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Investigations on nanostructured $LiMnPO_4$ particles for cathodic material in Li-ion battery applications.

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ABSTRACT

The Nanostructured $LiMnPO_4$ (LMP) material was synthesized successfully by the use of glycol and water as solvents. The mixture of solvents yielded flower like shuttles of LMP nanomaterial and is being reported for the first time. The synthesized nanoflowers were characterized through various techniques to ascertain its phase and morphological analysis. Powder X-ray diffraction was carried out to confirm its phase. The formation of nanocrystalline nature was confirmed through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Energy dispersive analysis (EDAX) was used to confirm the elemental analysis and FTIR analysis was carried out to confirm the functional group present in the compound. The results of LMP were discussed in detail for its potential application in Lithium ion battery applications as a cathodic material.

Keywords: Li – ion battery, $LiMnPO_4$ nanomateiral, SEM, XRD, HRTEM, EDAX, FTIR.

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INTRODUCTION

Nanocrystalline materials have received an increasing amount of research interest in the recent decade. This unique size dependent has created an interest in the researcher's community which has opened a wide scope of research in the synthesis of materials. Of widely investigated compounds are cathodic material which finds application in lithium ion batteries (LIB) which have attracted large number of researchers for efficient design in LIBs [1]. The rapid development in high energy and high density rechargeable batteries with good safety, long cycle life and stability are an important criteria whereas cost-effectiveness is imperative for the next generation of portable electronics and various other wide spread applications like portable devices, power tools, electric vehicles, telecommunications. Apart from these, the LIBs provide light-weight and highly efficient power supplier which possess high energy density and is more efficient than a single large battery [2-3].

In the recent past few years synthesis of one-dimensional (1D) porous structures have received broad research interests for their promising properties in sensors, catalysis, bioengineering and also in the protection of environmental applications such as water purification and solvent purification applications [4-8]. There were efforts to synthesize cathodic material in the form of nanocrystalline form for its application in lithium battery in which porous materials find wide applications [9-13].

There is variety of commercially available cathodic material of which layered materials of oxides of rock salt such as lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$) and lithium ion phosphate ($LiFePO_4$) were widely used. Recently spinel ($LiMn_2O_4$) and olvine structure $LiMPO_4$ (M – transition metal) have gained much attraction due to its better thermal stability and low cost nature. Their better electrochemical properties and lower toxicity when compared to lithium cobalt oxide have attracted nanocrystalline researchers to synthesize it in different shapes and size to suit their applications [4].

Lithium is a light weight metal in the periodic table and thus acts as an easy metal charge carrier in battery applications. The strong covalent P-O bonds in the phosphate-based materials favour the LMP materials and thus increases their thermal stability and facilitates a stable operation of the battery especially at higher operation temperatures [14-15]. Apart from lower toxicity and low cost nature, they also possess the olivine structure which facilitates the higher stability and thereby increases the energy capacity [16-18]. Most batteries use aqueous electrolyte which restricts their operation voltage in the range of 1-2 volt whereas lithium ion batteries are operating in a non-aqueous electrolyte which favours their use in the operation voltage of about 4 volts.

In the present investigation, $LiMnPO_4$ was synthesized by wet chemical method to achieve uniform nanocrystalline form and to obtain thermodynamically stable structure with stronger bonding. The structural and micro-structural properties of the synthesized LiMnPO4 nano-particles were carried out using powder XRD and SEM, HRTEM analysis. The bonding nature was investigated through FTIR analysis and the results were discussed in detail.

EXPERIMENTAL

In the present investigation, $LiMnPO_4$ (LMP) was synthesized by mixing ethylene glycol and water in the ratio 15: 5. Lithium hydroxide (LiOH) and manganese sulphate monohydrate ($MnSO_4.H_2O$) were mixed in the 1:1 ratio in the acidic solution which contains orthophosphoric acid (H_3PO_4). The mother solution containing the mixture of solvents was stirred continuously to achieve homogeneous solution for the synthesis. The final mother solution with the homogeneous mixture is then transferred to the Teflon autoclave. The autoclave is sealed and kept in the muffle furnace for about 150°C for 12 hours to obtain complete nanocrystalline precipitate. The collected precipitate is then washed and dried in vacuum drying oven at 120°C for 24 h. The dried samples were then used for further characterization testing and for fabrication of cathodic materials. Figure 1 shows the flow chart for the current investigation of $LiMnPO_4$ nanoparticles.

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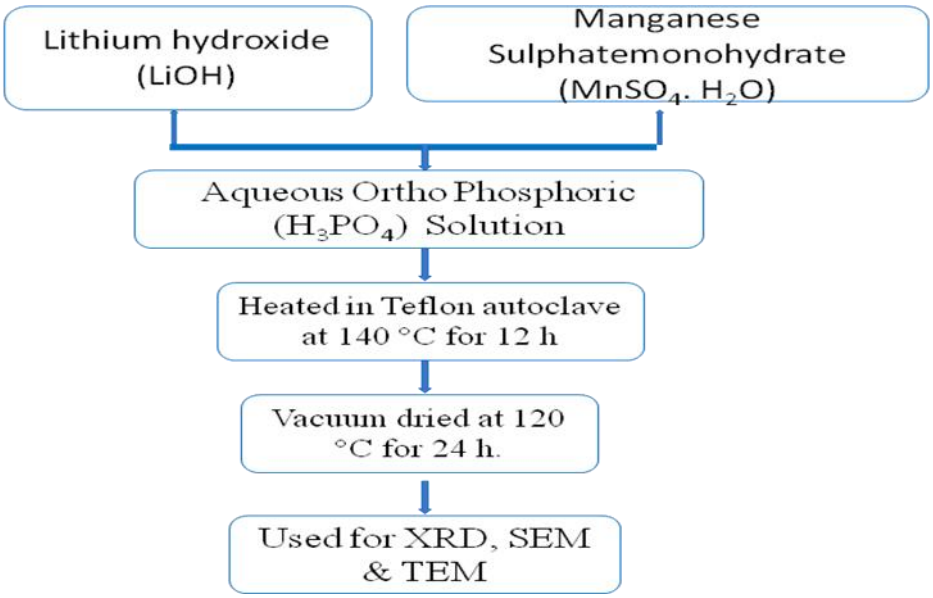
Figure 1: Flow chart for the current investigation of $LiMnPO_4$ nano-particles.



RESULTS AND DISCUSSION

Crystal Structure and Morphology

The structural characterization, phase identification and the crystalline size of the LMP nano-particles were investigated by powder-XRD analysis from PAN analytical Philips equipped with Cu – Ka radiation source (lambda = 1.5405 Å) was employed for measuring the intensity of the XRD patterns, to identify the phase purity and phase structure of crystalline. The morphology of the synthesized compound was carried out by the use of JEOL JSM – 6360LV, Scanning Electron Microscopy (SEM fitted with energy dispersive analysis (EDAX) spectrum). The nanocrystalline nature was confirmed by the use of JOEL 2010F HRTEM, Japan with 200kV operating voltage was used to capture the TEM images Transmission Electron Microscopy (TEM). The FTIR spectrum was recorded on the powder using spectrophotometer in the range of 4000-400cm^{-1} with 2cm^{-1} resolution for 20 scans.

Powder XRD pattern of LiMnPO4 (LMP) nano-particles

The powder XRD pattern of the $LiMnPO_4$ (LMP) nano-particles obtained is shown in Figure.2.The observed broad XRD peaks indicates that the peaks possess higher full-width half maximum (FWHM) which confirms the compound crystallizes in nanocrystalline form. The peaks were indexed to an orthorhombic crystal structure with space group of Pmnb of LMP (as compared to the standard patterns of JCPDS data No. 740375 [19].

The particle size was calculated from the FWHM values and thereby the use of Debye- Scherrer equation, ($D = k/\beta \cos\theta$ - where, β is the line broadening at half the maximum intensity in radians and θ is the Bragg angle) confirms that the crystalline sizes of pure $LiMnPO_4$ crystalline powder sample was found to be 65nm.

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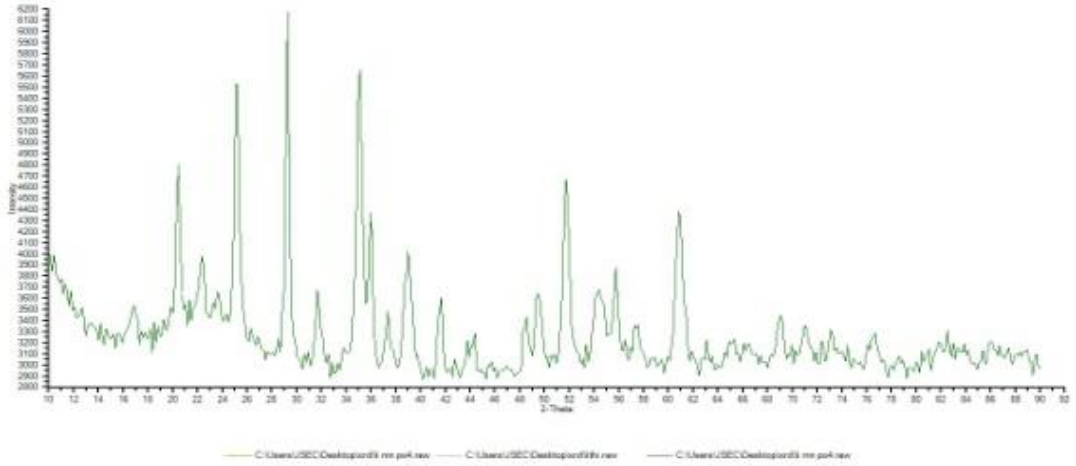

Figure 2: Powder XRD pattern of the $LiMnPO_4$ nano-particles.

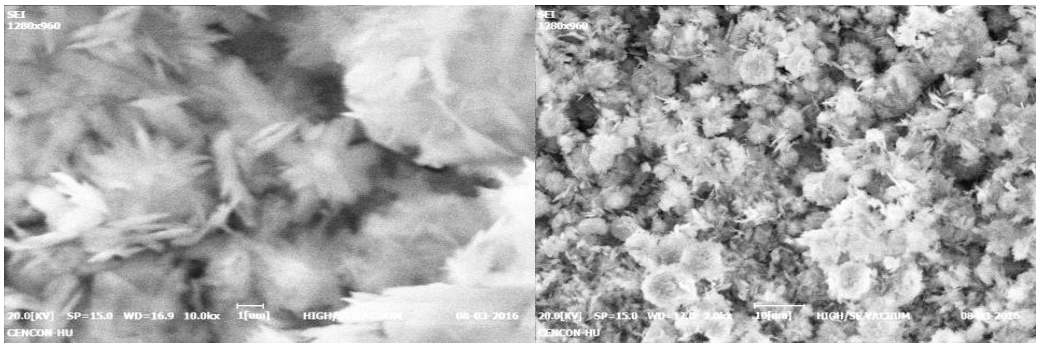

Figure 3: SEM Photographs of $LiMnPO_4$ with lower magnification

SEM and HRTEM of LiMnPO4 nanoparticles

Scanning electronic microscopy was performed to detect the morphology of the synthesized nano grains and also to measure the size of the particles. SEM image of LMP nano-particle is shown in Figure. 3. The SEM analysis indicates that the size of the synthesized LMP varies between 50 – 100 nm which is clearly seen in Figure.3. SEM Photographs of LiMnPO4 with lower magnification Transmission Electron Microscope with energy dispersive spectroscopy (TEM-EDS), and EDAX spectrum was taken for the LMP nano powder and the average crystalline sizes were found to be around 50 nm in thickness. Figure.4. shows the images obtained from the TEM instrument with different magnifications of the lithium manganese phosphate.

Transmission Electron Microscope with energy dispersive spectroscopy (TEM-EDS), JOEL 2010F HRTEM, Japan with 200kV operating voltage was used to capture the TEM images and EDAX spectrum was taken for the LMP nano powder and the size of the nanoparticles were found to be with an average size of 50nm in thickness. Figure.4. shows the TEM images of the LMP with different magnifications.

The presence of elements in the LMP was obtained from the EDAX spectrum which is shown in the Figure.5. It can be clearly seen from the graph that the elements of Mn, O and P were present in the required composition.

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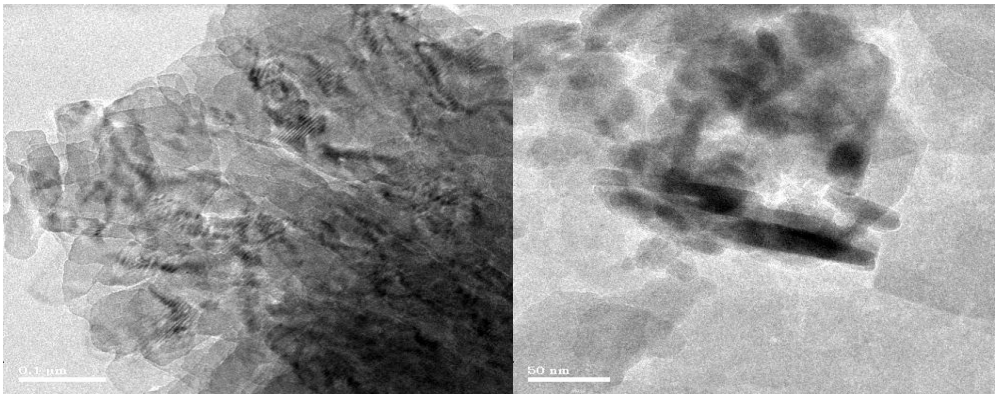

Figure 4: shows HRTEM images of the $LiMnPO_4$ nanoparticles at two different magnifications.

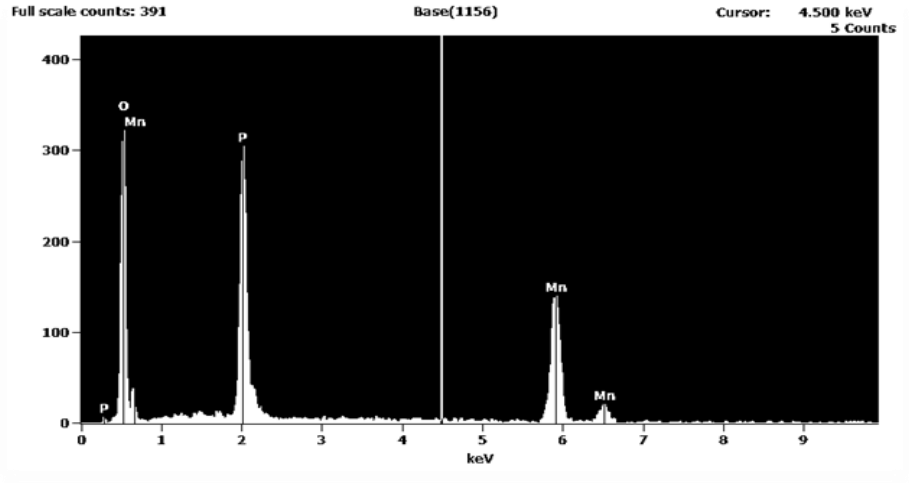

Figure 5: EDAX Studies of $LiMnPO_4$.

Fourier transform infra – red spectroscopy (FTIR) of LiMnPO4 nanoparticles

The FTIR spectrum of the LiMnPO4 samples calcined at 120°C is presented in Figure.6. The peak around 3416 cm^{-1} represents the O-H stretch which arises due to the moisture in the synthesized compound. The intensive band at 1624cm^{-1} attribute to the C-H bend and the band present at 1124cm^{-1} and 1064cm^{-1} attribute to the C-O stretch. 580 cm^{-1} may be assigned to the vibrations of PO_4-3. Thus, the presence of phosphorous oxide (PO_4-3) structures is confirmed from the FTIR analysis. These preliminary investigations suggest that the present method could be adopted for the large scale synthesizes of lithium manganese oxide for cathodic materials in lithium ion battery applications.

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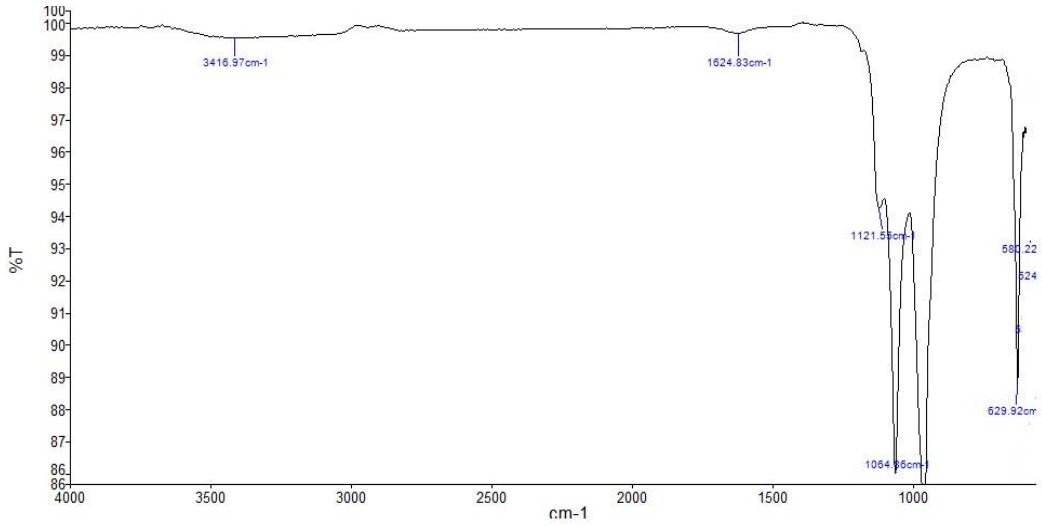

Figure 6: FTIR spectrum of LMP nano-particles

CONCLUSION

The Nanocrystalline form of Lithium manganese phosphate (LiMnPO4 - LMP) were synthesized from a very simple technique and the morphologies changes by adjusting the ratios of the glycol to water in the mixture of solvent mixture system. With the variation in the ratio of the glycol to water, the crystallization of the shuttles obtained of the LMP also varies. This variation of the particles morphologies may be mainly due to the viscosity and the dielectric constant of the solvents used which is the main cause to influence the final products.

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REFERENCES

[1] G Schmid (2004), Nanoparticles: From Theory to Applications, Wiley.
[2] S.W. Lee, C. Carlton, M. Risch, Y. Surendranath, S. Chen, S. Furutsuki,A. Yamada, D.G. Nocera, Y. Shao-Horn, J. Am. Chem. Soc. 134 (2012)16959 - 16962.
[3] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144(1997) 1188–1194.
[4] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithiumbatteries, Nature 414 (2001) 359–367.
[5] S.Y. Bae, H.W. Seo, J.H. Park, H. Yang, B.S. Kim, Chem. Phys. Lett. 376 (2003) 445–451.
[6] F. Li, J.B. He, W.L. Zhou, J.B. Wiley, J. Am. Chem. Soc. 125 (2003) 16166–16167.
[7] Z.D. Xiao, L.D. Zhang, X.K. Tian, X.H. Fang, Nanotechnology 16 (2005) 2647– 2650.
[8] Y.J. Yang, G.W. Meng, X.Y. Liu, L.D. Zhang, Z. Hu, C.Y. He, Y.M. Hu, J. Phys. Chem.C 112 (2008) 20126–20130.
[9] S.R. Li, N. Yesibolati, Y. Qiao, S.Y. Ge, J.F. Zhu, C.H. Chen, J. Alloys comp. 520(2012) 77–82.
[10] H. Ma, Z.Q. Yuan, F.Y. Cheng, J. Liang, Z.L. Tao, J. Chen, J. Alloys comp. 509 (20) (2011) 6030–6035.
[11] M.M. Rahman, J.Z. Wang, M.F. Hassan, Z.X. Chen, H.K. Liu, J. Alloys comp. 50 (17) (2011) 5408–5413.
[12] X.Y. Fan, Y. Li, J.J. Wang, L. Gou, P. Zhao, D.L. Li, L. Huang, S.G. Sun, J. Alloy comp. 493 (1–2) (2010) 77–80.
[13] X.Y. Fan, F.S. Ke, G.Z. Wei, L. Huang, S.G. Sun, J. Alloys comp. 476 (1–2) (2009)70–73.
[14] S. Franger, C. Bourbon, F. L. Cras, J. Electrochem. Soc., 151 (2004) A1024.
[15] M. Yonemura, A. Yamada, Y. Takei, N. Sonoyama, R. Kanno, J. Electrochem. Soc., 151 (2004) A1352.
[16] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J.Electrochem.Soc., 144(1997) 1188.
[17] M. Konarova, I. Taniguchi, Mater. Res. Bull., 43 (2008) 3305.

[18] D. Wang, H. Buqa, M. Crouzet, G. Deghenghi, T. Drezen, I. Exnar, N.H. Kwon, J.H.Miners, L. Poletto, M. Gratzel, J. Power Sources, 189 (2009) 624.
[19] Chiwon Kang, Mumukshu Patel, Baskaran Rangasamy, Kyu-Nam Jung , Changlei Xia, Sheldon Shi, Wonbong Choi, J.Power sources, 299 (2015) 465-471.