

A novel approach to exploit LiFePO_4 compound as an ambient temperature high capacity anode material for rechargeable lithium batteries

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Abstract

An ever first attempt has been made to investigate the possible anode performance characteristics of LiFePO_4 , popularly known so far as an environmentally compatible and economically viable lithium battery cathode material. The compound LiFePO_4 has been synthesized via solid state method and explored for the first time as an anode material against lithium metal through the present study. Surprisingly, an initial capacity of ~ 620 mAh/g has been exhibited by LiFePO_4 anode, which is about 4–5 times higher than the capacity of the corresponding LiFePO_4 cathodes. Also an excellent coulombic efficiency value of 99% has been shown by the compound, especially upon extended cycling. The extraordinarily higher specific capacity values of LiFePO_4 anodes may be exploited suitably for practical lithium battery applications.

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1. Introduction

LiFePO_4 , identified for the first time as a promising battery electrode material by Padhi et al. [1] has further seen tremendous growth, especially in the recent lithium battery related R&D activities. Despite the cheaper, safer and non-toxic nature of LiFePO_4 cathode with an apparently appreciable theoretical specific capacity value (170 mAh/g), certain critical and hampering problems that are concerned with the stringent synthesis conditions, inherent low electronic conduc-

tivity and slower lithium diffusion kinetics, etc., remain as challenging issues only till date [2,3]. It is well known that literature is replete with numerous synthetic approaches [2–4], which have been made with a view to prepare the title compound in its pure and conductive form. Such an effort includes microwave synthesis [4], hydrothermal method [2], spray produced LiFePO_4 [5], emulsion drying approach [6], co-precipitation technique [7] and soft chemistry route [8] apart from the solid state method [3,9–11] of synthesizing LiFePO_4 , wherein addition of carbon [12], sucrose [13], Cu/Ag powder [14] or the deployment of optimum synthesis temperature [15,16] has been implemented to improve the conductivity of native LiFePO_4 synthesized through any one of the mentioned methods. However, the room temperature

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electrochemical properties of LiFePO_4 cathodes, especially when $x > 1$ and under significant loadings remain with unsatisfactory results only [10].

On the other hand, it is quite surprising that no attempt has so far been paid towards the wide possibility of exploring the anode performance characteristics of LiFePO_4 , despite the extensive research being carried out on the cathode behavior of the same. Therefore such an effort to understand the possible extent of exploitation of LiFePO_4 as a potential lithium battery anode gains paramount importance. Hence, the present investigation was aimed at the exploration and exploitation of LiFePO_4 compound as an ambient temperature anode for rechargeable lithium batteries, which is an ever first attempt of this kind. Towards this intriguing interest, the compound LiFePO_4 was synthesized via solid state method and subjected further to physical as well as electrochemical anode performance characterization studies.

2. Experimental

2.1. Synthesis procedure

Stoichiometric amounts of Li_2CO_3 , $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ were mixed thoroughly along with 10 wt.% carbon and the mixture was ball milled for about 12 h to ensure intimate and homogenous mixing. The added carbon is expected to form a uniform surface coating over the reactant mixture which may prevent the formation of unacceptable impurities, developed along with the required LiFePO_4 product at the final step. The ball milled fine powders of the precursor mixture was subjected initially to a lower calcination temperature of 450 °C for 6 h and subsequently to 750 °C for 3 h (rate of heating: 5 °C per minute) with the deployment of periodical and intermittent grinding after every 3 h duration. The ultra fine powders obtained after the high temperature calcination of 750 °C was collected from furnace and subjected further to systematic characterization studies.

2.2. Structural and morphological characterization

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 10–110° at a scan rate of 0.1°/s. Surface morphology of the particles was examined through SEM images obtained from Jeol S-3000 H Scanning Electron microscope and the charge–discharge studies were carried out using MACCOR charge–discharge cycle life tester. BET surface area measurements were performed on a Micromeritics BET surface area analyzer

and the actual size of the particles was measured using Malvern easy particle size analyzer.

2.3. Electrochemical characterization

The anode electrode was prepared and used as described elsewhere [17].

3. Results and discussion

3.1. Structural results – PXR D studies

A striking similarity in the PXR D pattern of LiFePO_4 synthesized through the present study has been observed (Fig. 1) with the standard orthorhombic olivine type LiFePO_4 with a $Pnma$ space group. Based on the reports of Kim et al. [18], it is believed that the effect of carbon coating has restricted the undesirable conversion of iron and hence resulted in the phase pure formation of LiFePO_4 . Presence of trace impurities due to lithium orthophosphate (Li_3PO_4) [19] has also been excluded in the present study, due to the intimate mixing of precursor via ball milling and the deployment of optimum synthesis temperature (750 °C) with intermittent grinding of reactant mix-

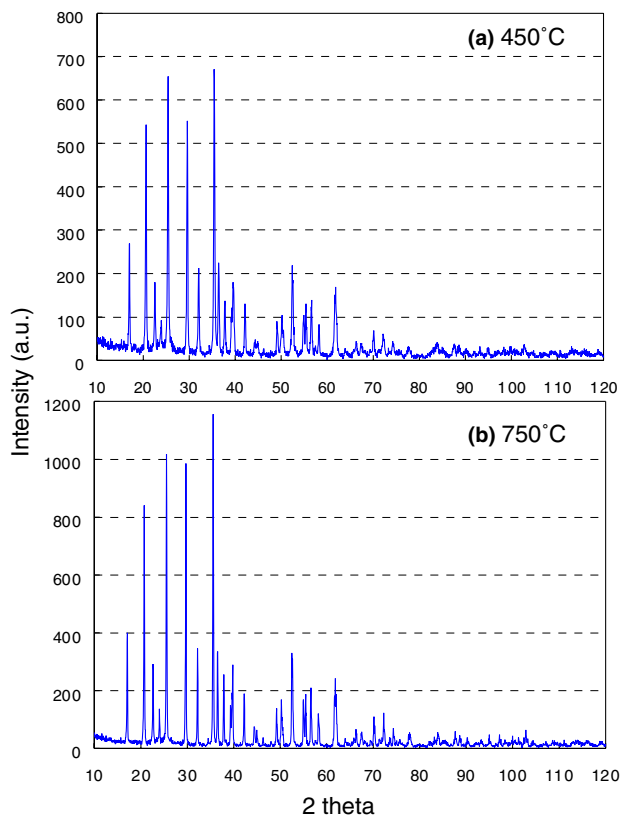


Fig. 1. XRD pattern exhibited by LiFePO_4 synthesized at: (a) 450 °C; (b) 750 °C.

ture. Although the process of crystallization commences at 450 °C Fig. 1(a), the contents of the furnace were heated to 750 °C (3 h), as the furnace heating at 700 °C has been reported to be accomplished with more ordering of iron at that specific temperature [10]. As expected, an enhanced degree of crystallinity and better phase purity of LiFePO_4 have been realized at 750 °C, which are evident from the sharp and symmetric diffractograms of increased intensity (Fig. 1(b)). The expected parasitic peaks due to Fe(II, III) pyrophosphates, especially when heated above 700 °C [3] were also found to be absent, thus confirmed the presence of single phase LiFePO_4 without any undesirable iron impurities. Also, the variation in the lattice parameter values of LiFePO_4 synthesised at 450 °C ($a = 10.361$; $b = 6.008$; $c = 4.701$ Å) and at 750 °C ($a = 10.378$; $b = 6.011$; $c = 4.714$ Å) has substantiated the fact that the high temperature calcination at 750 °C has imparted better crystallinity to the LiFePO_4 powder [6]. The average grain size D calculated using Scherrer's formula was found to be 120 nm, which is also comparable with the reported results of Zanes et al. [12].

3.2. Morphological results – SEM analysis

SEM images of LiFePO_4 synthesised at 450 and 750 °C are furnished in Figs. 2(a) and (b), respectively. The appearance of denser surface structure due to carbon coating is obvious from Fig. 2(a). Similarly, the presence of individual particles with an average particle size of 1 μm is evident from Fig. 2(b), despite the high calcination treatment of 750 °C at which phase pure LiFePO_4 has been synthesised. Based on the encouraging result that the particle size does not encounter the presence of either finer (<1 μm) or coarser particles (>20 μm) of LiFePO_4 , it is considered that the synthesized compound is suitable for usual electrode preparation techniques [19]. The estimated BET surface area value was about 19.3 m^2/g . and the actual size of all the 100% particles were found to reside well within the 1–3 μm range.

3.3. Electrochemical characterisation results

3.3.1. Charge–discharge studies

The charge–discharge behavior of LiFePO_4 anodes examined at room temperature (25 °C) is appended in Fig. 3. The flat discharge curves with large voltage plateaus suggest that charge–discharge proceeds as a two phase reaction, a behavior which is very much similar to that of LiFePO_4 cathodes [20,21]. However, a maximum capacity of ~620 mAh/g has been exhibited by LiFePO_4 anodes, which is approximately 4–5 times higher than the corresponding room temperature specific capacity values of LiFePO_4 cathodes [22]. Interestingly, the high specific capacity LiFePO_4 anodes possess significant cyclic reversibility with an acceptable fade in

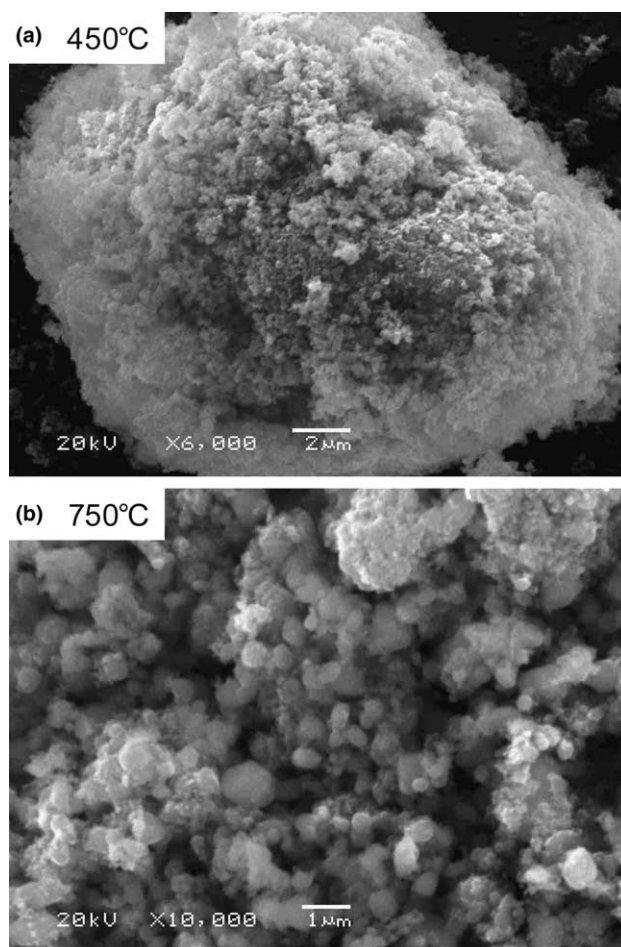


Fig. 2. SEM images of LiFePO_4 synthesized at: (a) 450 °C; (b) 750 °C.

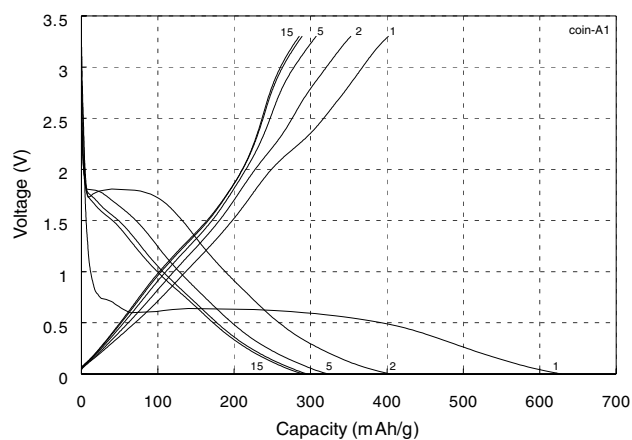


Fig. 3. Charge–discharge behavior of LiFePO_4 anode synthesized at 750 °C.

capacity values (<20%) upon ambient temperature cycling (up to 20 cycles), which is evident from Fig. 4. Similarly, the LiFePO_4 anodes exhibited a coulombic efficiency of 99%, especially upon progressive cycling (Fig. 4), which is also higher than that of LiFePO_4 cathodes (96%).

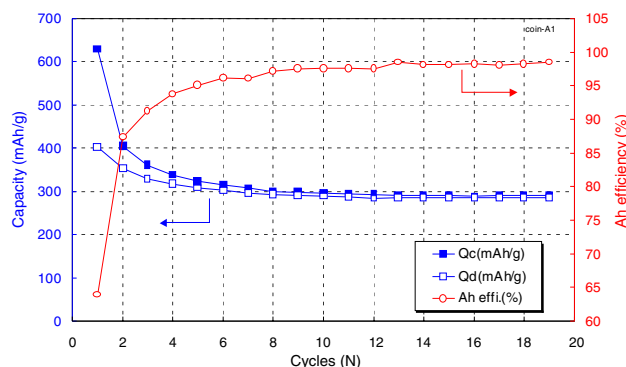


Fig. 4. Capacity vs cycleability behavior of LiFePO_4 anode in $\text{Li}|\text{LiFePO}_4$ cell.

Eventually, for a low cathode loading level of 5–20 mg/cm^2 of LiFePO_4 , only 70% of theoretical capacity value has been realized by Yang et al. [10]. On the other hand, the present study attributes to an average capacity of at least 300 mAh/g , against an average anode slurry coating of 10 mg/cm^2 of LiFePO_4 powder per disc, which is about 1.7 times higher than the theoretical capacity of LiFePO_4 cathode. Also, it is noteworthy that the first cycle irreversible capacity loss behavior of LiFePO_4 anodes is well within the acceptable limit ($\sim 33\%$), compared to the reported capacity loss values [23] of metal oxide anodes (35–40%). However, this unavoidable initial fade in capacity could presumably be related to the structural variations or loss of contact between the conductive binder [8] and the active material particles resulting from volume variations during lithium extraction. Similarly, with due modifications to combat the reduced capacity retention behavior (observed upon extended cycling) of LiFePO_4 anodes at room temperature, a remarkable breakthrough in the field of alternative anodes for rechargeable lithium batteries could be anticipated shortly.

4. Conclusion

Phase pure and better performing crystalline LiFePO_4 has been synthesized and investigated systematically for the anode performance characteristics against lithium metal. The LiFePO_4 anodes exhibited an unassumingly higher specific capacity value of ~ 620 mAh/g , with a permissible capacity fade up to 20 cycles. An appreciable coulombic efficiency of 99% has been observed with the room temperature cycling behavior of LiFePO_4 anodes. Based on the high specific capacity values, excellent coulombic efficiency and significant cycling behavior, the LiFePO_4 anodes qualify themselves as potential lithium battery anode candidates to be con-

sidered favorably for practical lithium battery applications and for commercial exploitation in the near future.

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