Rapid and Facile Synthesis of Mn Doped Porous LiFePO₄/C from Iron Carbonyl Complex

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ABSTRACT:

Porous Mn-doped LiFePO₄/C cathode material was synthesized by facile and fast microwave assisted solid state reaction from iron carbonyl complex using citric acid as reducing agent and source of carbon. The microstructure and electrochemical performance were systematically investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), Raman spectroscopy, charge-discharge cycling, cyclic voltammogram and electrochemical impedance spectroscopy. It was found that the as-prepared composites have a single phase of orthorhombic olivine-type structure and Mn²⁺ has successfully introduced into the M₂(Fe) sites. The electrochemical properties of LiFe_{0.99}Mn_{0.01}PO₄/C were compared with bare LiFePO₄ and LiFePO₄/C composite prepared by identical route. Compare to as-prepared LiFePO₄/C composites, LiFe_{0.99}Mn_{0.01}PO₄/C demonstrates a remarkable electrochemical property in terms of discharge capacity, electrochemical reversibility and cycling performance with an initial discharge capacity of 163.2 mAh·g⁻¹ at a discharge rate of 0.1 C. It also performed excellent even at higher current densities. The improved electrochemical performance was attributed to the smaller particle size,

porosity, the enhancement of the P-O bond and the facilitation of Li^+ ion “effective” diffusion, induced by Mn^{2+} -substitution.

Keywords: Mn-doped LiFePO_4/C , microwave heating system, iron carbonyl complex, porosity.

1. INTRODUCTION:

Olivine structure LiFePO_4 has received considerable attention as a cathode material for lithium ion batteries because of its low cost, good stability and environmental friendliness [1-4]. It has a flat potential plateau at 3.4 V versus Li/Li^+ and a high theoretical capacity of 170 mAh g^{-1} . However, the practical use of LiFePO_4 is highly limited due to its intrinsic low electronic conductivity and slow lithium ion diffusion which lead to poor rate capability [5-7]. Several strategies have been devised to overcome the inherent limitations of LiFePO_4 , including the particle fining [8, 9], creating conductive coating (carbon or metal) on the particles [10, 11], and doping with alien ion [12-15]. Fe-site doping is considered to be an effective way to improve the rate performance of LiFePO_4 , resulting due to increased in ionic mobility and diffusion coefficient.

Sun *et al.* [13] proposed that the rate capability of LiFePO_4 was significantly enhanced by doping Vanadium. Ge *et al.* [14] reported that Ni doped LiFePO_4/C nano-composite delivers high capacity up to $150 \text{ mAh}\cdot\text{g}^{-1}$ at 15 C, retaining 93% even after 7200 cycles. Many researchers found that the electrochemical activity of Mn could be greatly improved in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ [16-18]. Nakamura *et al.* mention that the 0.05 substitution of Fe^{2+} by Mn^{2+} shows higher capacity than pristine LiFePO_4 and on further increasing amount of Mn^{2+} specific capacity shrinks [18]. Hence in our investigation only 0.01 of Fe^{2+} is replace by Mn^{2+} composite to perceive the effect of low level substitution on electrochemical properties of LiFePO_4/C .

Currently microwave synthesis of ceramics and superconducting material and superfine nano-powders and catalysts [19] is fetching more reputation in material science. Microwave irradiation is highly favourable for solid state reaction since, in microwave substances are heated uniformly at molecular level compare to

conventional heating, where sample is heated from outer surface to the interior and thus resulting steep thermal gradient. Ganesh *et al.* [20] reported that the microwave do not change the nano crystalline size of the particles even after sintering, which is very important for commercial applications. Though the formation of LiFePO_4 by microwave is very fast it suffers from oxidation of Fe^{2+} , which can be controlled by heating with the inert gas flow or by coating raw material with activated carbon or carbonaceous substance [21]. However former way is discommodious, while the later unavoidably induces carbon residue.

In our work $\text{Fe}_2(\text{CO})_9$ is used as source of iron, which is on decomposition produces CO gas and sustain reducing atmosphere within the sample volume. Also we expect CO evolution will lead to the creation of pores in the final product, when it is escaping from reaction mixture. These pores will serve as channel for lithium intercalation and de-intercalation during charging–discharging of cell, which will further augment the specific capacity [22, 23]. In this research effort are taken to synthesize crystalline and porous $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ by facile and fast microwave synthesis method. The systematic studies were performed between bare LiFePO_4 , LiFePO_4/C and doped LiFePO_4/C composite to understand the effect of substitution as well as porosity on the electrochemical performance of the material.

2. MATERIALS

Mn doped $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite was prepared by microwave assisted solid-state reaction. The samples were synthesized from $\text{LiOOCCH}_3 \cdot 2\text{H}_2\text{O}$ (99% SCR, Shanghai, China), $\text{NH}_4\text{H}_2\text{PO}_4$ (99% SCR, Shanghai, China), $\text{Fe}_2(\text{CO})_9$ (99%, Jiangsu Tianyi Ultra-Fine Metal Powder Co. Ltd, Jiangsu, China), MnO_2 (99% SCR,

Shanghai, China) along with citric acid (99% SCR, Shanghai, China) as carbon source.

3. EXPERIMENTAL:

3.1 Synthesis of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$

The stoichiometric mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Fe}_2(\text{CO})_9$ was mixed in agate mortar with pestle for 30 minutes. The homogeneous mixture obtained was heated to 80°C in oven for 10mins and ground thoroughly with $\text{LiOOCCH}_3\cdot 2\text{H}_2\text{O}$, MnO_2 and citric acid for another 30 minutes. The mixture obtained was ball milled for 15 hours in ethanol and subsequently dried at 70°C in oven. The free flowing powder obtained is compressed (12 MPa) to pellets and heated in sealed quartz crucible. Similar procedure was followed to synthesize bare LiFePO_4 as well as LiFePO_4/C composite. Microwave irradiation of all the mixtures was executed in a specially designed single mode microwave furnace at 2.45 GHz and 136 W for 10 minutes.

3.2 Characterization of LiFePO_4/C synthesized.

The crystalline phase of the pristine and Mn-doped sample was analyzed by powder X-ray diffraction (PANalytical X'Pert Pro) which was performed using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Data were collected from 10 to 80° in 2θ , with a step size of 0.017 and 1.0 s per step. The microstructure of the powder samples product was observed by scanning electron microscope (JSM-5610LV) and JEM-2010 transmission electron microscope (TEM), whereas surface of the compress pellet was analyzed by Hitachi field-emission scanning electron microscope (FE-SEM S-4800). The Raman spectroscopic (INVIA RENISHAW laser Raman spectroscope) analysis was performed with a system utilizing 632.5 nm incident radiation and a $50\times$ aperture (N.A.=0.75) resulting approximately a $2 \text{ }\mu\text{m}$ diameter sampling cross section.

3.3 Electrochemical measurements

A cathode working electrode for electrochemical testing was prepared by mixing product with acetylene black and 5% solution of poly-tetrafluoroethylene (PTFE) in water, with weight ratio 80:10:10. Slurry prepared in isopropyl alcohol coated on thin aluminium sheet and dried in vacuum oven at 120 °C for 24 h. 2025 type coin cells were assembled using lithium foil as an anode, and 1 M solution of LiPF_6 in mixture of ethylene carbonate and dimethylene carbonate (1:1 v/v) as electrolyte in an argon filled glove box at room temperature. The two electrodes were held apart with separator (Celgard No 2402). Charge-discharge characteristic of the sample was cycled between 2.7 to 4.2 V by using battery test system (LAND CT2001A) at ambient temperature. Cyclic voltammetry (CV) and electrochemical impedance spectroscopic (EIS) measurement was performed on AutoPotentiostat30 system. The amplitude of the AC signal was 5 mV over the frequency range between 0.01 Hz and 100 kHz.

4. RESULTS AND DISCUSSION:

4.1 XRD

Fig.2 shows the XRD patterns of the as-prepared bare LiFePO_4 , LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composites. It was found that Mn-doped LiFePO_4/C is well crystallized in orthorhombic structure as the pristine sample and without any unexpected phase, such as Fe_2P or Mn-containing compounds [21]. All of the diffraction peaks match with the standard data for pure LiFePO_4 phase (PDF-40-1499). The peaks in the region 17.12, 20.72, 22.64, 23.99, 25.50, 29.62, 34.44, 35.52, 36.46 $\square$ 37.82, 39.24, 42.12, 49.12, 50.17, 52.54, 54.87, 55.37, 56.51, and 58.13 corresponds to (020), (011), (120), (101), (111), (121), (031), (131), (211), (140 $\square$, (041), (112), (302), (311), (042), (142), (160), (331), and (340) plane respectively.

This implies that the olivine structure of LiFePO_4 was well maintained during the preparation process.

As shown in Table-1, the unit cell parameters and unit cell volume of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ changed a little, *i.e.*, the length of *a*-axis, *b*-axis, *c*-axis and unit cell volume have increased. The increase in the unit parameters and unit cell volume of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ can be ascribed to the bigger ionic radius of Mn^{2+} (0.97 Å) compare to Fe^{2+} (0.92 Å). The results also indicate that Mn and Fe both occupy 4c sites at the tetrahedral Fe environment in $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ [22]. The expansion in the crystal lattice can provide more space for lithium intercalation/de-intercalation. When Fe^{2+} changes to Fe^{3+} during de-intercalation, the lattice collapses and limited lithium ion diffuses. In $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$, Mn^{2+} ions in the lattice may act as a pillar to prevent the collapse of the crystals during cycling and thus improve the electrochemical performance [24, 25].

4.2 Surface analysis

Fig.-3 a to c shows the typical SEM images of as prepared $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite with increasing magnification. From the Fig.- 3a it can be realized that, the product consist of porous agglomerations. The pores are clearly visible in higher magnification (Fig.-3 b & c). The morphology and size of LiFePO_4 was confirmed from corresponding SEM images. FE-SEM analysis of the sample confirmed that the porous agglomerations consist of non-uniform fine particles with the size ranged between 50nm and 300nm. The particles size and uniform distribution of conducting carbon are confirmed from TEM image (Fig.-4) of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$. The carbon web provide highly conductive channels for the electron mobility among LiFePO_4 active particles, and enhances the electronic conductivity of the composites [26]. ICP analysis of the $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ identifies the real composition of Li, Fe, and Mn in sample as 0.990, 0.996, and 0.0107 respectively, which are much closed to the intended value.

It is evident from the Fig-3 and Fig-4 that as synthesized material consist of porous agglomeration of smaller particles. The formation of pores can be attributed to evolution of CO gases during the decomposition of $\text{Fe}_2(\text{CO})_9$ [27, 28], which also take care of prevention of oxidation of Fe^{2+} . This qualitative picture of pores and voids of different dimensions has being confirmed with a quantitative analysis. Namely measurement of N_2 adsorption isotherms shows a large hysteresis (Fig.-5) for all three samples, which belong to type IV with a flat type hysteresis loop lacking of a clear plateau at saturation range. These results suggest those pores are distributed continuously in the meso and macro porous range [23]. Detailed analysis shows average pore size is 80-110 nm, i. e. in the macro porous range, and surface area is about 18-22 m^2g^{-1} .

4.3 Raman spectra

Raman spectrum recorded for LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite are exhibited in the Fig.-6. The carbon layer on LiFePO_4 crystals makes it difficult to see the details of the spectrum of the olivine structure of LiFePO_4 due to the diminution of the signals and the overlapping of the spectral bands [29], except few peaks corresponds to PO_4^{3-} and Fe-O bond. Two peaks at 1600 and 1336 cm^{-1} correspond to the G and D bands of carbon, respectively. The D band arises because of the disorder induced in sp^2 -bonded carbon, whereas the G band arises from the in-plane vibration of sp^2 carbon atoms [30,31]. However D and G bands of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ were observed at 1331 and 1597, 1331 and 1580 respectively. I_D/I_G value (the peak intensity ratio between 1336 and 1600 cm^{-1} peaks) generally provides a useful index to compare the degree of crystallinity of various materials, i. e. smaller the ratio of I_D/I_G higher the degree of carbon ordering in the material. For LiFePO_4/C I_D/I_G ratio is 1.15, but for $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ it is increased to 1.19. Since

I_D/I_G ratios of both the samples are very closed, effect of carbon coating on electrochemical properties of the samples will be equivalent. This confirms, the increment in specific capacity observed in $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ is purely due to doping of Mn^{2+} .

4.4 Electrochemical properties of synthesized LiFePO_4

Fig.-7 shows the comparative initial galvanostatic charge/discharge curves of pristine and Mn-doped LiFePO_4/C cathodes, which were operated at 0.1C current density in the voltage range of 2.5–4.2V(vs. Li^+/Li). There is no observable charge/discharge plateau associated with the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox couple in Fig-7. This indicates that $\text{Fe}^{2+}/\text{Fe}^{3+}$ is practically the only redox couple that contributes to the electrochemical reaction in the $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ cathode. It is also found that $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ exhibits the highest discharge capacities of $163.2 \text{ mAh}\cdot\text{g}^{-1}$, compare to 153.1 and $63.4 \text{ mAh}\cdot\text{g}^{-1}$ of LiFePO_4/C and LiFePO_4 respectively. Higher capacity suggested that, almost the full Fe^{2+} amount in $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ was electrochemically utilized at 0.1 C rate, indicating that the utilization of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction was improved with Mn-doping. The first cycle performance of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ at various current rates is presented in Fig-8. Due to the limited lithium diffusion and electronic conduction, the discharge capacity decreased with increasing current rates. Though Mn doped sample contain limited graphitic domain, exhibited good performance on capacity retention even after 50 cycles (Fig-9a) at various current rates indicate structure of the sample is very stable and substitution of Mn truly influencing electrochemical performance of LiFePO_4 .

The improved cycling performance of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ may be mainly ascribed to the smallest particle-size as well as the macro porous network. Size reduction of LiFePO_4 and larger particle with porous agglomeration would shorten

electronic conduction path and consequently facilitate the intercalation process of lithium ions, resulting in improve the charge and discharge kinetic [32-35]. On the other hand, Mn^{2+} substitution may induce Li^+ defect in LiFePO_4 and residue of $\text{Fe}^{2+}/\text{Fe}^{3+}$ coexistence state due to the balance of electrical valency. Such defects are favorable for the diffusion of Li^+ in solid phase and enhance electrical conductivity. As a result, high discharge capacity and good reversibility were obtained.

To get insight into the kinetics of lithium intercalation/deintercalation, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out at room temperature. Fig.-10 shows the CV curves of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composites at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$ in the 2.5-4.3 V (vs. Li^+/Li). For the LiFePO_4/C cathode, the oxidation and reduction peaks centre at 3.645 and 3.245 V, respectively. The potential separation between the two peaks is 0.400 V. However, in the case of the $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ cathode, the oxidation and reduction peaks centre at 3.574 and 3.283 V, respectively, with a potential separation of 0.291 V, less than that observed for LiFePO_4/C . This strongly support the higher polarization observed for LiFePO_4/C during first charge-discharge cycle reported in the Fig.-7. Both composites exhibiting, two-phase charge-discharge reaction of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple [36,37]. It can be found that $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ demonstrates a better step in oxidation-reduction process than the pristine one and the polarization defined as potential difference between the anodic and the cathodic peaks was reduced with the Mn^{2+} substitution. These behaviors tend to indicate that kinetic limitations on the electrochemical redox reaction were relaxed with the substitution [38, 39]. No other peaks were seen, which indicates an absence of electro active iron impurities. Furthermore, the integration of the area under the anodic and cathodic peaks suggests

that an equal quantity of lithium ions might be reversibly de-inserted and re-inserted into $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite during the charge-discharge cycling.

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Electrochemical impedance spectroscopy was registered on the coin cells in the fully charge state. The typical Nyquist plots of the as-prepared pristine and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ electrodes are shown in Fig.11A. The overall shape of Nyquist plot is composed of a depressed semicircle in the high frequency region and an oblique straight inclined line in the low frequency region. The semicircle part at high frequencies is attributed to the lithium-ion transfer resistances at the interface between the cathode particles and an electrolyte [39] and the linear part at low frequencies is attributed to the diffusion of Li^+ in the LiFePO_4 electrode materials [18]. Fig.11B depict simplified equivalent circuit model which was employed to analyze the impedance spectra, where the symbols, R_s , R_{ct} , and Z_w , denoted the solution resistance, charge-transfer resistance and Warburg impedance, respectively. Constant phase element (CPE) is placed to represent the double layer capacitance and passivation film capacitance. Significant decrease of R_{ct} from 162.97Ω in LiFePO_4/C to 78.70Ω in $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite indicates the enhancement of the charge-transfer reaction of the LiFePO_4/C on Mn^{2+} -substitution and improved transportation of electrons.

5. CONCLUSION

Substitution of iron by manganese in olivine-structure LiFePO_4/C composite was successfully prepared through a carbothermal reductive solid state reaction, using microwave as heating source. Analysis from XRD and SEM show that as-prepared

composites are well crystallized in orthorhombic structure and cell volume as well as the morphology varies on Mn doping. Among the as-prepared composites, $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite shows the highest reversible capacity. Taking into account all the analyses and results presented above, it can be concluded that the enhancement of chemical performance is due to successful substitution of Mn^{2+} at Fe^{2+} site in LiFePO_4 . In $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$, Mn^{2+} ions in the lattice may act as a pillar to prevent the collapse of the crystals during cycling and thus improving the electrochemical performance.

Acknowledgments

The research was supported by Chinese National Science Foundation (51172175, 51072147) and Hubei Science & Technology Plan (2012FFB05107, 2013BKB006).

References:

1. Yamada, A., Chung, S. C., Hinokuma K., 2001. Optimized LiFePO_4 for lithium battery cathodes. J. Electrochem. Soc. 148, A224-A229.
2. Andersson, A. S., Thomas, J. O., 2001. The source of first-cycle capacity loss in LiFePO_4 . J. Power Sou. 97-98, 498-502.
3. Padhi, A. K., Nanjundaswamy, K. S., Goodenough J. B., 1997. Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. J Electrochem Soc 144, 1188-1194.
4. Padhi, A. K., Nanjundaswamy, K. S., Masquelier, C., Okada, S., Goodenough, J. B., 1997. Effect of Structure on the $\text{Fe}^{3+} / \text{Fe}^{2+}$ Redox Couple in Iron Phosphates. J. Electrochem. Soc. 144, 1609-1613.
5. Chung, S. Y., Bloking, J. T., Chiang, Y. M., 2002. Electronically conductive

- phospho-olivines as lithium storage electrodes. *Nat Mater* 1,123-128.
6. Yu, D. Y. W., Fietzek, C., Weydanz, W., Donoue, K., Inoue, T., Kurokawa, H., Fujitani, S. , 2007. Study of LiFePO_4 by Cyclic Voltammetry. *J Electrochem. Soc.* 154, A253-A257.
 7. Andersson, A. S., Kalska, B., Haggstrom, L. , Thomas, J. O., 2000. Lithium extraction/insertion in LiFePO_4 : an X-ray diffraction and Mössbauer spectroscopy study. *Solid State Ionics*,130,41-52.
 8. Huang, Y. H., Ren, H. B. , Yin, S. Y. , Wang, Y. H., Peng, Z. H. , Zhou, Y. H., 2010. Synthesis of LiFePO_4/C composite with high-rate performance by starch sol assisted rheological phase method. *J. Power Sou.*, 195, 610-613.
 9. Rangappa, D., Sone, K., Kudo, T., Honma, I. 2010. Directed growth of nanoarchitected LiFePO_4 electrode by solvothermal synthesis and their cathode properties. *J. Power Sou.*, 195, 6167-6171.
 10. Mi, C. H., Cao, Y. X., Zhang, X. G. , Zhao, X. B., Li, H. L., 2008. Synthesis and characterization of $\text{LiFePO}_4/(\text{Ag}^+ \text{C})$ composite cathodes with nano-carbon webs. *Powd. Tech.*, 181,301-306.
 11. Zhang, B., Wang, X. J., Li, H., Huang, X. J., 2009. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material synthesized by chemical reduction and lithiation method. *J Power Sou* 189, 476-479.
 12. Ou, X. Q., Liang, G. C. , Wang, L. , Xu, S. Z., Zhao, X., 2008. Effects of magnesium doping on electronic conductivity and electrochemical properties of LiFePO_4 prepared via hydrothermal route. *J Power Sou* 184 ,543-547.
 13. Sun, C. S., Zhou, Z., Xu, Z. G., Wang, D. G., Wei, J. P., Bian, X. K., Yan, J., 2009. Improved high-rate charge/discharge performances of LiFePO_4/C via V-doping. *J. Power Sou.* 193,841-845.

14. Ge, Y. C., Yan, X. D., Liu, J., Zhang, X. F., Wang, J. W., He, X. G., Wang, R. S., Xie, H. M., 2010. An optimized Ni doped LiFePO_4/C nanocomposite with excellent rate performance. *Electrochim. Acta* 55, 5886-5890.
15. Wu, L., Li, X. H., Wang, Z. X., Wang, X. J., Li, L. J., Fang, J., Wu, F. X., Guo, H. J., 2010. Preparation of synthetic rutile and metal-doped LiFePO_4 from ilmenite. *Powd. Technol.* 199, 293-297.
16. Yamada, A., Kudo, Y., Liu, K. Y., 2001. Reaction Mechanism of the Olivine-Type $\text{Li}_x(\text{Mn}_{0.6}\text{Fe}_{0.4})\text{PO}_4$. *J. Electrochem. Soc.* 148, A747-A754.
17. Li, G. H., Azuma, H., Tohda, M., 2002. Optimized $\text{LiMn}_y\text{Fe}_{1-y}\text{PO}_4$ as the Cathode for Lithium Batteries. *J. Electrochem. Soc.* 149, A743-A743.
18. Nakamura, T., Sakumoto, K., Okamoto, M., Seki, S., Kobayashi, Y., Takeuchi, T., Tabuchi, M., Yamada, Y., 2007. Electrochemical study on Mn^{2+} -substitution in LiFePO_4 olivine compound. *J. Power Sou.* 174, 435-441.
19. Yang, L., Lu J., 2003. *Chemical World*, 3, 165.
20. Ganesh, L., Johnson, R., Rao, G. V. N., Mahajan, Y. R., Madhavendra, S. S Reddy, ., B. M., 2005. Microwave-assisted combustion synthesis of nanocrystalline MgAl_2O_4 spinel powder. *Ceram. Int.* 31, 67-74.
21. Park, K. S., Son, J. T., Chung, H. T., Kim, S. J., Lee, C. H., Kim, H. G., 2003. Synthesis of LiFePO_4 by co-precipitation and microwave heating. *Electrochem. Commun.* 5, 839-842.
22. [Pei, Z.](#), [Zhang, X.](#), [Gao, X.](#), 2013. Mixed-Solvent Thermal Synthesis of Porous LiFePO_4 . *J. Nanosci. Nanotechnol.* Apr.13(4), 3142-3248.
23. Dominko, R., Bele, M., Gaberscek, M., Remskar, M., Hanzel, D., Goupil, J. M., Pejovnik, S., Jamnik, J., 2006. Porous olivine composites synthesized by sol-gel technique. *J. Power Sou.* 153, 274-280.

24. Shin, H. C. , Park, S. B., Jang, H., Chung, K. Y., Cho, W. I. , Kim, C. S., Cho, B. W., 2008. Rate performance and structural change of Cr-doped LiFePO_4/C during cycling. *Electrochim Acta* 53, 7946-7951.
25. Liu, H., Cao, Q., Fu, L. J. , Li, C., Wu, Y. P. , Wu, H. Q. , 2006. Doping effects of zinc on LiFePO_4 cathode material for lithium ion batteries *Electrochem Commun* 8, 1553-1557.
26. Mi, C. H., Zhang, X. G. , Zhao, X. B., Li, H. L. ,2006. Synthesis and performance of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4/\text{nano-carbon}$ webs composite cathode. *Mater Sci Eng. B*,129, 8-13.
27. Naik, A., Zhou, J., Gao, C., Wang, L., 2014. Microwave Synthesis of LiFePO_4 from Iron Carbonyl Complex. *Electrochim. Acta* 142,215-222.
28. Naik, A., Zhou, J., Gao, C., Wang, L., 2014. Microwave Assisted Solid State Synthesis of LiFePO_4/C using two Different Carbon Sources. *Int. J. Elect. Sci.*, 9, 6124-6133.
29. Markevich, E., Sharabi, R., Haiket, O., 2011. Raman spectroscopy of carbon-coated LiCoPO_4 and LiFePO_4 . *J. Power Sou.* 196(15), 6433-6439.
30. Lu , Z. G. , Lo, M. F. , Cheng, C. Y. , 2008. Pulse Laser Deposition and Electrochemical Characterization of $\text{LiFePO}_4\text{-C}$ Composite Thin Films. *J. Phys. Chem. C* 112, 7069-7078.
31. Park, K. C. , Hayashi, T., Tomiyasu, H., Dresselhaus, M. S. , 2005. Progressive and invasive functionalization of carbon nanotube sidewalls by diluted nitric acid under supercritical conditions. *J. Mater. Chem.*,15,407-411.
32. Herle, P. S., Ellis, B., Coombs, N., Nazar, L. F., 2004. Nano-network electronic conduction in iron and nickel olivine phosphates. *Nat Mater* 3,147-152.
33. Delacourt, C., Poizot, P., Morcrette, M., Tarascon, J. M., Masquelier, C., 2004.

One-Step Low-Temperature Route for the Preparation of Electrochemically Active LiMnPO_4 Powders. *Chem. Mater.* 16, 93-99.

34. Li, L. J. , Li, X. H., Wang, Z. X., Wu, L., Zheng, J. C. , Guo, H. J. , 2009. Stable cycle-life properties of Ti-doped LiFePO_4 compounds synthesized by co-precipitation and normal temperature reduction method. *J. Phys. Chem. Solids*, 70, 240-247.
35. Gibot, P., Cabanas, M. C. , Laffont, L. , Levasseur, S., Carlach, P. , Hamelet, S., Tarascon, J. M., Masquelier, C., 2008. Room-temperature single-phase Li insertion/extraction in nanoscale Li_xFePO_4 . *Nat. Mater* 7(10),741-747.
36. Kang, H. C., Jun, D. K., Jin, B., Jin, E. M., Park, K. H., Gu, H. B., Kim, K. W. , 2008. Optimized solid-state synthesis of LiFePO_4 cathode materials using ball-milling. *J. Power Sou.* 179, 340-346.
37. Liao, X. Z. , Ma, Z. F. , Gong, Q., He, Y. S., Pei, L., Zeng, L. J., 2008. Low-temperature performance of LiFePO_4/C cathode in a quaternary carbonate-based electrolyte. *Electrochem. Commun.* 10, 691-694.
38. Yin, X. G. , Huang, K. L. , Liu, S. Q. , Wang, H. Y. , Wang, H., 2010. Preparation and characterization of Na-doped LiFePO_4/C composites as cathode materials for lithium-ion batteries. *J. Power Sou.* 195, 4308-4312.
39. Zhang, W. K., Hu, Y. L., Tao, X. Y., Huang, H., Gan, Y. P. , Wang, C. T. , 2010. Synthesis of spherical LiFePO_4/C via Ni doping. *J Phys Chem Solids* 71, 1196-1200.

CAPTIONS

Table-1 Calculated lattice parameters of LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$

Fig.-1 Flow chart for preparation of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composites

Fig.-2 X-ray diffraction patterns of material synthesized

Fig.3 a) ,b) , c) are SEM $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ at different magnification, d)FE-SEM of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$

Fig.-4 TEM image of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$.

Fig.-5 Typical nitrogen adsorption isotherms of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$, LiFePO_4/C and LiFePO_4

Fig.6 Raman spectrum recorded for LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ composite

Fig.7 The initial charge/discharge curves of a) LiFePO_4 b) LiFePO_4/C c) $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ recorded at 0.1C current density.

Fig.8 The initial charge/discharge curves of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ recorded at different current densities.

Fig.-9 Reversible capacity of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$, and LiFePO_4 during continuous cycling at 0.1 to 10C (the cell was charge and discharge with the same current density).

Fig. 10 Cyclic voltammograms of the $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ and LiFePO_4/C electrodes at a scan rate of $0.1\text{mV}\cdot\text{S}^{-1}$

Fig.-11 A) Electrochemical impedance spectra of the LiFePO_4/C and $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4/\text{C}$ cathodes B) corresponding equivalent circuit model

TABLE

Table-1

Lattice Parameter	Samples		
	LiFePO ₄ /C	LiFe _{0.99} Mn _{0.01} PO ₄ /C	Padhi <i>et. al.</i> ³
a (Å)	10.3193	10.3415	10.3344
b (Å)	5.9856	6.0037	6.0083
c (Å)	4.6812	4.7084	4.6931
Volume of unit(Å ³)	289.1446	292.3316	291.4048

FIGURES

Fig.-1

Fig.-2

Fig.3

Fig.-4

Fig.-5

Fig.6

Fig.7

Fig.8

Fig.-9

Fig. 10

Fig.-11