

# STRUCTURAL AND ELECTROCHEMICAL PERFORMANCE OF CITRIC ACID CARBON COATED ASSISTED LITHIUM IRON PHOSPHATE/GRAPHENE OXIDE CELL FOR LITHIUM ION BATTERY APPLICATIONS

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**Abstract-** To investigate and enhance the efficiency of the LiFePO<sub>4</sub>/C sample with graphene oxide anode in the form of pouch type cell. XRD measurement has been performed for LiFePO<sub>4</sub>/C sample to analyse the structure of the sample. Surface of the LiFePO<sub>4</sub>/C sample shows with mono-dispersed particles which helps to progress the performance of the LiFePO<sub>4</sub>/C sample. The average particles size of the sample is 3.5 μm, which has been confirmed by particle size analyser. Impedance and charge/discharge analysis were performed for LiFePO<sub>4</sub>/C/graphene oxide full cell. LiFePO<sub>4</sub>/C/graphene oxide sample exhibits the high initial discharge capacity of 121 mAh/g with capacity retention of 84 % after 100 charge/discharge cycles. Lithium iron phosphate cathode and graphene oxide anode serves as a good cathode and anode material for Lithium ion battery applications.

**Keywords-** LiFePO<sub>4</sub>/C, Graphene oxide, Full cell, Lithium ion batteries.

## 1. INTRODUCTION

Lithium ion batteries are the most promising candidates in the applications of electric and hybrid vehicles and also it possesses major part in the reduction of greenhouse gas emissions [1]. LiFePO<sub>4</sub> is an olivine-type phosphate material which is acting as a good cathode material in rechargeable lithium ion batteries. LiFePO<sub>4</sub> has many advantages such as low cost, environmental friendliness and high thermal stability. Moreover, LiFePO<sub>4</sub> cathode material exhibit a high theoretical capacity (170 mAh/g) and having the flat discharge voltage at 3.4 V against lithium [2-4]. Eventhough, if the current density increased, then the LiFePO<sub>4</sub> may be concerned with capacity loss owing to diffusion-controlled kinetics of the electrochemical mechanism. Two methods are playing an important role

to reduce the poor conductivity problem; one is that to moderate the grain size in which reduce the diffusion path distance for electrons and Li<sup>+</sup> ions. In the second case, the coating of carbon with LiFePO<sub>4</sub> cathode particles [5-7] or some other dopants [8]. Coating with carbon particles can work as interaction bridges and nucleation sites for the production of LiFePO<sub>4</sub> [9]. By covering the surface of LiFePO<sub>4</sub> particles with carbon has been used to refine the electrochemical efficiency of LiFePO<sub>4</sub> [10]. High temperature sintering for a protracted period is vital strategy to achieve the high conductive carbon. At high temperature, no surviving hydroxyl or carbonyl is present on the surface of the carbon and also there is no chemical bonds on surface like oxygen bridge bonds between carbon and LiFePO<sub>4</sub> [11]. Controlling the size of the carbon treated LiFePO<sub>4</sub> is beneficial factor in the electrochemical performance. Consequently, when including the high surface area carbon reduces the tap density and the energy density [12-14]. There are several carbon additives are used such as glucose [15], ethylene glycol [16], ascorbic acid [17,18] etc., to improve the LiFePO<sub>4</sub> cathode material behaviour. Among them, citric acid was employed for producing high efficiency cathode material because of low cost. Different synthesis techniques are available for preparing LiFePO<sub>4</sub> including solid-state reactions and solution methods [19-23]. Solid state method is an easy preparation method with low cost and high yield. Zhouguang Lu et al [24] have developed citric acid and ammonium assisted olivine LiFePO<sub>4</sub> particles and they accomplished a proficient surface morphology. Moreover, commercially used anode material for lithium ion batteries is graphite owing to its structural stability when cycling and flat potential profile. In spite of good electrochemical performance of graphite it exhibits a small capacity of 372 mAh/g [25]. However, graphene exhibits the high capacity which is

double times higher than the capacity of graphite. Consequently, graphene based anodes holds the capability to replace graphite anodes [26]. Many researchers were developed their work in chemically modified graphene like graphene oxide (GO), reduced graphene oxide (rGO) both anode and cathode [27]. But few researchers are reported their work in full cell lithium ion batteries. In our present work, we have examined the performance of citric acid coated lithium iron phosphate (LFP/C) cathode material with commercial graphene oxide (GO) serves as an anode material for full cell lithium ion battery applications.

## 2. EXPERIMENTAL TECHNIQUES

### 2.1. MATERIAL PREPARATION

Carbon coated Lithium iron phosphate was synthesized by using conventional solid state method. Stoichiometric amounts of  $\text{LiCO}_3$ ,  $\text{FePO}_4$  and citric acid (10%) were well grounded for 1 hour by using a mortar and pestle. The obtained powder was pressed into pellet and heated by two steps sintering process in tubular furnace (air atmosphere). Pre-sintering and final sintering were performed at  $450^\circ\text{C}/5\text{h}$  and  $850^\circ\text{C}/12$  hours. The obtained LFP/C was grounded well.

**2.2. CHARACTERISATION DETAILS** For structural analysis, XRD (XPRT-PRO) studies were carried out for  $\text{LiFePO}_4/\text{C}$ . The morphology of the synthesized sample was evaluated by using JSM-6390 (SEM). FTIR was taken to investigate the functional groups of the prepared samples. To investigate the particle size of the sample particle size analyser (SALD-2300) was used.

### 2.3. ELECTROCHEMICAL CHARACTERISATION

To prepare GO and LFP/C electrodes 80% Active material, 10% PVDF and 10% carbon black were grounded well then few drops of N-methyl pyrrole done was added to make a slurry. Cathode material (LFP/C) was coated onto a aluminium foil and anode material (GO) was coated onto a copper foil. Both the electrodes were dried under vacuum atmosphere at  $80^\circ\text{C}$  for 12 hours. The electrolyte was 1M Lithium perchlorate in EC:DMC (1:1). A pouch cell was assembled with the above mentioned cathode and anode. The above mentioned electrolyte was injected into the pouch cell when placed inside an argon filled glove box. The full battery was cycled between 0.1 to 1.4 V range in battery cyler (Biologic BCS-815)

## 3. RESULTS AND DISCUSSION

### 3.1 STRUCTURAL ANALYSIS

To investigate the crystal structure of the LFP/C sample, the XRD analysis was performed. The XRD pattern LFP/C was illustrated in figure 1. LFP belongs to orthorhombic olivine structure with Pnma space group. Sharp peaks perceived from the XRD pattern shows the crystalline nature of the sample. All the peaks are well matched with the JCPDS card number (81-1173) and previous reported data[28]. Absence of carbon related peaks indicated that the carbon presented in amorphous nature. The grain size of LFP/C sample is 54 nm calculated by using Scherrer's formula.

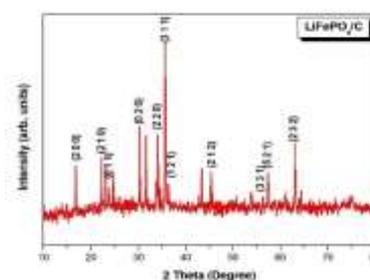
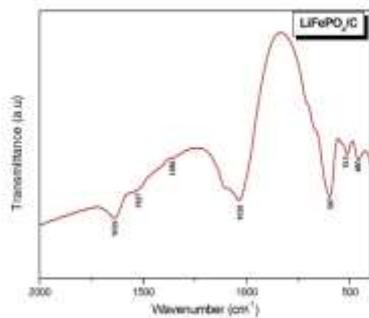


Fig. 1 XRD pattern of LFP/C.

### 3.2.FTIR ANALYSIS

The external information about pure  $\text{LiFePO}_4$ , Adipic and Citric acid coated  $\text{LiFePO}_4$  can be attained from FTIR spectroscopy. Vibrational modes are dependent on the point group symmetry of the cations in the oxygen host matrix. Generally, vibrational modes comes from motion of cation with respect to their oxygen neighbours [29]. Figure 2 shows FTIR spectra of LFP/C. The absorbance band in  $1035\text{ cm}^{-1}$  is the evidence for intra molecular stretching motion of phosphate anions [30]. The bands at 460 and  $513\text{ cm}^{-1}$  can be attributed to vibrations of P-O bonds. The band at  $597\text{ cm}^{-1}$  can be assigned to vibration mode of atomic P-O bonds[31]. All absorbance bands existence in the region of  $1400\text{-}1700\text{ cm}^{-1}$  shows the vibration of olivine  $\text{LiFePO}_4$ . Weak peaks observed in the  $1400\text{-}1600\text{ cm}^{-1}$  region is the

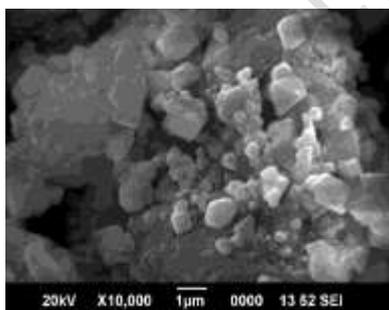
evidence for absorbance of residual carbon[32].



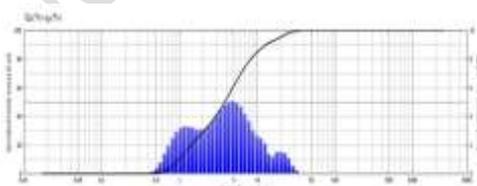
**Fig. 2 FTIR analysis of LFP/C.**

### 3.3 SURFACE MORPHOLOGY

The microsphere particles are arranged on the surface of LFP/C sample with homogenous morphology. The SEM image of LFP/C is shown in figure 3 (a). The average particle size of the sample is 3.5 $\mu\text{m}$  which is shown in figure 3 (b) which has been also confirmed by using particle size analyser. The grain size of the sample is 54 nm which is obtained from the XRD analysis. The average particle size of the sample is greater than the grain size of the sample which clearly designates the polycrystalline nature of the sample. Moreover, particles of LFP/C sample showed with sufficient space for moving charge carriers which is the evidence for better performance of LFP/C sample.



**Fig. 3 (a) SEM image of LFP/C.**

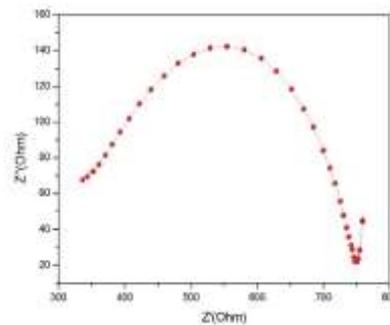


**Fig. 3 (b) Particle size analysis of LFP/C.**

### 3.4.1 IMPEDANCE ANALYSIS

Figure 4 shows the Nyquist plot of LFP/C/ GO full cell. Nyquist plot contains a semicircle and a

straight line present in the low-frequency part. In the middle frequency region the semicircle is assigned to charge transfer resistance ( $R_{ct}$ ). In the low frequency region, the straight line represents the Warburg impedance ( $Z_w$ ) which is associated to the diffusion of lithium ions. In the Nyquist plot, the depressed semicircle in the high frequency region attributed to lower resistance of LFP/C/GO full cell.



**Fig. 4 Impedance spectra of LFP/C/GO.**

### 3.4.2. ELECTROCHEMICAL ANALYSIS

The rate performance of LFP/C/GO has shown in figure 5. At the first cycle, the original specific discharge capacity has been attained at 121mAh/gat1 mA current rate which is 70% of its theoretical capacity. The cyclic behaviour of LFP/C/GO full cell is shown in figure 6. At 50<sup>th</sup> cycle it exhibits a excellent cyclic performance of 92% capacity retention calculated from its initial discharge capacity. LFP/C/GO full cell delivers 84 % capacity retention after 100 charge/ discharge cycles. Moreover, Carbon coatings can helps to form more stable solid electrolyte interphase (SEI) also used to avoid the direct interaction between the active material and electrolyte which is explained in schematic diagram 1[33]. The remarkably good discharge capacity, long cycle life indicates that the efficiency of LFP/C/GO full cell. This present study clearly indicates that graphene based anodes with LFP/C cathodes holds the good capability.

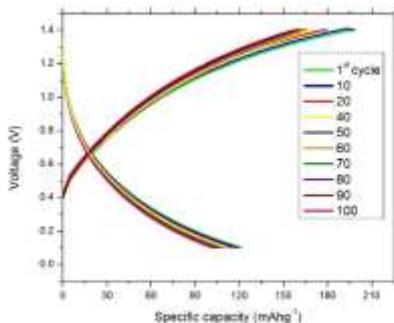


Fig.5 Charge/discharge profile of

LFP/C/GO.

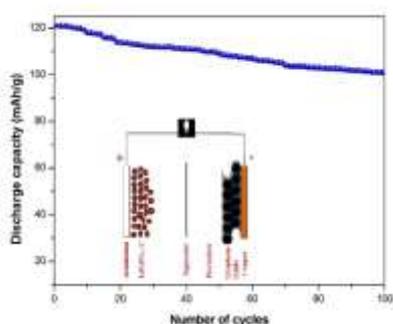
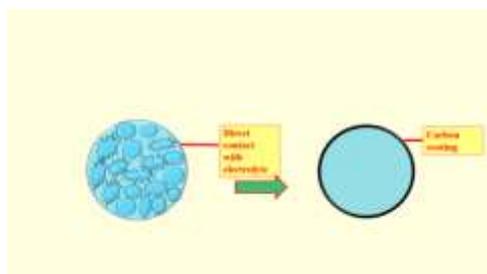


Fig. 6 Cyclic stability of LFP/C/GO.



Schematic diagram 1. Comparison between carbon coated and non-coated samples.

## 5. CONCLUSION

Citric acid coated lithium iron phosphate was successfully synthesized by using conventional solid state method. Full cell lithium ion battery was made by using LFP/C which employed as a cathode material and commercial graphene oxide was serves as a anode material in argon filled glove box. The particle size of LFP/C sample is 3.5  $\mu\text{m}$  which is confirmed from particle size analyser. LFP/C/GO full cell exhibits a initial discharge capacity of 121 mAh/g and displays an excellent cyclic performance of 84% capacity retention after 100 charge/discharge cycles.

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