https://doi.org/10.15623/ijret.2018.0712002 Received: 27-09-2018, Accepted: 06-11-2018, Published: 29-11-2018

SYNTHESIS AND CHARACTERIZATION OF $LiFePO_4$ BY FLAME SPRAY PYROLYSIS – A LI-ION BATTERY CATHODE MATERIAL

Mallika Rani Parimi[1]

[1]*Assistant Professor, Department of Chemical Engineering, Anil Neerukonda Institute of Technology & Sciences, Visakhapatnam, India*

Abstract

Flame Spray Pyrolysis is a method used in the synthesis of $LiFePO_4$ with subsequent heat treatment in tubular furnace for Li-ion battery application as cathode material. The crystal structure, morphology of $LiFePO_4$ synthesized by Flame Spray Pyrolysis was studied by X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM). From the Debye-Scherer equation, $LiFePO_4$ particles obtained by this method are pure, homogeneous and well-crystallized with size ranging from of 25 – 60nm. FESEM data reveal that the particles are in spherical morphology with primary particle size ranging from 15-75nm.

***Keywords: -** $LiFePO_4$, Flame Spray Pyrolysis, XRD, FESEM, Cathode, Nano particles.*

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1. INTRODUCTION

In our day to day life, the demand for energy is growing due to which the utilization of non-renewable energy resources is increasing. But these fuels are predicted to decline steadily at about 2-3% a year. So it is crucial for human to pursue technological development that utilizes limited energy resources to reduce the burden on environment. Batteries are one such alternate energy sources, secondary batteries like Li-ion batteries have a wide range of applications in domestic purposes like portable electronics, electric vehicles, power grids, etc. Li-ion batteries are superior to conventional secondary batteries as they are lighter, have superior energy density, lower self-discharge (5% per month), no memory effect, high electrochemical potential, high capacity, durability, flexibility in design, prolonged service life, larger number of charge/discharge cycles, better environmental friendliness, and higher safety when compared to other batteries[5]. Lithium metal being an alkali is very active and has low density, large specific capacity, high electrochemical potential, high electro negativity, high energy density [16]. First commercial lithium ion battery was released by Sony Energy Tec Inc. in 1991[8,12] using $LiCoO_2$ as cathode and commercial graphite as anode. Li-ion batteries are used in Hybrid Electric Vehicles, Plug-in Hybrid Electric Vehicles and Electric Vehicles. Among various alternative cathode materials, lithium iron phosphate ($LiFePO_4$), discovered by Good enough in 1997[17] can be effectively used from very small particles down to the nano size because its reactivity. The batteries we are using in our present day life are all cobalt- based [6,19] but they are limited to portable devices due to capacity limitation, cost, safety, environmental issues. To overcome these limitations new advanced high capacities, low cost and environmental safe materials are needed. Olivine $LiMPO_4$ (M = Fe, Mn, Co and Ni) materials acts as alternative cathode material because of their thermal/chemical stability and low cost [20]. $LiFePO_4$ has a high theoretical capacity (170mAh/g) and operates at a cell voltage of 3.4V vs Li. However electronic conductivity is relatively low (10^{-9}S/Cm) which can be increased by doping $LiFePO_4$ with supervalent cations [3,21], coating $LiFePO_4$ with conductive materials such as carbons from organic precursors [11,18], and decreasing the particle size of $LiFePO_4$[4,13]. $LiFePO_4$ can be synthesized by various methods like High temperature solid state method [1], Co Precipitation [1], Mechanochemical activation [16], Carbothermal reduction [16], Template method [2], Hydrothermal [7], Flame Spray Pyrolysis [15], Spray Drying [10], Sol-Gel Spray Drying [9], Microwave heating [16], etc. A relatively flat discharge profile can be obtained using $LiFePO_4$.

This paper deals with synthesizing cathode material $LiFePO_4$ by using Flame Spray Pyrolysis method. The Flame spray pyrolysis is specifically chosen because of the possibility of obtaining nano sized particles, due to which the diffusion length decreases thereby facilitating easy Li-ion mobility from the active material. Three reaction steps occur during the electrochemical process: Li ion diffusion within solid state electrode material, a charge transfer reaction at the interface between the electrode and electrolyte, and Li ion movement in the electrolyte. Among these 3 steps, the first step, Li ion diffusion within the solid state electrode material is keen in enhancing the kinetic properties by decreasing the diffusion length in the material which can be done by making the material down to nano-size dimensions [14]. But the composite $LiFePO_4$ electrode material acts like an insulator because of its poor electronic conductivity which affects the electrochemical performance of the battery. To overcome this defect of poor conductivity, carbon coating can be done across the particles which would ultimately result in increased conductivities of the composite material.

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2. Synthesis of $LiFePO_4$ by Flame Spray Pyrolysis Method

2.1 Experimental Procedure

Flame Spray pyrolysis is a generic process which has good control in particle morphology and can produce a wide array of high purity nanopowders. The principle followed in Flame Spray Pyrolysis is that the particles are produced by decomposing precursor molecules at high temperatures which is similar to that of combustion. A typical flame spray pyrolysis system [15] is composed of a precursor solution reservoir, droplet generator/atomizer, reactor, and collection unit. Precursor solutions of aqueous/non-aqueous solvents in which the liquid feed containing metal precursors are dissolved and carried by an oxidizing gas into a reactor/flame zone in which droplets are evaporated and decomposed into solid particles. The unit set up at the ARCI is capable of producing oxide nanopowders at a rate of 1 kg/h. The unit setup and the schematic diagram is shown in Fig.1.

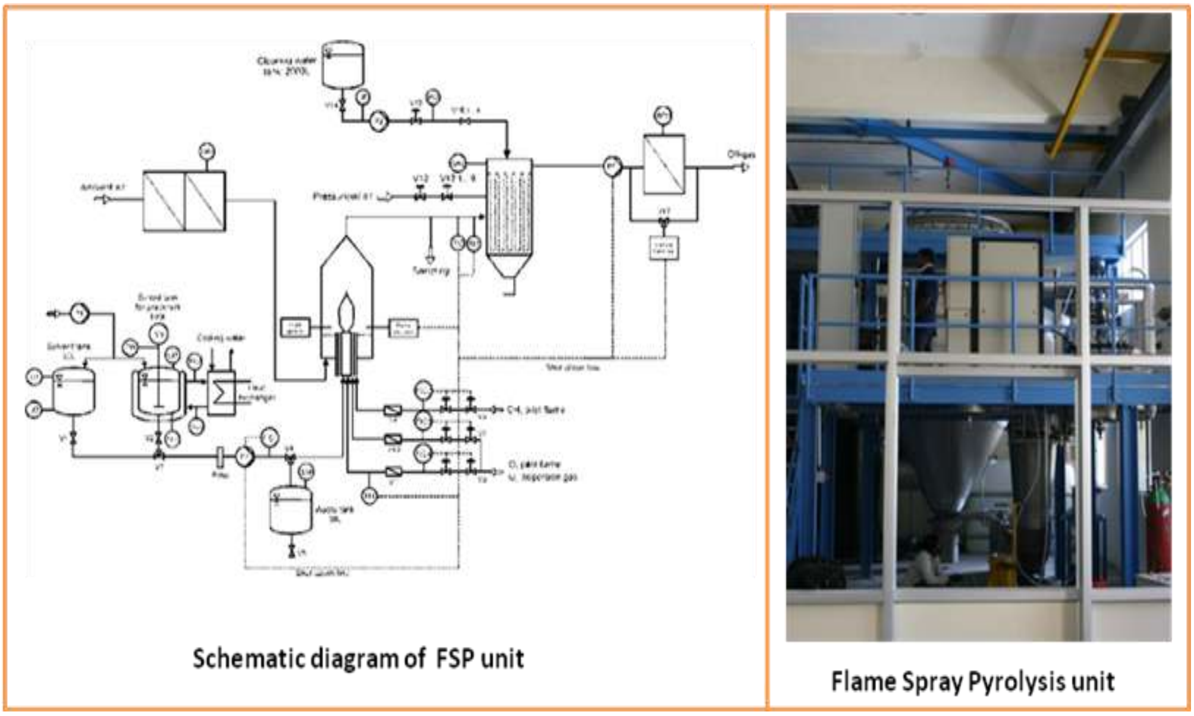

Fig 1: Flame Spray Pyrolysis unit

In the present synthesis, the precursor solution consists of metal nitrates $LiNO_3$, Fe $(NO_3)_3.9H_2O$ and H_3PO_4 (1:1:1M) dissolved in the organic solvents like ethanol/methanol, precursors are well mixed on magnetic stirrer till all the nitrates were dissolved. In this pilot flame spray pyrolysis plant, optimized conditions are followed for the synthesis of $LiFePO_4$. The precursor feeding range was 2-12 kg/h, an optimum of 8kg/h was delivered to the capillary of a two-phase atomizer (Series 970, Du¨sen-Schlick, Germany Capillary of 0.8mm dia.) with a microgear pump (HNP Microsysteme, Germany). The precursor feed was dispersed by using oxygen as dispersion gas at 80 l/min (60-120 l/min) at 2-3bar pressure drop. The supporting flame (diffusion flame) surrounding the nozzle was fed with methane at 5l/min (inner annulus) and oxygen at 5l/min (outer annulus). All these flow rates were controlled using calibrated mass flow controllers (Bronkhorst, Netherlands) and are reported at 25^{o}C and 1 atm. With progress in the process the metal precursor is sprayed with an oxidizing gas into the flame region, the sprayed droplets is combusted and is finally converted to nano sized metal composite which was sent for downstream operations. The temperature of the so formed nanoparticles was decreased by means of passing filtered ambient air so that the particles entering the bag house casing is maintained at a temperature of around 200^{o}C. By passing the pressurized air undergoing periodic pulses to a commercial bag-house filter (Mikropul, Germany) which contains 71 filter bags were automatically cleaned and due to which particles are collected at the bottom of the casing in to the particle collector of 257-mm diameter provided. The off-gas was passed through a HEPA police filter to prevent nanoparticle release into the environment.

The as synthesized $LiFePO_4$ powders heat treated in tubular furnace under inert atmosphere (Ar gas) at 600ºC for 6 h and thoroughly grounded in mortar, to yield crystallized $LiFePO_4$ particles. The XRD patterns of these samples were recorded using Cu-Kά (λ=1.5418 Aº (in 2θ)) radiation of an X-ray diffraction (XRD, Bruker D8- advance, Germany). The morphology of the powders was observed on a field emission scanning electron microscope (FE-SEM; Hitachi’s, S-4300 SE/N).

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3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Analysis

The crystallinity and the phase information of $LiFePO_4$ prepared by flame spray pyrolysis have been confirmed with the X-ray diffraction (XRD) method, as shown in Fig - 2. The as prepared powder (fig. 2c) shows no reflection indicates amorphous nature of the material. All the reflections (fig. 2b) can be attributed to the olivine structured $LiFePO_4$ (triphylite) (JCPDS no. 01-076-6355) that lacks any impurity phase after heat treatment.

From the Debye-Scherer equation, the crystallite sizes were in the range of 25 – 60nm which are consistent with FESEM images. Therefore, a pure, homogeneous and well-crystallized $LiFePO_4$ composite is indicated for all the parameters discussed in experimental method.

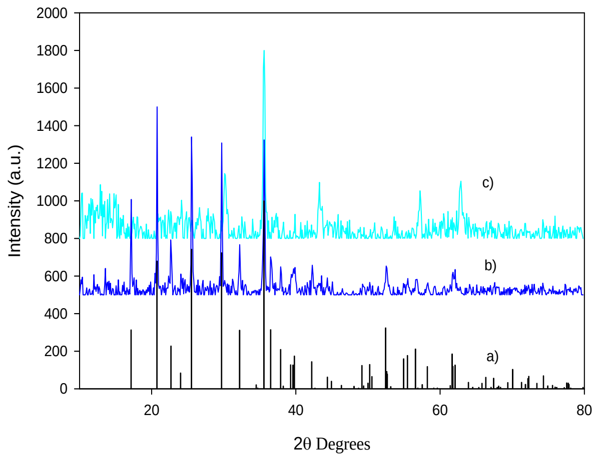

Fig 2: XRD pattern of $LiFePO_4$ sample (a) Standard data (JCPDF 01-076-6355) (b) Heat treated $LiFePO_4$ (c) As prepared $LiFePO_4$ by FSP

3.2 Morphological Analysis

Fig - 3. (a-f) shows the FESEM images of the $LiFePO_4$ samples synthesized by flame spray pyrolysis method by keeping the parameters constant at a precursor concentration of 1M, precursor feeding rate of 8kg/h and O_2 dispersion rate of 80l/min. The FESEM data reveal that the particles are in spherical morphology with primary particle size ranges from 15-75nm. As the particle size decreases, the diffusion path length decreases resulting in easy diffusion mechanism of lithium ion and electron through the interphase during electrochemical reaction, thereby improving the performance of the cell.

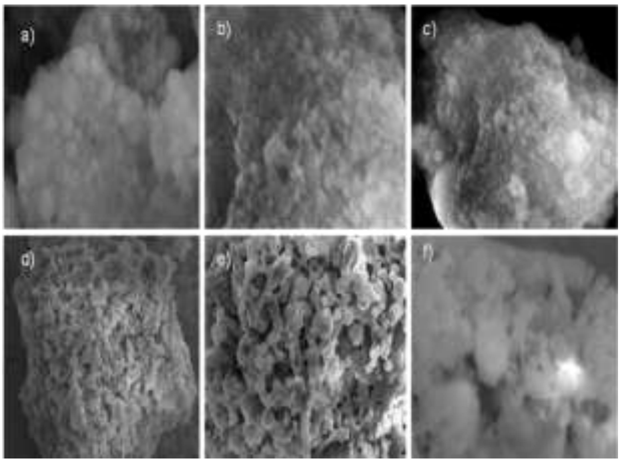

Fig 3: FESEM images of as prepared $LiFePO_4$ cathode prepared by FSP (a-c) As synthesized (1M - Concentration, precursor feeding rate - 8 kg/h and O_2 dispersion - 80 l/min) and (d-f) heat treated $LiFePO_4$ (Tubular furnace – Ar atmosphere at 600°C for 6h)

Bulk scale synthesis was done for 40 litres of precursor solution and produced $LiFePO_4$ powder of 0.75kg. The XRD profiles and FESEM data showed similar strategies as that for test run. Fig -4,5 represents the XRD profiles and FESEM data for the bulk produced $LiFePO_4$.

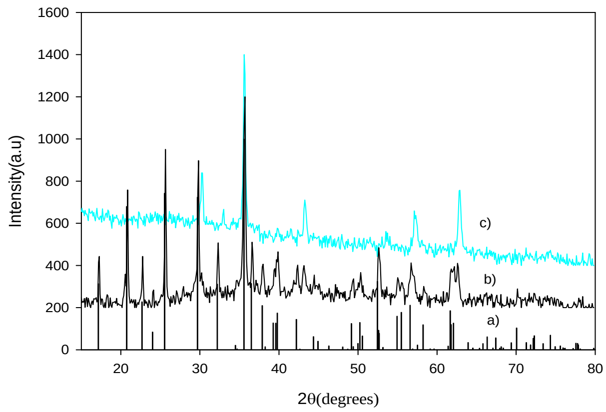

Fig 4: XRD pattern of $LiFePO_4$ sample (Bulk Production) (a) Standard data (JCPDF 01-076-6355), (b) Heat treated $LiFePO_4$ (c) As prepared $LiFePO_4$ by FSP

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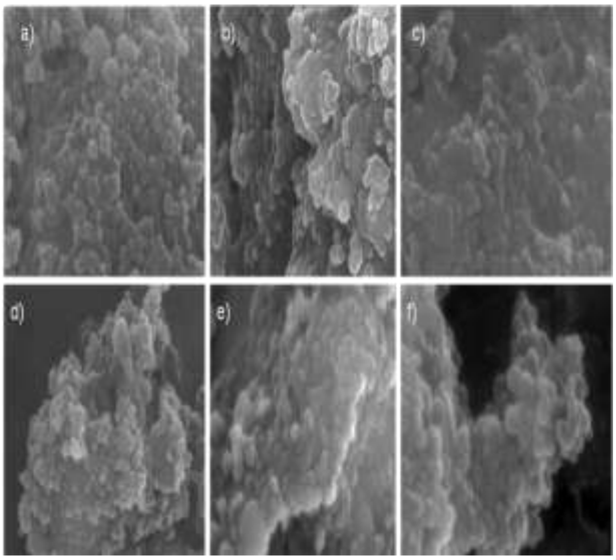

Fig 5: FESEM images of as prepared $LiFePO_4$ cathode (Bulk production) prepared by FSP (a-c) As synthesized (1M - Concentration, precursor feeding rate - 8 kg/h and O_2 dispersion - 80 l/min) and (d-f) heat treated $LiFePO_4$ (Tubular furnace – Ar atmosphere at 600^{o}C for 6h).

3. CONCLUSION

From this study, it is seen that Flame Spray Pyrolysis can be regarded as one of the most effective technique in producing $LiFePO_4$ nano particles down to 15nm size. As $LiFePO_4$ nano particles are used in Li-ion battery application as a cathode material this size reduction decreases diffusion length which would thereby easily facilitate Li-ion mobility from the active material cathode to anode and vice versa in a battery assembly. X-ray diffraction analysis also revealed that the $LiFePO_4$ particles obtained by this method are pure, homogeneous and well-crystallized with size ranging from of 25 – 60nm.

Abbreviations and Acronyms

FSP - Flame Spray Pyrolysis
FESEM - Field Emission Scanning Electron Microscopy
XRD - X-Ray Diffraction
JCPDF - XRD Software reference for $LiFePO_4$
JCPDS - XRD Software reference for $LiFePO_4$
HEPA - High Efficiency Particulate Air
ARCI - International Advanced Research Centre for Powder Metallurgy and New Materials

REFERENCES

[1] Borong Wu, Yonghuan Ren and Ning Li, “$LiFePO_4$ Cathode Material”, School of Chemical Engineering and Environment, Electric Vehicles The Benefits and Barriers, InTech, 2011, ISBN:978-953-307-287-6.

[2] Charles R. Sides, Fausto Croce, Vaneica Y. Young, Charles R. Martin, and Bruno Scrosati, “ A High-Rate, Nanocomposite $LiFePO_4$/Carbon Cathode”, Electrochemical and Solid-State Letters, 2005, vol.8(9), pp.A484-A487.

[3] Chung, S. Y., Bloking, J. T. and Chiang, Y. M., “ Electronically conductive phosphor-olivines as lithium storage electrodes”, Nature Materials, 2002, vol.1, pp. 123-128.

[4] Delacourt, C., Poizot, P., Levasseur, S. and Masquelier, C., “ Side effects on carbon-free $LiFePO_4$ powders the key to superior energy density”, Electrochemical and Solid State Letters, 2006, vol. 9(7), pp.A352-A355.

[5] Doktor der Naturwissenschaften, “Synthesis of nanosized, electrochemically active lithium transition metal phosphates”, Dissertation, ULM University, 2011.

[6] D. Aurbach, B. Markovsky, A. Rodkin, E. Levi, Y. S. Cohen, H. J. Kim, M. Schmidt, “On the capacity fading of $LiCoO_2$ intercalation electrodes: The effect of cycling, storage, temperature and surface film forming additives”, Electrochim. Acta, 2002, vol. 47(27), pp. 4291-4306.

[7] En Mei Kim, Kyung-Hee Park, and Hal-Bon Gu, “Electrochemical Characteristics of LiFePO4 with Conductivity Materials for Lithium Polymer Batteries”, J. Advanced Engineering and Technology, 2008, vol.1(1), pp. 107-111.

[8] E. Plichta, M. Salomon, S. Slane, M. Uchiyama, D. Chua, W. B. Ebner, and H. Lin, “ A rechargeable Li/Li_xCoO_2 cell”, Journal of Power Sources, 1987, vol.21(1), pp. 25-31.

[9] Feng Yu, Jingjie Zhang, Yanfeng Yang, Guangzhi Song, “Porous micro-spherical aggregates of $LiFePO_4$/C nano composites: A novel and simple template-free concept and synthesis via sol-gel-spray drying method”, Journal of Power Sources, 2010, vol. 195(19), pp.6873–6878.

[10] Feng Yu, Jingjie Zhang, Yanfeng Yang, Guangzhi Song, “Preparation and Characterization of mesoporous $LiFePO_4$/C microsphere by spray drying assisted template method”, Journal of Power Sources, 2009, vol.189(1), pp.794–797.

[11] Herle P. S., Ellis B., Coombs N. and Nazar L. F., “ Nano-network electronic conduction in iron and nickel olivine phosphates”, Nature Materials, 2004, vol.3, pp.7152.

[12] J. N. Reimers, and J. R. Dahn, “Electrochemical and Insitu X-Ray Diffraction studies of Lithium intercalation in Li_xCoO_2”,J. Electrochem. Soc., 1992, vol. 139(8), pp. 2091-2097.

[13] Kim D. H. and Kim J., “Synthesis of $LiFePO_4$ nanoparticles in polyol medium and their electrochemical properties”, Electrochemical and Solid State Letters, 2006, vol. 9(9), pp. A439-A442.

[14] Kyu Tae Lee, Jaephil Cho, “Roles of nano size in lithium reactive nanomaterials for lithium ion batteries”, nanotoday, 2011, vol. 6, pp.28–41.

[15] N.A. Hamid, S. Wennig, S. Hardt, A. Heinzel, C. Schulz, H. Wiggers, “High capacity cathodes for lithium- ion batteries from nanostructured $LiFePO_4$ synthesized by highly-flexible and scalable flame spray pyrolysis”, Journal of Power Sources, 2012, vol.216, pp.76-83.

https://doi.org/10.15623/ijret.2018.0712002 Received: 27-09-2018, Accepted: 06-11-2018, Published: 29-11-2018

[16] Ozan Toprakci, Hatice A.K. Toprakci, Liwen Ji, and Xiangwu Zhang, "Fabrication and Electrochemical Characteristics of $LiFePO_4$ Powders for Lithium-Ion Batteries", KONA Powder and Particle Journal, 2010, vol.28, pp.50-73.

[17] Padhi A.K., Nanjundaswamy K.S. and Goodenough J. B., "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries", Journal of Electrochemical Society, 1997, vol.144, pp.1188-1194.

[18] Ravet N., Chouinard Y., Magnan J. F., Besner S., Gauthier M. and Armand M, "Electroactivity of natural and synthetic triphylite", J. Power Sources, 2001, vol.97-98, pp.503-507.

[19] T. Ohzuku, A. Ueda., "Solid-state redox reactions of $LiCoO_2$ (R_{3m}) for 4v secondary lithium cells" J. Electrochem. Soc., 1994, vol. 141(11), pp. 2972-2977.

[20] T. Ohzuku, S. Takeda, M. Iwanaga, " Solid-state redox potentials for $Li[Me_{0.5}Mn_{1.5}]O_4$(Me:3d-transitional metal) having spinel framework structures: A series of 5volt materials for advanced lithium-ion batteries", J. Power Sources, 1999, vol. 81-82, pp. 90-94.

[21] Yang S., Song Y., Ngala K., Zavalij P. Y. and Whittingham M. S., "Performance of $LiFePO_4$ as lithium battery cathode and comparison with manganese and vanadium oxides", Journal of Power Sources, 2003, vol. 119-121, pp.239-24.