CHAPTER 3

Investigation on the synthesis and characterization of olivine structured LiMPO₄/C composite cathodes (M=Fe & Co) for facile lithium intercalation behavior
3.1 Background and motivation

In spite of more than 20 years of research on Li-ion insertion/deinsertion compounds, only few candidates have been identified as potential cathodes. For example, layered LiCoO$_2$, multimetal oxide family LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$, spinel LiMn$_2$O$_4$ and its derivatives along with olivine structured LiMPO$_4$ cathodes receive attraction amongst researchers, especially for their comparable electrochemical performance, as required by the modern techno commercial society. Particularly, olivine structured LiFePO$_4$ has emerged as one of the leading cathode candidates for high power lithium ion cells, as the covalently bonded PO$_4$ group offers excellent thermal stability, while Fe is inexpensive and environmentally benign. The main drawback of LiFePO$_4$ is its low electronic and lithium-ion conductivity added with stringent synthesis methodology. It is well known that the low electronic conductivity ($\sigma_e=10^{-9}$ Scm$^{-1}$) and low lithium diffusivity ($D_{Li^+}=10^{-14}$ cm$^2$/s) issues of LiFePO$_4$ could be addressed significantly with the help of conductive material coating and particle size reduction respectively.

Towards this direction, coating of LiFePO$_4$ surface with Cu, Ag, carbon, or conducting polymers is reported to be very effective in improving the electronic conductivity of the powder [2]. Although metal additives may significantly improve the electronic conductivity of LiFePO$_4$, it is difficult to achieve a uniform metal dispersion on the surface of LiFePO$_4$ [2]. Metal oxidation to form insulating films and/or soluble ions that might interfere with the negative electrode cycleability are certain issues to be considered seriously, whereas carbon coating is free from such intracies. Because, carbon is well known for its stability and compatibility and use in the preparation of composite cathode. Furthermore, use of a high-cost metal additive is not suitable for large-scale applications of LiFePO$_4$ products. Similarly, conductive
polymers such as polypyrrole generally have poor mechanical properties and instability [3]. Although recently poly-(3,4-ethylenedioxythiophene) (PEDOT) chemically grown on partially de-lithiated LiFePO₄ seems to lead to good cycleability [4], by comparison, carbon coating has been particularly attractive with respect to its high conductivity using carbon concentrations as low as 0.5–3 wt.% [5–8]. Its low cost, simplicity of introduction during or after the LiFePO₄ synthesis, its proven use as a conductive additive in composite electrodes and its chemical stability in the battery are the salient features due to which the same has been widely considered.

Similarly, size reduction of cathode active material to nanoscale dimension has been pointed out by John Goodenough et al. as one of the effective techniques to solve the kinetic problems of LiFePO₄ [9] due to shorter lithium ion diffusion path length. Many other researchers also attempted to mitigate lithium diffusion limitations in LiFePO₄ by reducing the particle size with a view to shorten the diffusion length. Recent studies show that ionic diffusion constant depends on particle size and the diffusion in nanosized particles is reported to be much faster than in micrometre-sized particles or bulk [10]. However, the higher surface area arising from the smaller nanoparticle size also results in other undesirable effects such as low material packing density of the cathode and potential electrode/electrolyte reactions [11,12].

Among the various synthesis methods, hydrothermal (HDT) approach, popularly known for producing nano crystalline LiFePO₄/C with controlled morphology [13, 14] requires a careful manipulation of parameters such as concentration, pH, pressure and temperature. In addition, such a low temperature synthesis method may lead to Li⁺ ion diffusion related problems, especially when iron atoms occupy the lithium site [15] and the suitability for large scale synthesis is debatable.
Although the size reduction strategy has been employed to improve the performance of LiFePO$_4$ in many studies, recent reports indicate that the specific capacity of LiFePO$_4$ has no clear dependence on the particle size in the range of 50–400 nm [16, 17]. For example, with the introduction of highly conductive carbon, some LiFePO$_4$ materials with a larger particle size (150–300 nm) exhibited better performance than the materials of smaller size (30–100 nm). This is because Li-ion transport in these LiFePO$_4$ particles is not diffusion-controlled and the contribution of size reduction to the capacity of LiFePO$_4$ is therefore limited [16]. It has to be pointed out that the nano-sized particles do not necessarily always give excellent electrochemical performance. For instance, it was found that in the hydrothermal synthesis, anti-site defects may form, which would block lithium ion transportation and lead to slow kinetics [18]. Considering these adverse effects of nanosized LiFePO$_4$ in practical applications, it is understood that an optimum particle size of LiFePO$_4$/C with controlled morphology is crucial to realize improved electrochemical performance.

A combination of carbon coating and reduced particle size with controlled morphology can improve the rate performance and material utilization of LiFePO$_4$ [19–20]. To achieve high capacity from low cost LiFePO$_4$ batteries with a suitable size, it is desirable to reduce the amount of carbon and to improve the quality of carbon coating. Identification and adoption of a suitable synthesis methodology with optimized synthesis parameters/conditions and type of carbon or carbon source to improve the electronic conductivity are reported to play a vital role in modifying the physical as well as electrochemical properties of LiFePO$_4$ cathode material. Therefore, attempts to modify solid-state synthesis methodology, surface modification of LiFePO$_4$ and newer solution assisted synthesis approach combined with the
segregation of Li$_3$PO$_4$ impurity to realize closer to the theoretical capacity value are discussed in this chapter regarding LiFePO$_4$ cathode.

The challenges remain in the development and commercialization of low-cost and stable LiFePO$_4$ cathode for lithium-ion batteries have provoked strong interest to investigate other members of the olivine like metallophosphate family LiMPO$_4$ (M = Mn, Fe, Co,Ni) [21-24] to explore the possibility of recommending them as potential cathode candidates. Among them, LiCoPO$_4$ is bestowed with certain inherent advantages that include higher red-ox potential (4.8 V vs. Li/Li$^+$), appreciable theoretical energy density of $\sim$ 802 WhKg$^{-1}$ (which is 1.35 times higher than that of LiFePO$_4$) [25-28], better electronic conductivity than LiMnPO$_4$ and lesser threat on electrolyte decomposition compared with that of LiNiPO$_4$ (with a red-ox potential of 5.1 V). The difference in the cell volumes between pristine and delithiated phases was reported to be about 2%, which is much lower in comparison with those of LiFePO$_4$/FePO$_4$ (7%) and LiMnPO$_4$/MnPO$_4$ (8.9%) [26, 27]. However, the structure evolution during delithiation of LiCoPO$_4$ is not completely resolved yet. Amine at al. reported the formation of a second olivine-like phase upon lithium extraction from LiCoPO$_4$ [21]. A two-phase mechanism of lithium extraction from LiCoPO$_4$ was confirmed by in-situ synchrotron diffraction [25]. On the other hand, ex-situ diffraction on other LiCoPO$_4$ samples annealed at low temperatures showed a pronounced amorphization of the cathode material after electrochemical delithiation [28]. Amorphization of cathode material was also observed upon chemical oxidation of LiCoPO$_4$ with NO$_2$BF$_4$[29]. In addition, coating of carbon on pristine LiCoPO$_4$ is not easy compared with that of LiFePO$_4$ [310], as the same has a major dependence on the selection of suitable synthesis approach and addition of desired amount of preferred type of carbon to form LiCoPO$_4$/C.
In this regard, despite the number synthesis methods that are reported on the carbon coated LiCoPO$_4$ cathode [31-37], Wolfenstine et al. [34] have reported the role of heating environment in forming highly conductive Co$_2$P phase ($\sim 10^{-1}$ Scm$^{-1}$) and the significance of Co$_2$P co-existing LiCoPO$_4$ cathode in exhibiting better electrochemical properties. Further, it is well known that the formation of dimensionally controlled nanocrystalline LiCoPO$_4$ is expected to improve the electrochemical behaviour due to shortened diffusion path length of lithium ions. With this back ground, synthesis and characterization of growth controlled LiCoPO$_4$/C nanorods consisting of in-situ formed Co$_2$P phase has been aimed through the present study.

3.2 Experimental section

3.2.1 Solid State Fusion (SSF) Method and subsequent surface modification of LiFePO$_4$ to prepare composites: Stoichiometric amounts of Li$_2$CO$_3$ (Lithium carbonate), FeC$_2$O$_4$.2H$_2$O (Fe(II) oxalate) and NH$_4$H$_2$PO$_4$ (Ammonium dihydrogen phosphate) were mixed thoroughly and ball milled for two hours. Then the mixture was treated with a carbon source and heated initially at a lower calcination temperature of 300 °C for 8h. in Ar atmosphere to remove volatiles. The product thus obtained was ground again and sintered at 700 °C for a period of 8h. in Ar atmosphere (Fig. 1). The ultra fine powders of LiFePO$_4$ thus obtained were subjected to systematic characterization studies.

Further, the LiFePO$_4$ powder was mixed with calculated (2wt.%) amount of carbon (super P), metal (Cu) and metal oxide (CuO), ground well to ensure homogeneity and subjected to heat treatment. The mixture was furnace heated at 500 °C for 2h., ground well and collected as a composite consisting of LiFePO$_4$/additive.
Fig. 1 Steps involved in the solid state fusion method to synthesize LiFePO₄/C

3.2.2 Modified solid state fusion (MSSF) synthesized LiFePO₄/C: In MSSF method, a mixture consisting of stoichiometric amounts of lithium carbonate, iron (II) 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 nanorods of LiFePO₄/C composite material. Herein, Li₂CO₃ being a precursor for MSSF process acts as a source of lithium (to form LiFePO₄/C) and CO₃²⁻ anion to assist the carbonic acid driven one dimensional growth of rod like morphology (38).

3.2.3 Furnace heated and microwave irradiated gel derived LiFePO₄/C (solution assisted sol-gel approach):

Primarily, a precursor mix consisting of an appropriate amount of lithium acetate, iron (II) oxalate (dissolved in acid medium) and ammonium dihydrogen phosphate was added to hot water with stirring to get a thick solution. To the solution,
3g of gelling agent (viz. gelatin) was added and the process of stirring and heating was continued to get a thick gel. The gel thus obtained was treated further in two different modes, viz. conventional sol-gel approach (furnace calcination of gel in a mixture of Ar & H₂ – 90:10) and microwave assisted sol-gel approach (microwave irradiation of the gel) with a view to understand the effect of synthesis method upon physical as well as electrochemical properties of synthesized LiFePO₄/C compound (Fig. 2). Details pertinent to such treatment are given below

**Fig. 2** Flow chart of furnace heated and microwave irradiated gel derived LiFePO₄/C

**a) Conventional sol-gel method:** The formed gel was dried and furnace-heated to 300 °C for about 12 h. followed by higher calcination at 700 °C for about 8 h. in an atmosphere that contains a mixture of argon and hydrogen (90:10) along with the addition of 2wt.% of select carbon using alumina crucibles. The ultrafine LiFePO₄/C composite obtained after 700 °C was ground and subjected to characterization studies.

**b) Microwave assisted sol-gel:** The formed gel was dried and irradiated with microwave for about 12 min. followed by sintering at 700 °C for 1h. with the addition
of 2wt.% of chosen carbon. Ultrafine powders of LiFePO$_4$/C composite was collected and subjected to characterization studies.

3.2.4 Preparation of LiCoPO$_4$/C (Modified solid state fusion method): LiCoPO$_4$ has been prepared by three different routes, namely (a) conventional solid state fusion, (b) modified solid state fusion with the addition of carbonic acid (H$_2$CO$_3$) as growth inhibiting modifier, and (c) modified solid state fusion with a mixture of carbonic acid and ammonium bicarbonate (H$_2$CO$_3$+$\text{(NH}_4\text{)}_2\text{CO}_3$).

For conventional solid-state fusion route, stoichiometric amounts of lithium carbonate (Li$_2$CO$_3$), cobalt carbonate (CoCO$_3$) and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) (Alfa Aesar, 99%) were ball milled for 12 h. and the resultant powder was collected in a crucible. The powder was initially heated at 300 °C for 8 h. to eliminate the gaseous products and further calcined at 700 °C for 8 h. with an intermittent grinding to avoid particle agglomeration. The final product thus obtained was LiCoPO$_4$. Modified solid-state fusion procedure is quite similar to the aforesaid one, which involves the addition of growth inhibiting modifiers {either H$_2$CO$_3$ alone, or a solution of H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$} to cover or impregnate the solid precursor mixture in the crucible with the inhibitor solution. The content was sonicated for 30 min. to ensure the percolation of growth inhibitor solution throughout the precursor mixture. In other words, 30 ml of carbonic acid has been added to maintain the precursor mix in wet condition even after sonication and the amount of (NH$_4$)$_2$CO$_3$ used in the experiments was 1.5 g. Higher CO$_3^{2-}$ concentrations (aided by the addition of H$_2$CO$_3$ or H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ mix) confine the growth of crystals in one dimension, leading to porous LiCoPO$_4$ nanorods [39]. The escape of CO$_2$ gas and the growth inhibited formation of nanorods aided by the addition of H$_2$CO$_3$ are documented in our previous report [38].
LiCoPO₄ synthesized by different routes (labeled as Samples ‘A1’, ‘B1’ and ‘C1’ which were synthesized in air) was similarly synthesized in an argon atmosphere, with all other conditions unchanged, to produce Samples ‘A2’, ‘B2’ and ‘C2’. Subsequently, samples ‘A2’, ‘B2’ and ‘C2’ were treated further to obtain LiCoPO₄/C composite by the following procedure. The three LiCoPO₄ parent compounds (synthesized in argon atmosphere) were ball milled individually with 10 wt. % super P® carbon for approximately 12 h. The product was furnace heated at 500 °C (2 h.) in argon atmosphere to obtain respective LiCoPO₄/C composites (labeled as Samples ‘A3’, ‘B3’ and ‘C3’).

3.2.5 Electrode preparation and coin cell fabrication

a) LiFePO₄/C: The coin cells were fabricated with the LiFePO₄/C composite cathode, metallic lithium anode and a solution containing 1M LiPF₆ salt dissolved in1:1 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 tons 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.

b) LiCoPO₄/C: The synthesized powder was first mixed intimately with super P carbon black and polyvinylidene fluoride (binder) in 80:10:10 ratio respectively and the mix was treated with N-Methylpyrrolidin-2-one (solvent) to form a slurry. The slurry was cast uniformly on a thin aluminum foil and then dried for about 12 h. at 110°C. The dried foil was hot pressed and the circular electrode was punched out from the coated foil. Using such cathode electrode, 2032 coin cell was assembled in
an Argon-filled glove box and crimp sealed prior to characterization studies. Charge-Discharge study was carried out on such type of 2032 coin cell consisting of lithium anode, synthesized cathodes and a non-aqueous electrolyte containing 1M LiPF$_6$ dissolved in 1:1 v/v EC: DEC with a celgard separator.

3.2.6 Physical and electrochemical characterization: The LiMPO$_4$/C (M=Fe, Co) thus obtained were systematically characterized for their physical and electrochemical properties. X-ray powder diffraction pattern of synthesized compounds was recorded on a PANalytical X’pert PRO X-ray diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10–70° and at a scan rate of 3° per minute. Amount of carbon content in the final product was calculated using thermogravimetry analysis (TG) with a thermo balance model STA 409 PC in the temperature range 25–800 °C, using alumina crucibles, under air with a heating rate of 20 °C/min. Conductivity measurements were carried out using an LCR meter (Hioki-3532) in the 100 to 400 °C temperature range and a frequency range of 42 to 1 MHz. Surface morphology of synthesized samples were studied on a scanning electron microscope (JSM 6400, JEOL, Japan). Transmission electron microscopy (TEM) images were collected using a JEOL 2010F TEM operating at 200 keV. Raman spectrum was recorded using a Renishaw InVia Laser Raman Microscope. The oxidation state of elements in LiCoPO$_4$ compound was investigated by X-ray photoelectron spectroscopy (XPS) using an Mg Kα excitation source. Cyclic voltammetry study has been carried out on Autolab and charge-discharge studies were carried out using MACCOR or ARBIN charge-discharge cycle life tester.
3.3 Results and discussion

3.3.1 Surface modified LiFePO$_4$ synthesized by of solid state fusion method

Typical XRD pattern obtained for solid state synthesized LiFePO$_4$/additive (C/M/MO) is displayed in Fig. 3, which shows striking similarity with the standard JCPDS pattern No.: 81-1173, related to pristine LiFePO$_4$. The XRD pattern of LiFePO$_4$ shows the presence of well resolved and highly intense peaks, thus confirming the formation of highly crystalline LiFePO$_4$ without any impurities (Fig. 3a).

![X-ray diffraction pattern and SEM image of LiFePO$_4$/C synthesized using solid state fusion method](image)

Fig. 3 a) X-ray diffraction pattern and b) SEM image of LiFePO$_4$/C synthesized using solid state fusion method

The miller indices (h,k,l) of all the peaks are indexed as per JCPDS file number 81-1173. From search match analysis, the currently synthesized LiFePO$_4$ compound is found to possess orthorhombic structure and Pnma space group with the lattice parameter values of a=10.33, b=5.87, c=4.69. Fig. 3b shows the SEM image of as synthesized LiFePO$_4$ particles, wherein well defined grain boundaries are seen. Herein, it is believed that the presence of unevenly distributed particles of LiFePO$_4$ is due to the deployment of solid state fusion method, which in turn is expected to reflect adversely on electrochemical behavior.
Fig. 4 corresponds to the differential capacity vs. voltage plot of LiFePO$_4$/C composite cathode, recorded between 3.0-4.0V vs. Li/Li$^+$ at a current rate of 0.1C. Presence of an anodic peak at 3.39V and a corresponding cathodic peak at 3.46V signifies the presence of Fe$^{2+}$/Fe$^{3+}$ red-ox couple and hence confirms the typical two phase reaction between LiFePO$_4$ and FePO$_4$.

![Graphs](image)

**Fig. 4** Differential capacity vs. voltage plot and cycling behavior of (a & b) carbon, (c&d) Cu and (e &f) CuO modified LiFePO$_4$ cathode

The difference between anodic and cathodic peak potential is found to be ~0.07 V (Fig. 4a), thus demonstrating the lower polarization and excellent cycling reversibility of LiFePO$_4$/C composite cathode. Similarly, Cu and CuO coated LiFePO$_4$ cathode also exhibits anodic and cathodic peaks corresponding to the
presence of Fe$^{2+}$/Fe$^{3+}$ red-ox couple, but the difference between anodic and cathodic peak potentials are comparatively large i.e 0.1 and 0.9 V (Fig. 4c & e) for Cu and CuO coated LiFePO$_4$ cathodes respectively.

In other words, LiFePO$_4$/C cathode of the present study with 2wt.% carbon exhibits a specific capacity of 100 mAh/g (Fig. 4b) and the same cathode with 2wt.% Cu and CuO coating is found to exhibit a comparatively lesser capacity values of 50 and 45 mAh/g respectively (Fig. 4d & f). Hence, it is believed that the inferior capacity values and the observed large polarization behavior due to the lack of adequate electronic conductivity are surpassed partially in the present study by way of modifying the surface of LiFePO$_4$ with Cu or CuO. Further, it is understood that carbon coating is better than Cu or CuO coating for LiFePO$_4$ to improve the electrochemical properties.

3.3.2 Synergistic effect of carbonate anion directed shape controlled morphology and super P carbon in preparing LiFePO$_4$/C cathode – Modified solid state fusion method

It is well known that nano crystalline LiFePO$_4$/C with controlled morphology would exhibit improved electrochemical performance via. reduction of lithium diffusion path length and the strain associated with the two phase red-ox reaction between LiFePO$_4$ and FePO$_4$ [40]. Among the different morphologies of nanomaterials, one dimensional nano rods [41, 42] provide facile strain relaxation during battery charge and discharge, thus improving the cycleability of nano electrodes [43]. Therefore, identification of suitable synthesis methodology that offers one-dimensional nano rods of LiFePO$_4$/C and the type of carbon that improves the performance of LiFePO$_4$/C nano composite have been targeted through the present study.
Solid state fusion (SSF) method, known for commercial viability has negative influence on the electrochemical performance due to the unavoidable particle growth. The same has been discussed in the previous section also. Hence, exploration of a novel approach, viz. modified solid state fusion method (MSSF), also known as modified mechano thermal method (MMT) [38] to prepare morphology controlled LiFePO$_4$/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 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 [39]. Quite different from such reported attempts, simple addition of carbonic acid (H$_2$CO$_3$) that can liberate CO$_3^{2-}$ anion upon two step decomposition according to equations (1) and (2) has been explored in the present study to facilitate the growth inhibition effect.

$$\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad (1)$$

$$\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (2)$$

It is well known that addition of carbon improves the bulk conductivity of LiFePO$_4$ and impedes the agglomeration of particles significantly [44, 45]. Towards this direction, an optimum amount of (2wt.% ) different types of carbon viz. super P carbon, conducting and nickel coated graphite were added individually to form LiFePO$_4$/C composite cathode using MSSF synthesis approach.

**Synthesis method vs. Morphology-SEM study:**

Fig. 1(a &b) shows the FESEM images of LiFePO$_4$/C synthesized by SSF and MSSF methods, wherein a wide range of unevenly distributed particles (Fig. 5a) of 500 nm are obtained from SSF method. On the other hand, homogenous distribution
of nano rods of 200 nm size (Fig.5b) results from MSSF method, due to the increased concentration of \( \text{CO}_3^{2-} \) anion.

**Fig. 5** Schematic representation and FESEM images of LiFePO\(_4\)/C synthesized by (a) SSF method and (b) MSSF 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. 5b) that results from the unidirectional escape of \( \text{CO}_2 \) gas (as shown in Fig. 5) at high temperature. Formation of thin layer of carbon coating over the surface of LiFePO\(_4\) particles results from the addition of different types of carbon, viz., Super P, Conducting and Nickel coated graphite, thus avoids the agglomeration of rods even at 700 °C. Hence, the growth controlled nano rod formation of LiFePO\(_4\)/C may be attributed to the \( \text{CO}_3^{2-} \) inhibition effect and the carbon wiring effect.

**Phase characterization –XRD studies:** Powder X-ray diffraction (PXRD) pattern was recorded to confirm the phase pure formation of crystalline LiFePO\(_4\)/C compound (Fig. 6) synthesized via. MMT method containing 2 wt.% of different
types of carbon, viz. (a) Super P, (b) Conducting and (c) Nickel coated graphite. Absence of undesirable Fe(III) related impurity peaks confirms the formation of single phase LiFePO₄. LiFePO₄/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 LiFePO₄/C compound. However, the added carbons have no negative influence on the crystal structure of LiFePO₄. All the bragg peaks can be indexed to a pure and well crystallized LiFePO₄ 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 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 behavior.

![XRD pattern of LiFePO₄/C composite material synthesized by MSSF containing a) Super P carbon, b) Conducting graphite and c) Ni coated graphite](image)

**Fig. 6** XRD pattern of LiFePO₄/C composite material synthesized by MSSF containing a) Super P carbon, b) Conducting graphite and c) Ni coated graphite
Surface coating –TEM analysis: The presence of nano crystalline LiFePO$_4$/C composite with carbon coating is confirmed from TEM images (Fig. 7). TEM evidences the formation of uniform layer of carbon coating over native LiFePO$_4$ particle. The wiring effect of carbon in connecting the interfaces between LiFePO$_4$ particles [46] 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 [47] has been obtained, which is attributed to the significance of MSSF synthesis methodology.

![Fig. 7 Schematic representation of one-dimentional nano rod formation and the typical TEM images of LiFePO$_4$/C synthesized by MSSF method](image)

Electrochemical behaviour: Electrochemical performance of LiFePO$_4$/C composite cathodes containing three different types of carbon was carried out on 2032 coin cells individually. Fig. 8(i) depicts the voltage vs. capacity behavior of MSSF synthesized LiFePO$_4$/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 Li$^+$ extraction and insertion reaction between LiFePO$_4$ and FePO$_4$. Among the three composite cathodes, cells containing LiFePO$_4$/super P
carbon exhibits higher discharge capacity (160 mAh/g) value, compared with those of conducting (b) and nickel coated graphitic (c) carbons.

The cycling behavior of LiFePO$_4$/C cathodes at C/20 rate is furnished in Fig. 8(ii). An initial discharge capacity of 160, 129 and 100 mAh/g has been exhibited by LiFePO$_4$/C cathode with super P carbon (a), conductive graphite (b) and Ni coated graphite (c) respectively. Interestingly, LiFePO$_4$/super P composite cathode (a) delivered a capacity as high as 160 mAh/g (almost close to theoretical capacity of 169 mAh/g) with an excellent capacity retention (95%) and a negligible capacity fade (5%) up to 50 cycles.

![Electrochemical behavior of MSSF synthesized LiFePO$_4$/C cathodes](image)

**Fig. 8** Electrochemical behavior of MSSF synthesized LiFePO$_4$/C cathodes: i) Voltage vs. Capacity ii) Discharge Capacity vs. Cycle number and iii) Rate capability behavior of LiFePO$_4$/super P composite cathode

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Such an improved electrochemical behavior of LiFePO₄/superP composite cathode has been endorsed to the synergistic effect of nano rods (200 nm) derived from the CO₃²⁻ anion controlled morphology and the uniformly formed thin coating of super P carbon, desired for the effective wiring of LiFePO₄ particles. In order to further investigate upon the high rate performance of LiFePO₄/super P composite cathode, rate capability test was performed at various C-rates. Fig. 8(iii) shows that LiFePO₄/super P composite cathode exhibits a discharge capacity of 160 mAh/g at C/20 rate and slightly reduced capacity values of 152, 146, 135 and 122 mAh/g at higher C-rates such as C/10, C/5, C/2 and 1C respectively. From this, the suitability of MSSF synthesized LiFePO₄/super P composite cathode for high power applications is understood.

To conclude, a simple, an easy-to-adopt and a commercially viable MSSF synthesis route has been demonstrated to prepare morphologically controlled nano rods of LiFePO₄/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 LiFePO₄/C cathode exhibited higher discharge capacity (160 mAh/g). The estimable capacity retention and rate capability behavior of LiFePO₄/super P composite authenticates the synergistic effect of MSSF method and role of super P carbon in preparing the lithium intercalating olivine cathode with an improved electrochemical behavior.

3.3.3 LiFePO₄/C synthesized using solution assisted sol-gel method (Furnace heated and microwave irradiated gel derived LiFePO₄/C, hydrothermally removed Li₃PO₄ impurity)

Although solid state methods are simple to use, they are typically time and energy consuming techniques and often lead to larger particle size, low purity and
relatively poor electrochemical performance. Therefore, solution based methods are gaining importance, as they often result in smaller and more uniform particle size, higher purity, more homogeneous carbon coating and higher electrochemical capacity. Among the variety of solution based synthesis approaches, sol-gel method, known for producing meso/nano structured compounds has been chosen for the present study [48-51]. Sol-gel method, based on solution approach ensures the uniform distribution and an atomic level mixing of reactants and gelling agents. Such an intimate mixing of precursors renders phase pure final product with nano particles, which is the significance of sol-gel method. As a result, the sol-gel synthesized cathode is expected to exhibit enhanced electrochemical performance, due to shorter diffusion distances of the intercalating lithium ions.

![XRD pattern of LiFePO$_4$/C prepared using citric acid assisted sol-gel method](image)

**Fig. 9** XRD pattern of LiFePO$_4$/C prepared using citric acid assisted sol-gel method

XRD pattern of LiFePO$_4$ compound, derived from the furnace heated gel obtained from citric acid assisted sol-gel method is shown in Fig. 9. The miller indices (hkl) of all the peaks corresponding to LiFePO$_4$ are indexed as per the JCPDS
file number 81-1173. From search match analysis, it is deduced that the compound possesses orthorhombic structure with Pnma space group. X-ray diffraction pattern indicates small peaks between 20=20 and 25°, corresponding to Li$_3$PO$_4$ impure phase along with the formation of desired orthorhombic phase. However, XRD peaks corresponding to impurities such as Fe$_2$P and Fe$_2$O$_3$ are not observed. Li$_3$PO$_4$ impurity in LiFePO$_4$ has also been reported by Axmann et al. [52]. They reported the effect of Li stoichiometry on the specific capacity of LiFePO$_4$ and showed that excess amount of Li$_3$PO$_4$ leads to a capacity fade due to the increase in the inactive component in the material. Also, they attributed this fade to the occupation of the Li site by Fe atoms that blocks the diffusion of lithium kinetics.

![Fig. 10](image-url)  

**Fig. 10** Cycling behavior of LiFePO$_4$/C cathode and representative voltammogram (Inset) vs. Li/Li$^+$

Fig. 10 shows the charge/discharge behavior of citric acid assisted sol-gel derived LiFePO$_4$/C cathode at 0.1 C rate. The discharge capacity of Li|electrolyte|LiFePO$_4$/C cell is 108 mAh/g with an excellent capacity retention. Herein, the magnitude of capacity is inferior, which could be corroborated to the co-
existence of impure Li$_3$PO$_4$ phase. The CV of LiFePO$_4$/C cathode consists of anodic and cathodic peaks at 3.65 and 3.25 V respectively (Inset of Fig. 10), corresponding to the one-step reversible de-intercalation and intercalation of lithium ions (LiFePO$_4$/FePO$_4$). As a result, objective of this study becomes the formation of single phase LiFePO$_4$ using solution assisted sol-gel method, wherein segregation of Li$_3$PO$_4$ phase from LiFePO$_4$ or formation of LiFePO$_4$ phase without Li$_3$PO$_4$ is the prime concern to realise improved electrochemical behavior.

**Fig. 11** XRD patterns of LiFePO$_4$/C composite synthesized by gelatin assisted sol-gel method

Therefore, in yet another attempt to prepare single phase LiFePO$_4$, novel gelling agent i.e., gelatin to assist the sol-gel method has been tried with acetate and nitrate precursors. However, XRD pattern of gelatin assisted sol-gel derived LiFePO$_4$/C compound evidences the co-existence of impure Li$_3$PO$_4$ phase, irrespective of the
usage of different type of lithium source (in the form of lithium nitrate or lithium acetate) (Fig. 11), because formation of Li$_3$PO$_4$ is thermodynamically more feasible than LiFePO$_4$ phase. Simultaneously, the gel obtained from gelatin assisted sol-gel method has been treated in a different manner i.e., mode of heating has been changed from normal furnace heating to microwave irradiation, but the co-existence of Li$_3$PO$_4$ phase along with orthorhombic LiFePO$_4$/C phase (Fig. 12) could not be avoided.

![Fig. 12 XRD patterns of LiFePO$_4$/C composite synthesized by sol-gel (furnace heated) and microwave assisted sol-gel methods](image)

Interestingly, the charge/discharge behavior of LiFePO$_4$/C derived from the gel irradiated with microwave was found to be better than the one obtained from furnace heating (Fig. 13a). Such an improved electrochemical behaviour is believed to be due to the formation of nanoparticles with (resulting from microwave irradiation)
continuous carbon coating over the LiFePO₄ particles. However, XRD clearly reveals that removal of Li₃PO₄ impurity needs to be attended to obtain phase pure LiFePO₄, (corresponding to any type of solution assisted synthesis method) and hence the same has been investigated further by following different approaches.

Fig. 13 Cycling behaviour and representative cyclic voltammogram (inset) of LiFePO₄/C cathode produced by sol-gel and microwave assisted sol-gel methods

**Removal of Li₃PO₄ phase using water:** The solubility of Li₃PO₄ in neutral water is about 0.03 g/L and the complete removal of Li₃PO₄ impurities from the active material will require huge amount of water. So, washing with water is not a practical
solution to remove Li\textsubscript{3}PO\textsubscript{4} for a lab scale or large-scale process. As an alternative, acidic solution will definitely remove Li\textsubscript{3}PO\textsubscript{4} but it will also dissolve the LiFePO\textsubscript{4} base material [52]. With this background, two different approaches were adopted to dissolve Li\textsubscript{3}PO\textsubscript{4} without affecting the desired LiFePO\textsubscript{4} phase i.e., 1g of LiFePO\textsubscript{4}/C containing Li\textsubscript{3}PO\textsubscript{4} was treated with 100 ml of water (pH-5.5 ~ 6) and kept for stirring with heating at 80 °C for 36 h. Alternatively, 1g of same sample in 100 ml water was transferred to a hydrothermal set up and heated to 200 °C for 8h. to (possibly) remove Li\textsubscript{3}PO\textsubscript{4} impurity.

**Fig. 14** (a) XRD patterns of LiFePO\textsubscript{4}/C obtained from sol-gel method and LiFePO\textsubscript{4}/C treated further to remove Li\textsubscript{3}PO\textsubscript{4} impurity. (b) cycling behaviour of LiFePO\textsubscript{4}/C with and without Li\textsubscript{3}PO\textsubscript{4} (Inset: representative cyclic voltammogram of LiFePO\textsubscript{4}/C vs. Li/Li\textsuperscript{+})

X-ray pattern confirms that complete removal of Li\textsubscript{3}PO\textsubscript{4} phase from LiFePO\textsubscript{4}/C composite is possible using hydrothermal heating approach, as evident from Fig. 14a. On other hand, sample subjected to heating and stirring is found to
suffer from serious problems, as the said treatment has destroyed the original LiFePO$_4$ phase itself, which may be due to reaction of oxygen/water with LiFePO$_4$ in open atmosphere. Further, the magnitude of specific capacity exhibited by single phase (after removing Li$_3$PO$_4$ hydro-thermally) LiFePO$_4$/C composite cathode (151 mAh/g) is found to be better than the LiFePO$_4$/C composite with the co-existence of Li$_3$PO$_4$ phase (Fig. 14b). Hence, the dependence of discharge capacity values on the phase purity of LiFePO$_4$, as reported by Dahn et al [37], is understood from the present study also. In addition, a progressively consistent discharge behavior of LiFePO$_4$/C composite is observed, which may be correlated to the advantages of gelatin assisted sol-gel synthesis method and the complete removal of impure Li$_3$PO$_4$ phase in producing crystalline and single phase LiFePO$_4$/C particles that reduce the capacity fade upon cycling via improved and facile lithium diffusion kinetics.

3.3.4 A revisit on the phase pure LiFePO$_4$/C composite synthesized using gelatin assisted sol-gel method with an optimum temperature:

In an attempt to understand the effect of synthesis temperature upon phase purity and electrochemical properties of LiFePO$_4$/C composite cathode, the compound has been synthesized at four different temperatures, viz., 400, 500, 600 and 700 °C using gelatin assisted sol-gel method. The XRD pattern recorded for LiFePO$_4$/C synthesized at different temperatures is appended in Fig. 15. The diffraction patterns indicate that the crystal structure is identified to that of orthorhombic phase of LiFePO$_4$ for all the synthesis temperatures (JCPDS File No.: 81-1173). On the other hand, LiFePO$_4$/C synthesized at 400, 500 and 700 °C corresponds to a co-existence of impure Li$_3$PO$_4$ phase along with LiFePO$_4$, as understood from the presence of extra peaks at 20 = 23 and 40°. Interestingly, LiFePO$_4$/C synthesized at 600 °C matches
exactly with the orthorhombic structure, as understood from the striking similarity with JCPDS No: 81-1173.

![XRD pattern of LiFePO₄/C composite synthesized at different temperatures using gelatin assisted sol-gel method](image)

**Fig. 15** XRD pattern of LiFePO₄/C composite synthesized at different temperatures using gelatin assisted sol-gel method

From Fig. 16, presence of nanoparticles with definite grain boundaries is seen for LiFePO₄/C synthesized at 600 °C. Similarly, closely arranged spherical grains of LiFePO₄/C are seen from the TEM images of LiFePO₄/C synthesized at lower temperatures such as 400 and 500 °C. Despite the fact that spherical surface morphology is observed for LiFePO₄/C synthesized at different temperatures, formation of single phase is understood from the XRD pattern recorded for LiFePO₄/C synthesized at temperature a of 600 °C. Hence, the significance of gelatin assisted sol-gel process with an optimum synthesis temperature in controlling the growth and wider distribution of particles via. multistep and controlled rate of heating (2°C/min.) could be understood. The particle size analysis of LiFePO₄/C synthesized
at different temperature clearly evidences the presence of nano crystalline particles with $< 100$ nm size.

**Fig. 16** TEM images of LiFePO$_4$/C composites synthesized at different temperatures using gelatin assisted sol-gel method.

HRTEM images of the composite LiFePO$_4$/C synthesized by gelatin assisted sol-gel method in argon:hydrogen (90:10) atmosphere are furnished in Fig. 17.

**Fig. 17** HRTEM images of uniform coating of carbon on LiFePO$_4$ particles.
The high resolution TEM photographs authenticate the fact that the added 2wt.% super P carbon and the residual carbon derived from precursor as well as from gelling agent are effectively coated as a thin layer on LiFePO$_4$ particles corresponding to a thickness of \(~10 \text{ nm}\). Such an uniform coating of carbon layer (~10 nm) enhances the conductivity drastically by means of connecting the interface between LiFePO$_4$ particles.

Electrochemical studies were carried out on 2032 type coin cells fabricated using synthesized composite electrode as cathode and lithium as anode (reference and counter electrode). The cycling behavior of currently prepared LiFePO$_4$/C cathode at 0.1C rate is described in Fig. 18. The initial discharge capacity of LiFePO$_4$/C with a synthesis temperature ranging from 400 ~ 700 °C is found to be 165, 156, 155 and 140 mAh/g respectively. Especially, LiFePO$_4$/C cathode synthesized at 600 °C delivered an appreciable steady state capacity of 160 mAh/g (almost closer to the theoretical capacity of 169 mAh/g) with an excellent capacity retention, i.e., even after the 50th cycle, only 3% capacity fade has been observed. Other three composite cathodes also exhibited good capacity retention up on extended cycling, but the magnitude of capacity is not encouraging. The high specific capacity and good capacity retention observed with LiFePO$_4$/C composite could be endorsed to the advantageous effect of smaller particle size derived from gelatin assisted sol-gel method and the formation of single phase compound at a relatively lower temperature of 600 °C.

In order to further investigate the performance of LiFePO$_4$/C composite synthesized at 600 °C for its suitability in high rate applications, a systematic rate capability test was performed at various C-rates. Inset of Fig 18 shows that a discharge capacity of 145 mAh/g is observed at C/5 rate and the subsequent C-rate
capacity at C/2, C, 2C, 5C and 10C are found to be 135, 126, 80 and 64 mAh/g respectively. Such a high discharge capacity at high current rates is attributed to the combined effect of morphologically controlled nano particles and the formation of phase pure LiFePO₄ at 600 °C.

![Graph showing discharge capacity versus cycle number for LiFePO₄/C composite cathode synthesized at different temperatures and rate capability behavior of LiFePO₄/C cathode synthesized at 600 °C.]

**Fig. 18** Cycling behaviour of LiFePO₄/C composite cathode synthesized at different temperatures and rate capability behavior of LiFePO₄/C cathode synthesized at 600 °C.

To conclude, solution based gelatin assisted sol-gel synthesis route has been demonstrated to synthesize LiFePO₄/C composite possessing desired and homogeneously distributed spherical morphology with ~200 nm particle size. Among the different synthesis temperatures, the compound synthesized at 600 °C results in the formation of single phase (absence of Li₃PO₄) final product. The same LiFePO₄/C has been found to exhibit specific capacity (160 mAh/g) closer to theoretical capacity and an acceptable rate capability behavior, thus qualifying itself as yet another cathode for rechargeable lithium battery applications. Also, gelatin assisted sol-gel
method with a furnace heating of gel at 600 °C could be considered as a feasible synthesis approach to prepare better performing LiFePO₄/C cathode.

3.3.5 LiCoPO₄/C: Carbonate anion aided growth controlled synthesis of LiCoPO₄/C and its improved electrochemical behavior

The objective of this piece of work is to synthesize electrochemically better performing LiCoPO₄/C composite using a unique and modified solid-state fusion (MSSF) method. Role of growth inhibiting additives and heating atmosphere in forming growth controlled LiCoPO₄/C particles and the advantages co-existing Co₂P phase with LiCoPO₄/C have been studied in detail. Li₂CO₃ as a source of lithium and carbonate anion, (H₂CO₃ or (NH₄)₂CO₃ + H₂CO₃) as growth inhibiting modifier have been used along with chosen precursors in this synthesis. Intrigued by the interesting results obtained for LiFePO₄/C with the added growth inhibiting modifiers, this particular attempt has been made to prepare dimensionally growth controlled LiCoPO₄/C particles, with newer set of modifiers. Preparation of LiFePO₄/C consisting of co-existing Co₂P phase has been aimed by deploying suitable heating atmosphere during furnace treatment. Accordingly, an inert (argon) heating atmosphere has been chosen to trap the carbon within the particles and to facilitate the co-existence of the conductive Co₂P phase in the LiCoPO₄/C. Further, it has been aimed to individually examine the growth inhibiting additive (effect of CO₃²⁻ inhibition) on LiCoPO₄/C nanorod formation. Synergistic effect of synthesis methodology that renders the formation of LiCoPO₄ with desirable Co₂P as second phase, effect of growth inhibiting modifiers in forming nanorods and the encouraging effect of super P carbon (10 wt. %) to improve the electrochemical behavior of the LiCoPO₄/C cathode are investigated in detail.
Structural studies – XRD: The X-ray diffraction (XRD) patterns of the pristine LiCoPO$_4$ powder synthesized via. conventional solid state fusion (SSF) (Sample ‘A1’), modified solid state fusion with the addition of H$_2$CO$_3$ (Sample ‘B1’) and H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ (Sample ‘C1’) in an oxidizing (air) environment are shown in Fig. 19. All the reflections could be indexed on the basis of the ordered olivine structure with an orthorhombic Pnmb space group (ICDD pattern 32-0552). The sharp diffraction peaks illustrate that the obtained product is highly crystalline. The absence of second phases such as Co$_3$O$_4$ or Co$_2$P$_2$O$_7$ in the synthesized LiCoPO$_4$ powder indicates the formation of phase-pure samples [53].

Fig. 19 XRD patterns of the LiCoPO$_4$ synthesized in air and Ar atmosphere using (a) conventional and (b) modified solid state fusion method with the addition of growth inhibiting modifier viz. carbonic acid (H$_2$CO$_3$) and (c) with a mixture of carbonic acid and ammonium carbonate (H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$).
A more detailed analysis of the XRD pattern (in Fig. 19c) reveals the presence of Li$_3$PO$_4$ as a minor phase in Sample ‘C1’. No detectable reflections corresponding to Co$_2$P phase are present in all the synthesized samples (Fig. 19a-c), an indication that the oxidizing environment does not support its formation, a finding substantiated by Wolfenstein et al. [54]. An identical set of samples have been prepared in the argon atmosphere while keeping the other conditions unchanged to obtain Samples ‘A2’, ‘B2’ and ‘C2’.

Fig. 19 (d-f) shows the X-ray diffraction (XRD) patterns of the pristine LiCoPO$_4$ powder (Samples A2, B2 and C2) in Ar atmosphere. The presence of Co$_3$O$_4$ as a second phase together with the major olivine (LiCoPO$_4$) phase is observed in Sample A2 (conventional SSF) (Fig. 19d). The modified SSF method with the addition of H$_2$CO$_3$ produced a single phase (Fig. 19e) olivine structure (ICDD pattern 32-0552). Interestingly, LiCoPO$_4$ compound synthesized with the addition of H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ (Fig. 19f) showed LiCoPO$_4$ peaks along with those for the highly conductive Co$_2$P phase [55]. An increased concentration of CO$_3^{2-}$ anion (through the addition of (NH$_4$)$_2$CO$_3$) has influenced the formation of nanocrystalline LiCoPO$_4$ by co-producing Co$_2$P. Hence, the synergistic effect of CO$_3^{2-}$ ion concentration and the presence of an inert argon atmosphere in producing LiCoPO$_4$ as a major phase with the co-existence of conductive Co$_2$P has been understood.

**Conductivity Studies:** The ionic conductivity (ac) of the conventional (Sample A1, A2) and modified solid state fusion synthesized LiCoPO$_4$ (Samples B1, B2 and C1, C2) synthesized in air and argon atmospheres has been investigated in the temperature range 30 – 400 °C (Figs 20). The ionic conduction in the LiCoPO$_4$ cathode is due to movement of ions by hopping mechanism between the allowed sites. Irrespective of the synthesis conditions, for all samples, conductivity at low frequencies is frequency-
independent (characterized by a plateau in the curve), while at higher frequencies, a dispersion region is observed in the conductivity plot. The former and latter behaviour correspond to the DC and AC conductivity of the bulk LiCoPO$_4$ respectively. Extrapolation of the plateau to the $Y$-axis gives the DC conductivity [56]; values obtained at 100 and 400 °C are given in Table 1. At a higher temperature (400 °C), a two-fold increase in conductivity has been observed in all the LiCoPO$_4$ samples (Figs. 20) relative to that the values observed at lower temperature.

**Fig. 20** Conductivity studies of the LiCoPO$_4$ synthesized in air and Ar atmosphere using (a) conventional and (b) modified solid state fusion method with the addition of growth inhibiting modifier carbonic acid (H$_2$CO$_3$) and (c) with a mixture of carbonic acid and ammonium carbonate (H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$).

The highest conductivity was exhibited by LiCoPO$_4$ obtained in the presence of H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ and heat treated under argon atmosphere. This sample, which according to XRD analysis contained highly conducting Co$_2$P, showed an increase in conductivity from the order of $10^{-8}$ at 100 °C to $10^{-6}$ S/cm at 400 °C. Based on these results, it is understood that LiCoPO$_4$ sample synthesised in the presence of H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$ and heat treated under argon atmosphere has properties desirable.
for lithium intercalation behavior. Hence, samples (‘A3’, ‘B3’ and ‘C3’) are chosen for further studies.

**Table 1** Conductivity values of LiCoPO$_4$ compound synthesized using (a) conventional and (b) modified solid state fusion (SSF) method with the addition of growth inhibiting modifier carbonic acid (H$_2$CO$_3$) and (c) with a mixture of carbonic acid and ammonium carbonate (H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$) in air and argon atmospheres.

<table>
<thead>
<tr>
<th>Methodology / Sample</th>
<th>Atm.</th>
<th>Conductivity / ohm$^{-1}$ cm$^{-1}$ at 100 °C</th>
<th>Conductivity / ohm$^{-1}$ cm$^{-1}$ at 400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Conventional SSF / A1</td>
<td>Air</td>
<td>3.9 x 10$^{-9}$</td>
<td>2.0 x 10$^{-7}$</td>
</tr>
<tr>
<td>(b) Modified SSF with the addition of carbonic acid (H$_2$CO$_3$) / B1</td>
<td></td>
<td>9.1 x 10$^{-9}$</td>
<td>5.1 x 10$^{-7}$</td>
</tr>
<tr>
<td>(c) Modified SSF with the addition of carbonic acid (H$_2$CO$_3$) and ammonium carbonate (H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$) / C1</td>
<td></td>
<td>8.2 x 10$^{-9}$</td>
<td>3.4 x 10$^{-7}$</td>
</tr>
<tr>
<td>(a) Conventional SSF / A2</td>
<td>Argon</td>
<td>2.6 x 10$^{-9}$</td>
<td>6.8 x 10$^{-7}$</td>
</tr>
<tr>
<td>(b) Modified SSF with the addition of carbonic acid (H$_2$CO$_3$) / B2</td>
<td></td>
<td>4.5 x 10$^{-9}$</td>
<td>1.9 x 10$^{-7}$</td>
</tr>
<tr>
<td>(c) Modified SSF with the addition of carbonic acid (H$_2$CO$_3$) and ammonium carbonate (H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$) / C2</td>
<td></td>
<td>4.9 x 10$^{-8}$</td>
<td>6.3 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

**Microscopy & Spectroscopy Studies: SEM, TEM, Raman and XPS:** Fig. 5 shows the scanning electron microscopy (SEM) images of the LiCoPO$_4$/C nanocomposites prepared as described above in an argon atmosphere (Samples ‘A3’, ‘B3’ and ‘C3’). The presence of agglomerated LiCoPO$_4$ particles with spherical shapes is evidenced from the SEM images (Fig. 5a) of conventionally-synthesized (i.e., no modifier) sample (Sample ‘A3’). On the other hand, needle and rod-like morphologies are
observed (Fig. 5b-c) for samples synthesized by modified SSF (Samples ‘B3’ and ‘C3’).

The morphological transformation, from spherical to rod, implies that the crystal growth has been controlled to one dimension, when carbonate anions are present. A higher concentration of carbonate anions (Sample ‘C3’) led to the rod like morphology (Fig. 21c) The appearance of shiny particles in all images (Fig. 21a-c) corresponds to the presence of added super P® carbon in LiCoPO₄/C composite, which is in agreement with the expected behavior.

Fig. 21 SEM images of LiCoPO₄/C synthesized under argon atmosphere using (a) conventional (b) modified solid state fusion method with the addition of growth inhibiting H₂CO₃ modifier and (c) with a mixture of H₂CO₃+(NH₄)₂CO₃.
Fig. 22 TEM images of LiCoPO$_4$/C synthesized under argon atmosphere using (a) conventional (b) modified solid state fusion method with the addition of growth inhibiting H$_2$CO$_3$ modifier and (c) with a mixture of H$_2$CO$_3$+(NH$_4$)$_2$CO$_3$.

Transmission electron microscopy (TEM) images recorded for LiCoPO$_4$/C composites (Samples ‘A3’, ‘B3’ and ‘C3’) synthesized in argon atmosphere are shown in Fig. 22. Presence of nanocrystalline LiCoPO$_4$/C composite with an adherent carbon coating is evident from Fig. 22 (a-c). A change in morphology evidenced from the TEM images substantiates the SEM results. A thick layer of carbon coating seen in the TEM images illustrates the encapsulation of LiCoPO$_4$ particles by carbon layer. A continuous carbon coating on the surface of native LiCoPO$_4$ particles suggests the chosen synthetic conditions are optimum to form nanocomposites. The presence of carbon network interconnects the individual particles of LiCoPO$_4$, leading to carbon
wiring that enhances the electrochemical behavior of the synthesized LiCoPO₄/C composite cathodes.

It is well known that the electrochemical performance of any composite electrode depends upon the type and nature of carbon involved and hence Raman spectroscopy has been used to investigate the nature of super P® carbon used in this study.

![Raman spectroscopy graph](image)

**Fig. 23** Raman spectroscopy of LiCoPO₄/C (sample ‘B3’) composite with added super P® carbon as a carbon source

In this regard, LiCoPO₄/C (Sample ‘B3’) powder, obtained from the addition of H₂CO₃ and heat treated in argon atmosphere (which has been demonstrated to form a single phase compound, as indicated by XRD, Fig. 19b) has been chosen as a typical compound for Raman spectroscopy studies. The recorded spectrum (Fig. 23) shows two broad bands around 1598 (G-band) and 1332 cm⁻¹ (D-band), characteristic of ordered graphitic and amorphous carbon respectively [57, 58]. The ratio of the calculated peak intensities (I_D/I_G) demonstrates that amorphous carbon is dominant, which could favor lithium intercalation.
The sample ‘B3’ was further characterized by X-ray photoelectron spectroscopy (XPS) to confirm the oxidation state of the individual elements present in the compound (Fig. 24). Herein, peaks corresponding to those of Li (1s), Co (2p3/2), P (2p3/2) and O (1s) in the LiCoPO₄ cathode observed at the respective binding energy values correspond well with the reported values [59, 60]. Particularly, the Li (1s) spectrum consists of a peak at 55.8 eV that confirms the oxidation state of Li as +1 and the best fit for the Co 2p3/2 spectrum gives a binding energy value of 780.7 eV, which is consistent with the value reported to those for Co²⁺ ions by Tan et al. [59]. The XPS spectra for the P (2p) peak located at 134.1 eV is assigned to the P⁵⁺ related compounds [60]. The O (1s) XPS spectrum has a well defined peak at 531.0 eV, evidencing the presence of -2 oxidation state of O element in LiCoPO₄.

**Fig. 24** XPS spectra of Co (2p3/2), P (2p3/2) and O (1s) in LiCoPO₄/C (sample ‘B3’) compound.

**Electrochemical Studies: Charge-discharge and Rate capability tests**

Fig. 25a shows the typical galvanostatic charge-discharge profile of a lithium coin cell consisting of LiCoPO₄/C nanocomposite cathode coupled with a metallic
lithium anode. The cut-off voltages used for discharge and charge cycle are 3.0 and 5.1 V respectively. The cell was charged and discharged at a constant rate of 0.1 C. The charge-discharge characteristics for all the samples are similar in shape, exhibiting a plateau each at about 4.8 and 4.7 V respectively, corresponding to Co\(^{3+}/Co^{2+}\) red-ox couple. The observed small difference of 0.1 V between the charge and discharge plateau illustrates that the electrochemical polarization is small. This could be attributed to the formation of one dimensional and morphological growth controlled LiCoPO\(_4\) nanorods, which facilitate the faster diffusion of lithium ions.

Although the electrochemical characteristics appear to be similar, the discharge capacities are found to be different for the electrode material prepared by the chosen synthetic routes with a small potential drop. The higher charge and discharge capacity of 162 and 123 mAh/g were observed for the sample containing the highest concentration of carbonate anions (Sample ‘C3’). The charge and discharge capacities observed for sample ‘A3’ are found to be only 120 and 64 while those for ‘B3’ are 140 and 106 mAh/g respectively. Thus, the presence of H\(_2\)CO\(_3\)\((NH_4)_2CO_3\) enhances the one dimensional growth and the co-existence of Co\(_2\)P phase that influenced the electrochemical behavior of sample ‘C3’.

Figure 25b shows the initial discharge capacity of the LiCoPO\(_4\)/C (Sample ‘C3’) cathode as 123 mAh/g and the available capacity after 30 cycles is 109 mAh/g, corresponding to excellent capacity retention of 89 %. On the other hand, other LiCoPO\(_4\)/C (Samples ‘A3’ and ‘B3’) cathodes exhibited not only a lower initial capacity (64 and 106 mAh/g) but also some serious capacity fade to the extent of 20 and 13 % respectively after the completion of 30 cycles. The enhanced performance of the Sample ‘C3’ cathode is attributed to the synergistic effects of (a) controlled morphology derived from the modified solid state fusion method with the mixture of
growth inhibitors $\text{H}_2\text{CO}_3 + (\text{NH}_4)_2\text{CO}_3$, (b) co-existence of conductive $\text{Co}_2\text{P}$ phase resulting from argon atmosphere and (c) the carbon wiring resulted from externally added super P® carbon

**Fig. 25** Electrochemical behavior of LiCoPO$_4$/C cathodes (samples ‘A3’, ‘B3’ and ‘C3’) vs. Li/Li$^+$ (a) voltage vs. specific capacity (b) capacity vs. cycling and (c) rate capability behavior

Rate capability of LiCoPO$_4$/C (Samples ‘A3’, ‘B3’ and ‘C3’) cathodes has been investigated under the influence of C/10, C/5, 1C, 2C and 5C discharge rates and the results are given in Fig. 25c. It is evident that appreciable discharge capacity values of 122, 114, 102, 93 and 81 mAh/g have been exhibited by LiCoPO$_4$/C (Sample ‘C3’) cathode at C/10, C/5, 1C, 2C and 5C rates respectively against the lower capacity values of 106, 95, 86, 79 and 66 mAh g$^{-1}$ corresponding to
LiCoPO$_4$/C (Sample ‘B3’) cathode and those of 64, 52, 42, 31 and 21 mAh/g exhibited by LiCoPO$_4$/C (Sample ‘A3’) cathode. It seems that the influence of growth inhibitor H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ (Sample ‘C3’) in the LiCoPO$_4$/C cathode is to improve the electrochemical behavior. The cathode produced by this method is found to be suitable for high rate rechargeable lithium battery applications.

To sum up, simple and an easy-to-adopt modified solid state fusion method has been employed to achieve morphologically controlled growth of LiCoPO$_4$/C nanorods using H$_2$CO$_3$ + (NH$_4$)$_2$CO$_3$ growth modifiers and heat treatment in an inert (argon) atmosphere. The role of CO$_3^{2-}$ ion in controlling the growth of particles to form rod-like morphology is analysed from microscopic images. The presence of an argon atmosphere during furnace heating, especially with an increased concentration of CO$_3^{2-}$ ion, aids the formation of desirable Co$_2$P phase. Addition of super P® carbon (10 wt. %) to the LiCoPO$_4$ cathode resulted in an amorphous carbon coating with an improved electronic conductivity and electrochemical performance. A discharge capacity of 123 mAh/g with excellent capacity retention and good rate capability of LiCoPO$_4$/C cathode up to 5 C rate is attributed to the synergistic effect of controlled growth, co-existence of conductive cobalt phosphide (Co$_2$P) phase and the presence of amorphous carbon coating on LiCoPO$_4$ particles.

Conclusions

a) Conventional solid state fusion (SSF) method is not suitable to prepare electrochemically better performing LiFePO$_4$/C, despite the introduction of surface modifiers such as carbon(super P), metal (Cu) or metal oxide (CuO).
b) A simple, an easy-to-adopt and a commercially viable MSSF synthesis route has been demonstrated to prepare morphologically controlled nano rods of LiFePO₄/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 LiFePO₄/C cathode exhibited higher discharge capacity (160 mAh/g) and acceptable rate capability behavior up to 5C rate condition.

c) The major problem involved in the solution assisted synthesis approach to prepare LiFePO₄ is the co-existence of Li₃PO₄ impurity, whose formation is thermodynamically more feasible. Such an impure phase could be separated successfully from the desirable LiFePO₄ phase by way of fine tuning the reaction conditions and synthesis parameters. Further, single phase LiFePO₄ could be prepared by adopting an optimized synthesis temperature up on revisit i.e., phase pure LiFePO₄/C nanocomposite has been synthesized using gelatin assisted sol-gel method at a temperature of 600°C and the same has exhibited a steady state capacity of ~162 mAh/g for 50 cycles with negligible capacity fade and an acceptable rate capability behavior up to 10C.

d) Modified solid state fusion method has been employed to achieve morphologically controlled growth of LiCoPO₄/C nanorods consisting of conductive Co₂P phase using H₂CO₃ + (NH₄)₂CO₃ as growth inhibiting modifiers and heat treatment in an inert (argon) atmosphere. A discharge capacity of 123 mAh/g with an excellent capacity retention and good rate capability of up to 5C rate have been demonstrated, which are attributed to the synergistic effect of controlled growth, co-existence of conductive cobalt phosphide (Co₂P) phase and
the presence of amorphous carbon coating on LiCoPO$_4$ particles.

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List of Publications – CHAPTER 3


Manuscript under Preparation – CHAPTER 3

- Synthesis of phase pure LiFePO$_4$/C composite using gelatin assisted sol-gel method,