to be ~ 110 nm. Figure 4.16 shows the SEM images of carbon coated LiNiPO$_4$ nanorods taken at different magnifications. From figure 4.16, the particle size of the carbon coated LiNiPO$_4$ nanoparticles was found to be ~ 80 nm. XRD, FTIR, Raman and SEM results confirmed the formation of pure and carbon coated nanocrystalline lithium transition metal phosphates prepared by polyol process followed by novel resin coating process.
Figure 4.11: SEM image of the pure LiMnPO$_4$ nanorods in low magnification
Figure 4.12: a & b) SEM images of the carbon coated LiMnPO₄ nanorods
Figure 4.13: a & b) SEM images of the pure LiCoPO$_4$ nanoparticles at different magnifications
Figure 4.14: a & b) SEM images of the carbon coated LiCoPO$_4$ nanoparticles at different magnifications
Figure 4.15: a & b) SEM images of the pure LiNiPO$_4$ nanoparticles at different magnifications
Figure 4.16: a & b) SEM images of the carbon coated LiNiPO$_4$ nanoparticles at different magnifications
4.2.5 High resolution transmission electron microscope – energy dispersion X-ray spectroscopy (HRTEM-EDS)

Figures 4.17 & 4.18 show the HRTEM images and EDS spectra of the carbon coated LiMPO₄ (M=Mn & Co) nanoparticle samples. From figure 4.17a, the TEM micrograph provided the direct evidence for the uniform coating of thin carbon layer about 3 nm over the nanocrystalline LiMnPO₄ nanorods. Figure 4.17b shows the EDS spectra of carbon coated nanocrystalline LiMnPO₄ nanorods and it shows the presence of carbon peak. Figure 4.18 shows the TEM image of the carbon coated LiCoPO₄ nanoparticles with EDS spectra. From figure 4.18a, an uniform thickness of carbon coating was found to be around 5 nm. The EDS spectra confirmed the presence of carbon in carbon coated LiNiPO₄ sample, showing carbon peak in figure 4.18b. Figure 4.19 shows the EDS spectra of the carbon coated LiNiPO₄ nanoparticles and it confirmed the presence of carbon in coated sample. Hence, from the TEM micrographs, FTIR results and Raman spectra, it is concluded that an uniform coating of the thin layer of carbon over the nanocrystalline LiMPO₄ (M=Mn, Co & Ni) nanoparticles was achieved.
Figure 4.17: a) HRTEM images and b) EDS spectrum of the carbon coated LiMnPO₄ nanorods
Figure 4.18: a) HRTEM images and b) EDS spectrum of the carbon coated LiCoPO$_4$ nanoparticles
4.3 Conclusions

Effect of PVP (stabilizer) and experimental conditions for polyol as well as resin coating processes were investigated for the synthesis of nanocrystalline pure and carbon coated LiMPO₄ (M=Mn, Co & Ni) samples. A systematic study was carried out through XRD, FTIR, Raman, SEM and TEM-EDS analysis of prepared pure and carbon coated LiMPO₄ (M=Mn, Co & Ni) nanoparticle samples.
The crystalline phases and structure of pure and carbon coated LiMPO$_4$ (M=Mn, Co & Ni) nanoparticle were confirmed from the analysis of XRD and FTIR results. In FTIR spectra of all carbon coated LiMPO$_4$ (M=Mn, Co & Ni) nanoparticle samples showed evidence for the presence of carbon. SEM images gave information of the microstructure of both pure and carbon coated samples. FTIR and Raman spectra of all carbon coated samples confirmed the presence of carbon and dominated amorphous nature of the coated carbon. Microstructure, shape, size, carbon coating and presence of transition metals, P, O, and C in the carbon coated LiMPO$_4$ (M=Mn, Co & Ni) nanoparticles were confirmed from the SEM images, TEM –EDS and Raman spectral results. HRTEM images of carbon coated LiMPO$_4$ (M=Mn, Co & Ni) nanoparticle samples give the evidence for uniformity of thickness of carbon coating upon the nanoparticles. Using a polyol and resin coating processes, we have shown that the pure and carbon coating LiMPO$_4$ (M=Mn, Co & Ni) nano materials could be synthesized.
Reference


