



# One Pot Synthesis of $Zr^{4+}$ doped Carbon Coated $LiFePO_4$ Cathode Material for Rechargeable Li-ion Battery

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## Authors' contributions

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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## ABSTRACT

$Zr^{4+}$  doped carbon coated  $LiFePO_4$  cathode [ $C-LiZr_xFe_{1-x}PO_4$  (where  $x=0.02$ )] material were synthesized by a one pot solid-state synthetic route for its use in rechargeable lithium-ion battery. The carbon coating over the phosphate material was done using a natural precursor, camphor. The calcinations and sintering temperatures were set at  $450^\circ C$  and  $700^\circ C$ , respectively, which were selected from the TGA-DTA experiment. The synthesized materials were characterized by various spectroscopic techniques, such as; FTIR, Powdered XRD and SEM. Electrochemical studies of the synthesized materials were carried out by cyclic voltametry and charge-discharge behavior after preparing a laboratory model cell against lithium anode. It was found that  $C-LiZr_xFe_{1-x}PO_4$  (where  $x=0.02$ ) material coated with carbon from a natural precursor (camphor) shows better discharge capacity of  $159 \text{ mAhg}^{-1}$  during the first few cycles compare to that of pure  $LiFePO_4$ .

**Keywords:**  $Zr^{4+}$  doped carbon coated  $LiFePO_4$  cathode; camphor precursor; solid-state synthesis; Li-ion battery.

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## 1. INTRODUCTION

Lithium-ion batteries are the most popular [1] storage system for portable electronics devices, because of their high energy-to-weight ratios [2]. It has no memory effect and shows minimum loss of capacity when not in use. Besides consumer electronics, lithium-ion batteries are gaining its popularity in different fields like military applications, electric vehicles, and aerospace applications [1].

In commercial lithium-ion batteries,  $\text{LiCoO}_2$  is used as the cathode material, but cobalt is costly and toxic [3,4]. Therefore, scientists are searching for new cathode materials, which are efficient and cost effective [3,5-10]. A number of new cathode materials were proposed and tested for Li-ion batteries during the recent years [4]. But these materials can hardly be considered as ideal for Li-ion batteries.

During last decade, lithium iron phosphate ( $\text{LiFePO}_4$ ) has been found an attractive alternating cathode material for rechargeable lithium-ion batteries [11-16], due to low cost starting materials, environment friendly, excellent cycling performances, high theoretical capacity ( $170\text{mAhg}^{-1}$ ) and good operating voltage [2,11-14]. But the main drawbacks, with this material, are its poor electronic conductivity and low diffusion coefficient of lithium ions, which lead to its poor rate capability [13,14]. Efforts have been made to increase its conductivity by replacing the active component ( $\text{Fe}^{2+}$ ) with higher valence metal cations, such as,  $\text{Ti}^{4+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Zr}^{4+}$ ,  $\text{W}^{6+}$ ,  $\text{V}^{3+}$  etc. [17-19]. The improvement in electronic conductivity has been achieved by the cost of Faradic capacity. As a result, scientist are looking for the synthesis of nano  $\text{LiFePO}_4$  through different particle size controlled techniques like water-based [20-25], sol-gel [26-29], sonochemical [30,31] solvothermal [16], ionothermal [32] and in-situ carbon coated via solid-state synthetic method [33]. Most of the reported methods are lengthy and cost effective.

In the present study, we report a simple and straight forward solid-state synthetic method for the preparation of  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  cathode material from a natural carbon precursor (camphor). The motivation comes from the fact that pyrolysis of camphor shoots can produce fullerene, glassy carbon, carbon nano tubes, etc [34,35]. Admittedly, our method, for the synthesis of  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$ , is simple and more convenient compared to the sol-gel technique used by Wang et al [17].

## 2. EXPERIMENTAL

### 2.1 Material Synthesis Procedure

The chemicals,  $\text{Li}_2\text{CO}_3$  (Sigma-Aldrich, USA, 99.9%),  $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$  (Sigma-Aldrich, USA, 99.9%),  $(\text{NH}_4)_2\text{HPO}_4$  (Merck, USA, 99%) and  $\text{Zr}(\text{OC}_2\text{H}_5)_4$  (Sigma-Aldrich, USA, 97%) were used as received. A stoichiometric amount of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  were taken in an agate mortar-pestle and ground to make a fine powder. Small amount of acetone (Merck, USA, GR grade) was added to the mixture and ground it to make a homogeneous mixture. The homogeneous mixture was then transferred, once acetone was evaporated, into an alumina boat and calcined at  $450^\circ\text{C}$  for 5 hours inside a tubular furnace under Ar atmosphere. After cooling and grinding, the powder was placed again inside the tubular furnace and sintered at  $700^\circ\text{C}$  for 8 hours in Ar atmosphere. Thus a pure  $\text{LiFePO}_4$  was obtained.

C-LiZr<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub> (where x = 0.02) was obtained, after mixing the stoichiometric amount of the precursor materials following the same procedure as discussed above, but mixing camphor as the carbon source equivalent to 10 wt% of the bulk material.

## 2.2 Thermal Gravimetric Analysis

TGA-DTA (Thermal Gravimetric Analysis and Differential Thermal Analysis) curve was recorded with a thermo balance (Perkin Elmer, Sweden model number STA 6000), in the temperature range of 40°C – 950°C at a heating rate of 20°Cmin<sup>-1</sup> under nitrogen gas flow.

## 2.3 Structural and Morphological Characterization

The materials, as obtained, were characterized by FTIR, powdered XRD and SEM. FTIR spectrum was recorded on FTIR-8400S, Shimadzu (Japan) after grinding the material with KBr powder. Powder X-ray diffraction (XRD) was taken from a Ultima III Rigaku machine using Cu K $\alpha$  ( $\lambda=1.5406$  Å) radiation in the range of  $2\theta = 10^\circ$  - $90^\circ$  with scan rate 5° min<sup>-1</sup>. The particle size and morphology was examined through Scanning Electron Microscope (JEOL, JSM-6360, UK).

## 2.4 Electrochemical Characterization

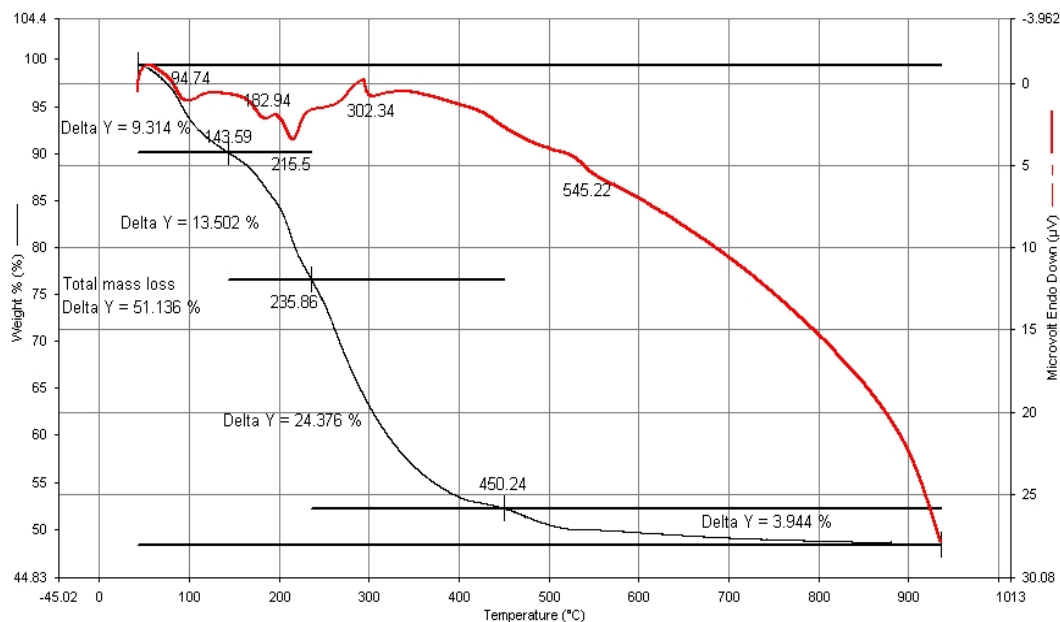
The electrochemical performances of the synthesized materials were carried out after fabricating a laboratory model coin type cell [36,37]. The cathode mixture was obtained by mixing the synthesized material with carbon black (Alfa Aesar, USA, 99.9%), graphite powder (Alfa Aesar, USA, 99.99%) and Polyvinylidene fluoride (PVDF) (Aldrich, USA) in the ration of 80:8:8:4 in presence of N-methyl pyrrolidone (NMP) (Merck, USA, 99.5%) as solvent [20-25]. The carbon black, graphite powder and the PVDF serve as conducting support and binder, respectively. The slurry, as obtained, was then spread over aluminum foil and the solvent, NMP, was removed by heating the foil coated with the slurry at 60°C under vacuum. The coated foil was then pressed using hydraulic press at 8 Tcm<sup>-2</sup> to achieve a better contact between the active material and the current collector [15]. The coated foil was finally heated at 80°C under vacuum for 12 hour to remove NMP completely and thus the positive electrode was ready for cell fabrication [5,11,12].

The cell was assembled inside a glove bag by purging dry argon gas. Li ribbon (Aldrich, USA, 99.9%) was pasted on a nickel foil to be used as an anode. LiPF<sub>6</sub> (Alfa Aesar, 98%), equivalent to one molar, was dissolved in 1:1 ethylene carbonate (EC) (Aldrich, 99.9%) and dimethyl carbonate (DMC) (Aldrich, 99.9%) mixture and used as the electrolyte and a porous polypropylene (PP) film soaked with the electrolyte was used as separator [25-28]. The electrochemical performance of the fabricated coin type cell was studied galvanostatically using a potentiostat/galvanostat, model VersaStat™II (Princeton Applied Research) within the potential window of 2.2 volts to 4.2 volts vs. Li.

## 3. RESULT AND DISCUSSION

Fig. 1 shows the TGA –DTA curve of the precursor materials. It is seen that the major mass loss occurs mainly in three steps. At the beginning 9.3% mass loss occurred in the temperature range of 40°C -143°C due to moisture removal. In the second step, another 13.5% mass loss occurred in the temperature range 143°C-296°C due to decomposition of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and removal of water of crystallization from the Fe (C<sub>2</sub>O<sub>4</sub>).2H<sub>2</sub>O crystal, whose

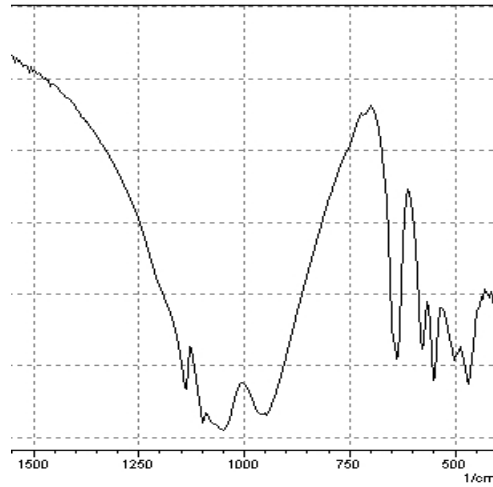
endothermic peak appeared at 215.5°C. Finally, 26.5% mass loss appeared in the temperature range 296°C-550°C due to decomposition of  $\text{Fe}(\text{C}_2\text{O}_4)$  and  $\text{Li}_2\text{CO}_3$ , and their corresponding endothermic peaks are seen at 302.3°C and 545.2°C, respectively. Above 550°C no appreciable mass loss is noted.



**Fig. 1. TGA-DTA of the precursor's mixture for synthesis of  $\text{LiFePO}_4$**

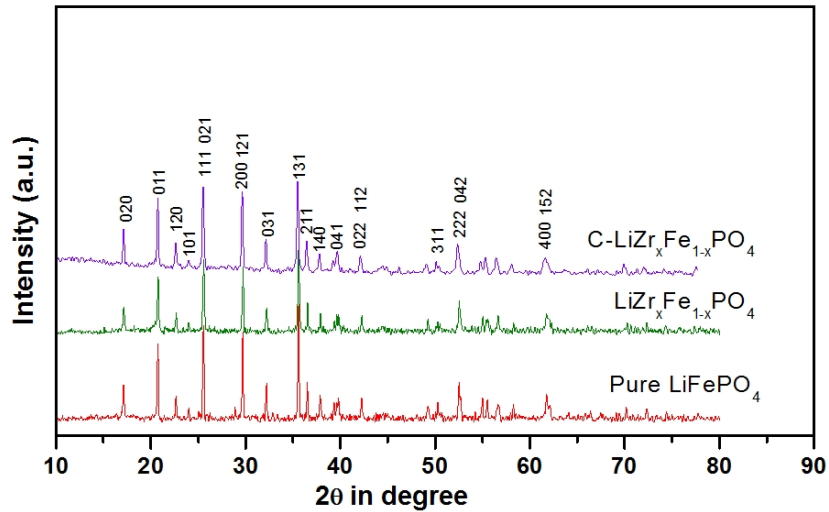
Thus, from the analysis of TGA-DTA curves, the calcinations temperature of the precursor mixture was set at 550°C, because maximum mass loss occurred within this temperature. Further, the sintering temperature was set at 700 °C for the crystalline particle to grow.

The FTIR signature of pure  $\text{LiFePO}_4$  in transmittance mode is shown in Fig. 2. The bands observed in this graph are well matches with the literature report of pure  $\text{LiFePO}_4$  [19,30] without any additional peaks. Thus, a phase pure  $\text{LiFePO}_4$ , using this solid-state method, has been successfully synthesized. No pattern change is observed with the doped sample, since the doping percentage is very small.



**Fig. 2. FTIR spectrum of synthesized pure LiFePO<sub>4</sub>**

The Fig. 3 shows the XRD pattern of C-LiZr<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub>, LiZr<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub> and pure LiFePO<sub>4</sub>.

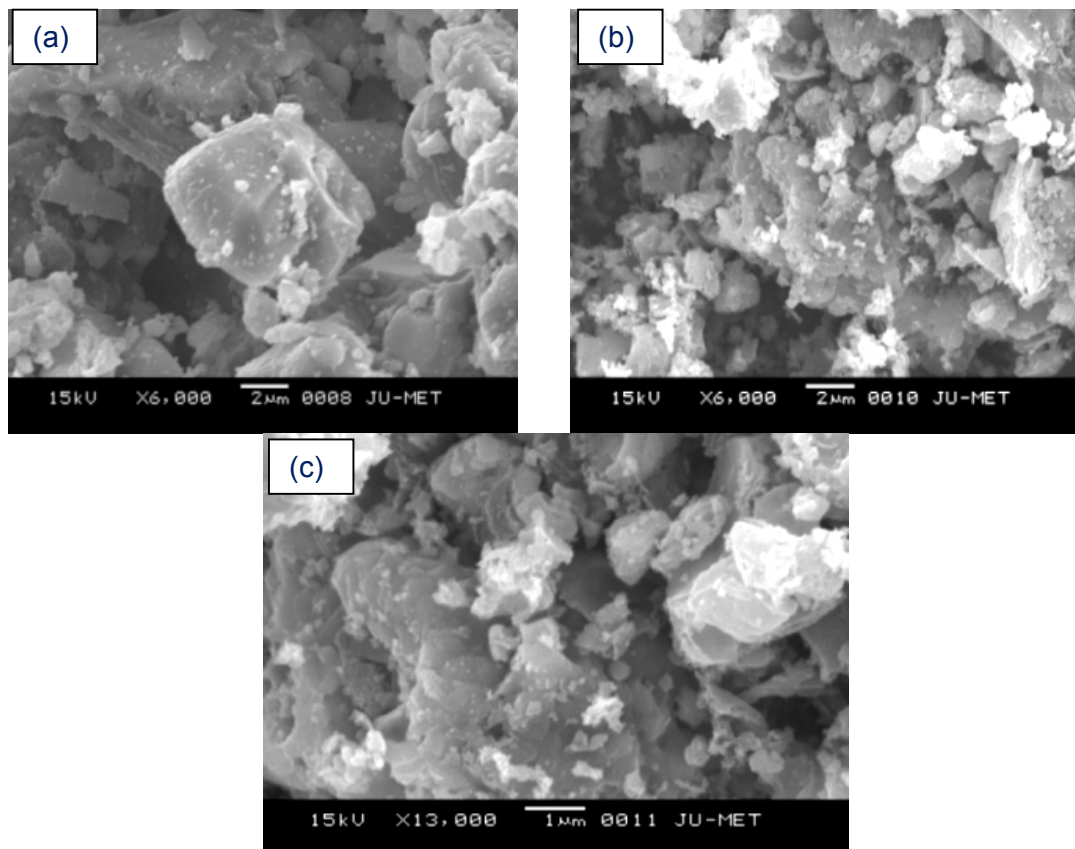


**Fig. 3. Powdered X-ray diffraction of the synthesized materials**

The observed pattern of the synthesized materials was compared with JCPDS data (file no.40-1499) and complete matches of the peak positions were observed. The materials are orthorhombic crystal structure with space group *Pnma*. The values of lattice are nearly close to the reported LiFePO<sub>4</sub> material (*a*=10.3221 Å, *b*=6.0051 Å, and *c*=4.6942Å) [15,38]. It is interesting to note that the XRD peak positions of these materials are exactly matches with the reported materials [17] obtained by sol-gel technique. Secondly, there is no shift in peak position, due to Zr<sup>4+</sup> doping, is observed [17], which indicates the proper doping in the lattice site and the doping concentration is low. However, close scrutiny shows that the XRD peaks obtained in the present study are more or less sharp, whereas XRD peaks of the material prepared by sol-gel technique [17] show peaks broadening, indicating nano material

formation. It is reported that in solid-state synthesis nano material often undergoes agglomeration, due to decaying at high temperature [15].

SEM images of the synthesized materials are shown in Fig. 4. A wide range of particle size distributions are observed in the SEM images. In case of pure  $\text{LiFePO}_4$ , the particle size varies from 200 nm to micron size, but for  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$ , it varies approximately from 100 nm - micron size. The formation of smaller particle, in case of  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  sample, may be due to retardation in crystal growth in presence of carbon and  $\text{Zr}^{4+}$  ion.



**Fig. 4. SEM images of pure  $\text{LiFePO}_4$  (a),  $\text{LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  (b), and  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  (c)**

Cyclic voltamograms, recorded with the prepared cell within the potential window of 2.2 - 4.2 volts vs. Li at a scan rate of  $0.5\ \text{mVs}^{-1}$  are shown in Fig. 5.

The peaks, observed at 3.49 V in the anodic scan and 3.33 V in the cathodic scan, are the characteristics of the removal and insertion of  $\text{Li}^+$  ion from/into the  $\text{LiFePO}_4/\text{FePO}_4$  structure. In case of pure materials the curves are broadening, but it became sharper with carbon coating and  $\text{Zr}^{4+}$  doping, indicating faster  $\text{Li}^+$  ion exchange. On the other hand, there is no change in redox position after doping with  $\text{Zr}^{4+}$  ions, indicating stable nature of the doping ions [17].

The laboratory model galvanic cells made out of the synthesized materials were charged and discharged at different current density. Fig. 6 shows the galvanostatic charge-discharge capacities at the rate of 0.1 C for the different materials.

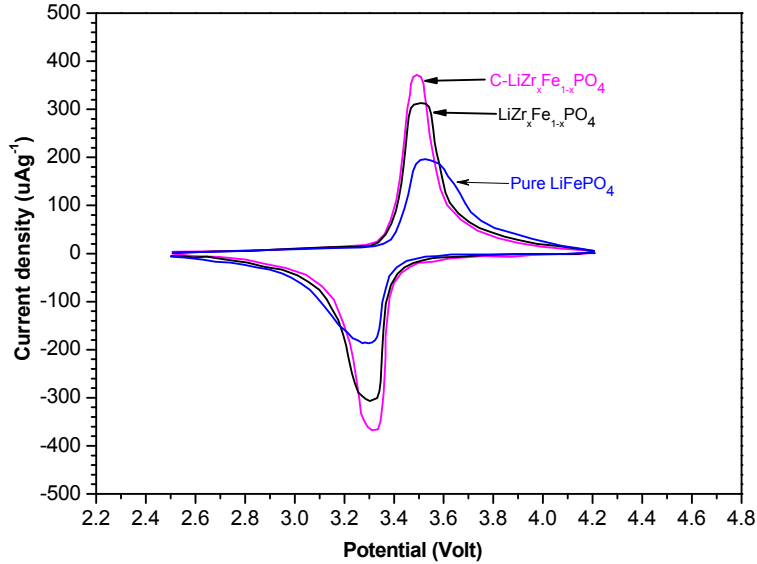


Fig. 5. Cyclic voltamograms of the synthesized materials vs. Li<sup>+</sup>/Li at scan rate of 0.5 mVs<sup>-1</sup>

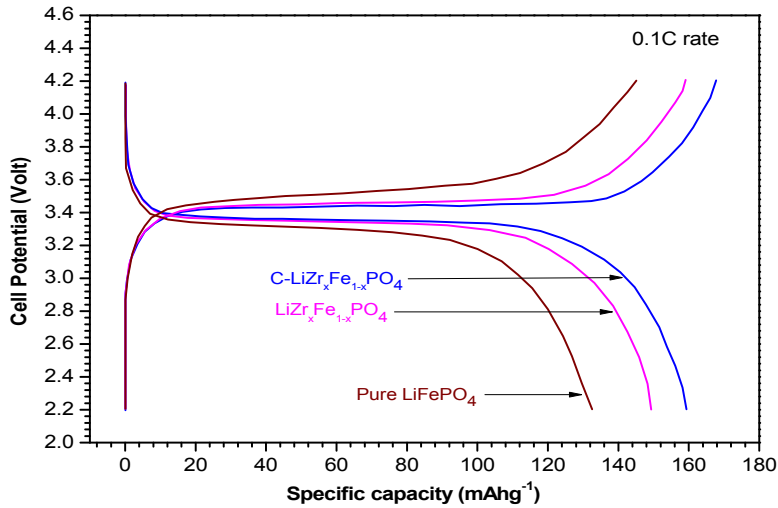
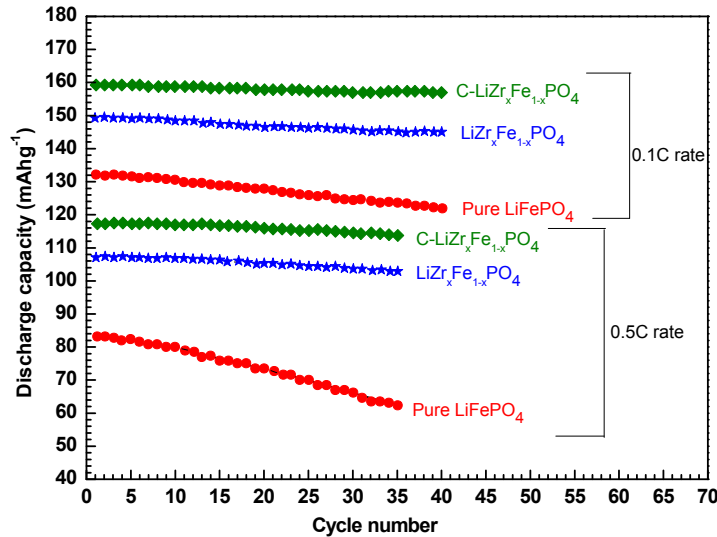


Fig. 6. Galvanostatic charge-discharge curve of the cells at 0.1C rate

The specific capacities of the prepared cells using different LiFePO<sub>4</sub> are found to be different. The C-LiZr<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub> shows higher specific capacity (159 mAhg<sup>-1</sup>) than LiZr<sub>x</sub>Fe<sub>1-x</sub>PO<sub>4</sub>.

$x\text{PO}_4$  and pure  $\text{LiFePO}_4$ . The capacities, observed for the  $\text{LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  and pure  $\text{LiFePO}_4$ , are  $149 \text{ mAhg}^{-1}$  and  $132 \text{ mAhg}^{-1}$ , respectively.

The same galvanic cells, fabricated out of the different synthesized materials, were charged-discharged about 40 cycles at 0.1 C rate and 35 cycles at 0.5 C rates and Fig. 7 presents the retention of capacity of each material with number of cycles.



**Fig. 7. Discharge capacities of different types of  $\text{LiFePO}_4$  cathodes at 0.1C and 0.5C rates**

The capacity fading is very high in case of pure  $\text{LiFePO}_4$  and it is very low with the material  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$ . This material does not undergo remarkable capacity fading up to 40 cycles.

#### 4. CONCLUSION

We demonstrated one pot (step) solid-state synthesis of  $\text{Zr}^{4+}$  doped carbon coated  $\text{LiFePO}_4$  [ $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  (where  $x=0.02$ )] cathode material using camphor as carbon source for its use in lithium-ion battery, which shows a good charge-discharge behavior indicating better  $\text{Li}^+$  exchange onto cathode material. The capacity is increased predominantly for  $\text{Zr}^{4+}$  ion doping which is further enhanced due to carbon coating. The capacity loss upon cycling is higher in case of pure material and this loss increases with increasing discharge rate. On the other hand,  $\text{C-LiZr}_x\text{Fe}_{1-x}\text{PO}_4$  retains its capacity with cycling at the higher discharge rate also.

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## COMPETING INTERESTS

Authors declare that there are no competing interests.

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