

# On the Synergistic Effect of Carbonate Anion Directed Shape Controlled Morphology and Super P Carbon in Preparing LiFePO<sub>4</sub>/C Cathode With Improved Lithium Intercalation Behavior

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A simple and carbonic acid directed modified mechano thermal (MMT) method is identified to produce morphology controlled nano rods of LiFePO<sub>4</sub>/C composite. The added carbonic acid plays a vital role in controlling the morphology (CO<sub>3</sub><sup>2-</sup> inhibition effect) and the formation of rod-like structure that results from the unidirectional escape of CO<sub>2</sub> gas upon calcination. MMT synthesized LiFePO<sub>4</sub>/C cathode containing 2 wt.% conducting graphite exhibits a nominal specific capacity of 129 mAhg<sup>-1</sup>, while the corresponding LiFePO<sub>4</sub>/C with 2 wt.% nickel coated graphite delivers 100 mAhg<sup>-1</sup> capacity. On the other hand, MMT synthesized LiFePO<sub>4</sub>/C composite cathode consisting of 2 wt.% super P carbon exhibits an appreciable capacity of 160 mAhg<sup>-1</sup> with an acceptable rate capability behaviour. The synergistic effect of shape controlled morphology (resulting from MMT synthesis approach) and the addition of super P carbon in improving the electrochemical behavior of LiFePO<sub>4</sub>/C composite cathode is demonstrated in the present study.

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**Keywords:** Modified mechano thermal (MMT) method, conventional mechano thermal (CMT) method, lithium iron phosphate, lithium batteries

## 1. INTRODUCTION

Lithium batteries dominate the field of advanced power sources wherein identification of cost-effective and safe cathodes with improved performance is the challenging issue. In this regard, olivine structured LiFePO<sub>4</sub> receives considerable attention in recent years, as the co-valency of phosphate group offers good thermal stability and the presence of iron makes it economically viable.

It is well known that nano crystalline LiFePO<sub>4</sub>/C with controlled morphology would exhibit

improved electrochemical performance via. reduction of lithium diffusion path length and the strain associated with the two phase redox reaction between  $\text{LiFePO}_4$  and  $\text{FePO}_4$  [1]. Among the different morphologies of nanomaterials, one dimensional nano rods [2,3] provide facile strain relaxation during battery charge and discharge, thus improving the cycleability of nano electrodes [4]. Therefore, identification of suitable synthesis methodology that offers one-dimensional nano rods of  $\text{LiFePO}_4/\text{C}$  and the type of carbon that improves the performance of  $\text{LiFePO}_4/\text{C}$  nano composite is targeted through the present study.

Among the various synthesis methods, hydrothermal (HDT) approach, popularly known for producing nano crystalline  $\text{LiFePO}_4/\text{C}$  with controlled morphology [5-6] requires a careful manipulation of parameters such as concentration, pH, pressure and temperature. In addition, HDT method may lead to  $\text{Li}^+$  ion diffusion related problems, especially when iron atoms occupy the lithium site [7] and the suitability of HDT method for large scale synthesis is debatable. On the other hand, conventional mechano thermal (CMT) method, known for commercial viability has negative influence on the electrochemical performance due to the unavoidable particle growth[8]. Hence, exploration of a novel approach, viz. modified mechano thermal (MMT) method to prepare morphology controlled  $\text{LiFePO}_4/\text{C}$  nano rods with a suitable carbon has been aimed through the study. Regarding the synthesis of electrode materials with controlled morphology, an excess supply of  $\text{CO}_3^{2-}$  anion is required to inhibit the growth of particles and the same has been attempted by adjusting the amount of lithium, addition of urea or ammonia bicarbonate [9]. Quite different from such attempts, simple addition of carbonic acid ( $\text{H}_2\text{CO}_3$ ) that can liberate  $\text{CO}_3^{2-}$  anion upon two step decomposition according to equations (1) and (2) is explored in the present study to facilitate the growth inhibition effect.



It is well known that the low electronic conductivity ( $\sigma_e=10^{-9} \text{ Scm}^{-1}$ ) and low lithium diffusivity ( $D_{\text{Li}^+}= 10^{-14} \text{ cm}^2\text{s}^{-1}$ ) issues of  $\text{LiFePO}_4$  [10-12] could be addressed significantly with the help of carbon coating and particle size reduction [13,14] than with super valent doping [15]. Because, addition of carbon improves bulk conductivity of  $\text{LiFePO}_4$  and impedes the agglomeration of particles significantly [16,17]. Towards this direction, an optimum amount of (2 wt.%) different types of carbon viz. super P, conducting and nickel coated graphite was added individually to form  $\text{LiFePO}_4/\text{C}$  composite cathode using MMT synthesis approach. The synergetic effect of MMT synthesis method and the type of carbon added in improving the electrochemical behavior  $\text{LiFePO}_4/\text{C}$  is better understood from a comparison of electrochemical performance of the same obtained from three different carbon sources.

## 2. EXPERIMENTAL

### 2.1. Synthesis procedure

In MMT method, a mixture consisting of stoichiometric amounts of lithium carbonate, iron oxalate and ammonium dihydrogen phosphate was treated with carbonic acid and 2 wt.% of carbon (super P/conducting graphite/ nickel coated graphite), ground well and furnace heated at 300 °C(8h.) in Ar atmosphere. The intermediate product received from furnace was further ground with an excess of carbonic acid and heat treated in Ar at 700 °C (5h.) to obtain nano rods of LiFePO<sub>4</sub>/C composite material. Herein, Li<sub>2</sub>CO<sub>3</sub> being a precursor for MMT process acts as a source of lithium (to form LiFePO<sub>4</sub>/C) and CO<sub>3</sub><sup>2-</sup> anion to assist the carbonic acid driven one dimensional growth of rod like morphology.

### 2.2. Physical and electrochemical characterizations

Phase characterization was done by a powder X-ray diffraction technique on a PANalytical X'pert PRO X-ray diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range 10–90° at a scan rate of 0.04° s<sup>-1</sup>. Surface morphology of the synthesized samples was studied on SEM [JSM 6400, JEOL, Japan] and Transmission electron microscopy (TEM) data was collected with a JEOL 2010F TEM operating at 200 keV. Charge discharge studies were carried out using MACCOR charge-discharge cycle life tester.

### 2.3. Electrode preparation and cell assembly

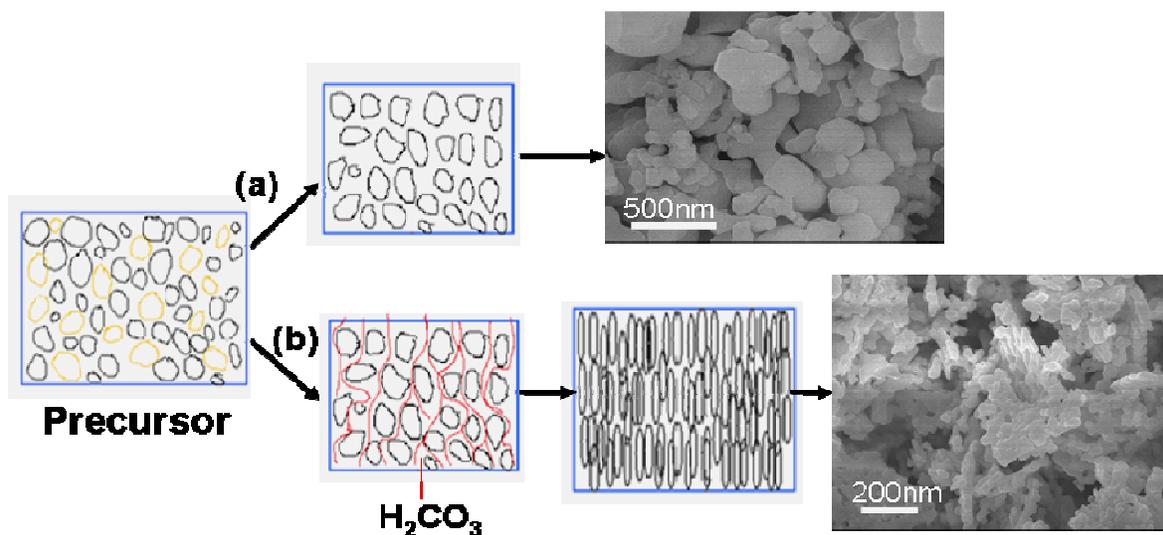
The coin cells were fabricated with the LiFePO<sub>4</sub>/C composite cathode, metallic lithium anode and a solution containing 1M LiPF<sub>6</sub> salt dissolved in 1:1 v/v diethyl carbonate (DEC)/ethylene carbonate(EC) as electrolyte along with Celgard separator. The cathodes were prepared by mixing 80 wt.% active material with 10 wt.% conductive carbon and 10 wt.% polytetrafluoroethylene (PTFE) binder, which was rolled into thin sheets using isopropanol. Circular electrodes were cut from the sheet, pressed over an Al mesh (3 ton of pressure). The electrodes typically had an active material content of 7~8 mg, and were dried under vacuum at 80 °C for more than 3 h. before assembling the cells in an argon-filled glove box.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis method vs. Morphology-SEM study

Fig. 1(a &b) shows the FESEM images of LiFePO<sub>4</sub>/C synthesized by CMT and MMT methods, wherein a wide range of unevenly distributed particles (Fig. 1a) of 500 nm are obtained from CMT

method. On the other hand, homogenous distribution of nano rods of 200 nm size (Fig.1b) results from MMT method, due to the increased concentration of  $\text{CO}_3^{2-}$  anion.



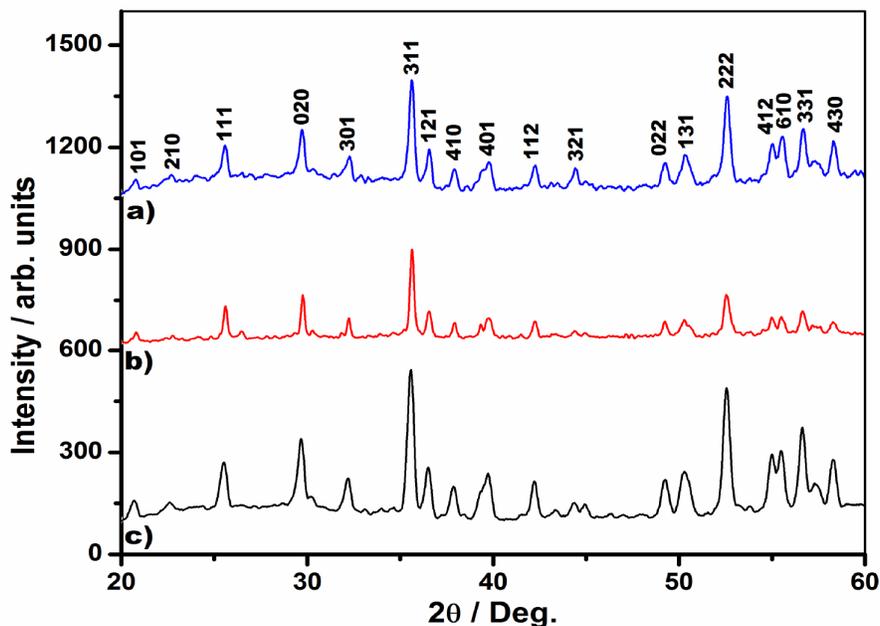
**Figure 1.** Schematic representation and SEM images of  $\text{LiFePO}_4/\text{C}$  synthesized by (a) CMT method and (b) MMT method

The added carbonic acid is believed to play a vital role in controlling the morphology ( $\text{CO}_3^{2-}$  inhibition effect) and the formation of rod-like structure (Fig.1b) that results from the unidirectional escape of  $\text{CO}_2$  gas (as shown in Fig.1) at high temperature. Formation of thin layer of carbon coating over the surface of  $\text{LiFePO}_4$  results from the addition of different types of carbon, viz., Super P, Conducting and Nickel coated graphite, thus avoiding the agglomeration of rods even at 700 °C. Hence, the growth controlled nano rod formation of  $\text{LiFePO}_4/\text{C}$  may be attributed to the  $\text{CO}_3^{2-}$  inhibition effect and the carbon wiring effect. Since  $\text{LiFePO}_4/\text{C}$  prepared from MMT method using different types of carbon exhibit similar surface morphology (Fig. 1b), it is understood that the morphology of MMT synthesized  $\text{LiFePO}_4/\text{C}$  has no dependence on the type of carbon being added.

### 3.2. Phase characterization –XRD studies

Powder X-ray diffraction (PXRD) pattern was recorded to confirm the phase pure formation of crystalline  $\text{LiFePO}_4/\text{C}$  compound (Fig.2) synthesized via. MMT method containing 2 wt% of different types of carbon, viz. Super P(a), Conducting (b) and Nickel coated graphite (c). Absence of undesirable Fe(III) related impurity peaks confirms the formation of single phase  $\text{LiFePO}_4$ .  $\text{LiFePO}_4/\text{C}$  compounds synthesized with different types of carbon show striking similarity with each other and also with the standard JCPDS pattern. Hence, PXRD study does not indicate (as that of SEM results) the preferred type of carbon that can be added to improve the performance of  $\text{LiFePO}_4/\text{C}$  compound. However, the added carbons have no negative influence on the crystal structure of  $\text{LiFePO}_4$ . All the

Bragg peaks can be indexed to a pure and well crystallized  $\text{LiFePO}_4$  phase, possessing an ordered olivine structure with a Pnma space group (JCPDS file No: 81-1173). The calculated lattice parameter values, viz.  $a=10.33$ ,  $b=6.01$  and  $c=4.69$  Å (Fig.1a) are found to be in good agreement with the standard values. Similarly, diffraction peaks corresponding to the presence of 2 wt%. carbon, being an insignificant amount is not seen in XRD, which is also a known behaviour.



**Figure 2.** XRD pattern of  $\text{LiFePO}_4/\text{C}$  composite material synthesized by MMT containing a) Super P carbon, b) Conducting graphite and c) Ni coated graphite

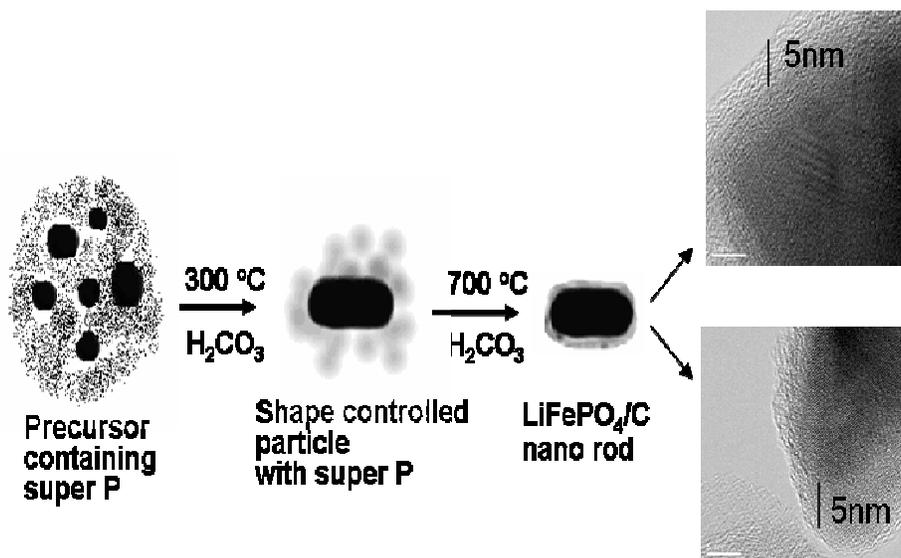
### 3.3. Surface coating –TEM analysis

The presence of nano crystalline  $\text{LiFePO}_4/\text{C}$  composite with carbon coating is confirmed from TEM images (Fig. 3). TEM evidences the formation of uniform layer of carbon coating over native  $\text{LiFePO}_4$  particle. The wiring effect of carbon in connecting the interfaces between  $\text{LiFePO}_4$  particles [18] is widely reported to enhance the electronic conductivity remarkably, especially with such an uniform carbon coating. A desirable coating thickness (5 nm) required for mixed conducting property [19] has been obtained, which is attributed to the significance of MMT synthesis methodology.

### 3.4. Electrochemical behaviour

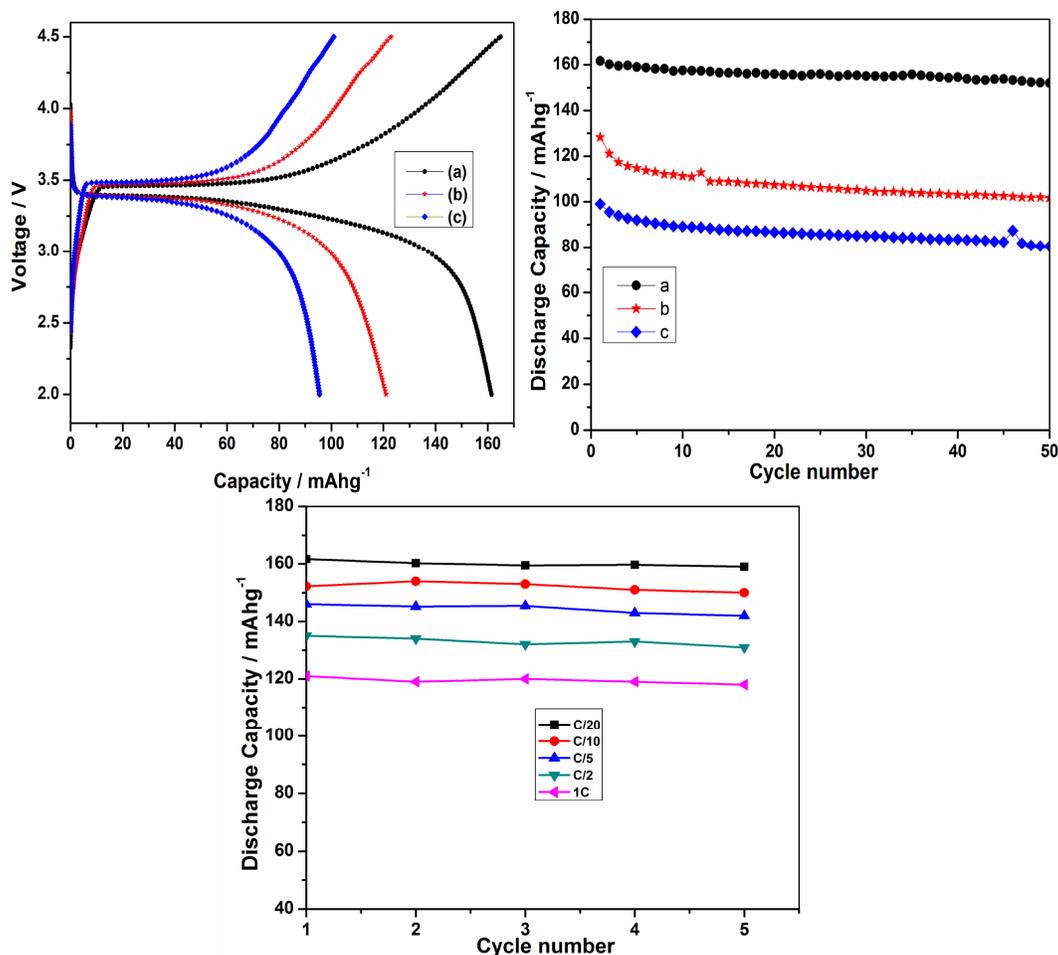
Electrochemical performance of  $\text{LiFePO}_4/\text{C}$  composite cathodes containing three different types of carbon was carried out on 2032 coin cells individually. Fig. 4(i) depicts the voltage vs. capacity behavior of MMT synthesized  $\text{LiFePO}_4/\text{C}$  composite cathodes, wherein well defined charge

and discharge plateaus were observed around 3.4 V for all the three cathodes. The appearance of 3.4 V plateau indicates the two phase nature of  $\text{Li}^+$  extraction and insertion reaction between  $\text{LiFePO}_4$  and  $\text{FePO}_4$ . Among the three composite cathodes, cells containing  $\text{LiFePO}_4$ /super P carbon exhibits higher discharge capacity ( $160 \text{ mAhg}^{-1}$ ) values, compared to those of conducting (b) and nickel coated graphitic (c) carbons.



**Figure 3.** Schematic representation of one-dimensional nano rod formation and the typical TEM images of  $\text{LiFePO}_4/\text{C}$  synthesized by MMT

The cycling behavior of  $\text{LiFePO}_4/\text{C}$  cathodes at C/20 rate is furnished in Fig. 4(ii). An initial discharge capacity of 160, 129 and  $100 \text{ mAhg}^{-1}$  have been exhibited by  $\text{LiFePO}_4/\text{C}$  cathode with super P carbon (a), conductive graphite (b) and Ni coated graphite (c) respectively. Interestingly,  $\text{LiFePO}_4$ /super P composite cathode (a) delivered a capacity as high as  $160 \text{ mAhg}^{-1}$  (almost close to theoretical capacity of  $169 \text{ mAhg}^{-1}$ ) with an excellent capacity retention (95%) and a negligible capacity fade (5%) up to 50 cycles. Such an improved electrochemical behavior of  $\text{LiFePO}_4$ /superP composite cathode has been endorsed to the synergistic effect of nano rods (200 nm) derived from the  $\text{CO}_3^{2-}$  anion controlled morphology and the uniformly formed thin coating of super P carbon, desired for the effective wiring of  $\text{LiFePO}_4$  particles. In order to further investigate the high rate performance of  $\text{LiFePO}_4$ /super P composite cathode, rate capability test was performed with various C-rates. Fig 4(iii) shows that  $\text{LiFePO}_4$ /super P composite cathode exhibits a discharge capacity of  $160 \text{ mAhg}^{-1}$  at C/20 rate and slightly reduced capacity values of 152, 146, 135 and  $122 \text{ mAhg}^{-1}$  are obtained at higher C-rates such as C/10, C/5, C/2 and 1C respectively. From this, the suitability of MMT synthesized  $\text{LiFePO}_4$ /superP composite cathode for high power applications is understood.



**Figure 4.** Electrochemical behavior of MMT synthesized  $\text{LiFePO}_4/\text{C}$  cathodes: i) Voltage vs Capacity ii) Discharge Capacity vs Cycle number and iii) Rate capability behavior of  $\text{LiFePO}_4/\text{super P}$  composite cathode

#### 4. CONCLUSION

To conclude, a simple, an easy-to-adopt and a commercially viable MMT synthesis route has been demonstrated to prepare morphology controlled nano rods of  $\text{LiFePO}_4/\text{C}$  with 200 nm particle size. Among the different types of commercial carbons (super P carbon, conducting graphite and Ni coated graphite) used to prepare the title compound, super P carbon coated  $\text{LiFePO}_4/\text{C}$  cathode exhibited higher discharge capacity ( $160 \text{ mAhg}^{-1}$ ). The excellent capacity retention and rate capability behavior of  $\text{LiFePO}_4/\text{super P}$  composite authenticates the synergistic effect of MMT method and super P carbon in preparing the lithium intercalating olivine cathode with an improved electrochemical behavior.

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