



ELECTROCHEMICAL PERFORMANCE OF LiFePO_4 BY RHODIUM DOPING

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Abstract:

An attempt was made to synthesis Rhodium (Rh) doped LiFePO_4 for Li Ion battery application as cathode candidate, $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$ ($x=0.01-0.03$). The cathode material is prepared by mixture of 75% active material, 20% acetylene black and 5% polyvinylidene Fluoride (pvdf) as binder made syrup with few drops of N-Methylene -2-Pyrrolidine. The best electrochemical performance was identified where $x=0.02$ ($\text{LiRh}_{0.02}\text{Fe}_{0.98}\text{PO}_4$ with specific capacity of 159.8 mAhg^{-1} and the capacity fade is only 0.5% after 50 cycle.

Keyword: Li- Ion Battery, LiFePO_4 , Rhodium, capacity fade, electrochemical study.

Introduction:

The increasing demand for portable devices has motivated towards advance Li^+ batteries with high energy density. Currently and most extensively used electrode material for rocking chair batteries are LiCoO_2 cathode and carbon anode was first described by Muzushima et al (1) Due to the toxicity, high cost, safety concern and lower amount of Li^+ insertion reversibly (2) LiCoO_2 is limited to small Li^+ battery applications. There has been deep research on developing new cathode material such as LiMn_2O_4 (3,4) Lithium Nickel based oxide (5) and Layered LiMnO_2 (7,8,9) compounds etc., LiNiO_2 existing two structural modification of which only one is electrochemically active and only few cycles are possible at higher capacities (10). Iron based cathode materials are ideal for future Lithium batteries in terms of low cost and eco friendly nature. Layered LiFeO_2 Synthesized in not suitable and exhibits low average voltage Vs Li^+/Li (8). A group of poly anion XO_4^{3-} ($\text{X}=\text{S}, \text{P}, \text{As}, \text{Mo}$) which combine with lithium and iron has been reported recently (11,12). The stabilization of structure and in turn $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential has been achieved by large polyanion. Among them LiFePO_4 with of the theoretical capacity of 170 mAh/g has an olivine structure (11). However the LiFePO_4 has poor rate performance due to its low chemical conductivity ($\approx 10^{-9} \text{ Scm}^{-1}$) and slow Li^+ diffusion in solid state in alleviated by carbon coating (13), Ion doping (14) are increases the electrical conductivity to $4.8 \times 10^{-2} \text{ S cm}^{-1}$ (15).

The good electrochemical performance is not only by high electrical conductivity of active material but may depend on the ability of Li^+ ion diffusion in the electrode bulk. The rate performance of V-doped LiFePO_4 has repeated as 70 M Ahg^{-1} at 20c rate (16). Only 3.2% capacity fading was observed at 2C rate even after 100 cycle by doping Ti at Fe site (17) The P-type semi conductivity has increased by doping small amount of Ti^{4+} in LiFePO_4 was reported (18) Yourong wang et al. (19) observed that Ru doped LiFePO_4 shows high specific capacity of 101 mAh/g at 5C rate. Low Co content ($\text{LiFe}_{0.8}\text{Co}_{0.2}\text{PO}_4$), the capacity shows limited but detectable enhancement with respect to LiFePO_4 and rich in Co content show far lower initial capacity and rapid fading was identified by N. Penazzi et. al., (20). The Initial specific capacity is about 177 and 167 MA hg^{-1} after 150 cycle in achieved with 2.5% zno doped Li Fe Po_4 cathode (21). To the best of our knowledge there has been no reports on Rh doped LiFePO_4 . Thus the present investigation is aimed at synthesis and evaluate the electrochemical performance of LiFePO_4 and $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$. ($x=0-0.03$)

Experimental:

Microwave aided hydrothermal synthesis of active material is a new attempt yield high place purity. The required amount of Lithium acetate, Ferrous acetate and Ammonium di hydrogen phosphate in deionized water with constant stirring with the flow of N₂ gas through tube to ensure reductive atmosphere. The dense slurry was transfer in to muffle furnace for 15 hrs at 120° C the green dried deposit was pressed into pellets followed by microwave irradiation operated at 2.45 GHZ and 500 W for 10min through activated carbon (22) which is microwave absorber.

The phase purity of prepared compounds were confirmed by XRD with Cu K α radiation. (Philips PW 1700) with rate of 2°/min. The particle morphology was examined by SEM. (Ititachi S-800) operated at 15 Kv. EDS is implemented for evaluating the composition and distribution of elements in the synthesized material.

Positive electrode was prepared by a mixture of 75% active material, 20% acetylene black as conductor and 5% polyvinylidene fluoride (Pvdf) as binder are made a syrup with few drops of N-methyl-2 pyrrolidine, casting on Aluminium foil as current collector and drying in vaccum at 120°C for 25hrs. The counter electrode was graphite pressed on Al foil. Micro porous polyethylene film was used as separator. Lithium hexa fluoro phosphate (LiPF₆) in 1:1 volume ratio of EC:PC is used as electrolyte. The electrochemical performance of active material was evaluated using a coin type cell (CR 2032). Cyclic voltammtry (CV) measurements were performed using EG&G instruments, model 6310 at a scanning rate of 0.1 mV/sec. Electrochemical impedance spectroscopy (EIS) of the fresh electrodes of prepared sample were measured using three electrode cell in the frequency range from 0.1Hz to 100kHz and excitation voltage was 5mV. Charge/Discharge tests were performed between 2.5V and 4.2V using Automatic cycle life tester, Won-A-Tech instruments, Model WPG 100 Potentiostate/ Glavanostate.

Results and Discussion:

The XRD pattern of the synthesized LiRhFePO₄ (where x = 0 to 0.03) were given in fig1. Diffraction peaks of samples are in full accord with the ordered LiFePO₄ olivine structure indexed to the orthorhompic pmnb space group (JCPDS No.40-1499). Rhodium doping does not affect the Lattice structure of LiFePO₄ due to its low concentration but it affect slightly the lattice parameter of LiFePO₄. The structural refinement of the sample allow us to show the variation of lattice parameters were summarized in table1. When the replacement of Fe²⁺ by Rh³⁺ leads to enlarge of unit cell because of the variation in the ionic radii Fe²⁺ $\approx$ 74 pm and Rh³⁺ 80 pm. Decreases in the unit cell volume during Li⁺ deintercalation due to the conversion of Fe²⁺ to Fe³⁺ the latter being small radii than former will collapse the lattice and low Li⁺ diffusion results. But Rh³⁺ doped sample will prevent the collapse of crystal by means of pillar effect. This is similar to that of Ru doped iron phosphate (19). The most favorable concentration of Rh for a better pillar effect and cyclic capability was identified as 0.02.

Table 1: Calculated crystal parameter of LiFe_{1-x}Rh_xPO₄ (x= 0.00 – 0.03)

Li Rh _x Fe _{1-x} Po ₄	a/nm	b/nm	c/nm	V/(nm) ³
0	1.0333	0.6011	0.4692	0.2914
0.01	1.0342	0.6031	0.4710	0.2937
0.02	1.0349	0.6038	0.4720	0.2949
0.03	1.0852	0.6042	0.4723	0.2954

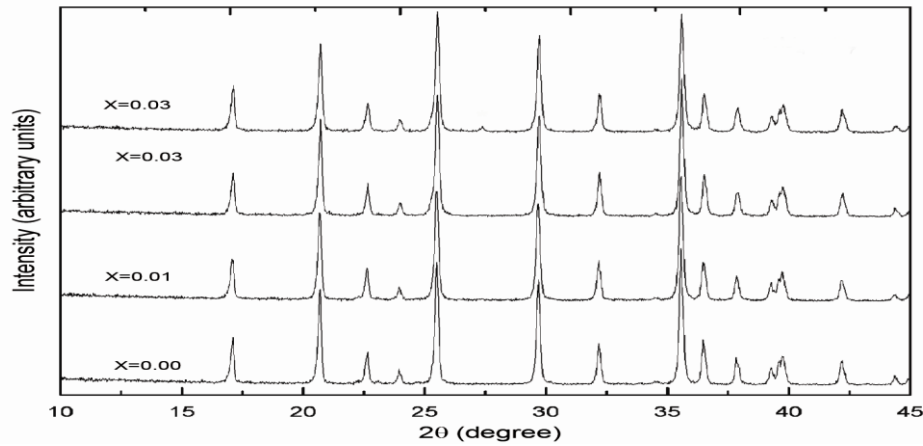


Figure 1: XRD pattern of $\text{LiFe}_{1-x}\text{Rh}_x\text{PO}_4$ ($x = 0.00, 0.01, 0.02, 0.03$)

The morphology of $\text{LiFe}_{1-x}\text{Rh}_x\text{PO}_4$ is shown in fig2. The particle morphology of samples are near spherical and the average crystal size although there are slight agglomeration and a small quantity of fragments. Addition of carbon source during microwave irradiation results in unique morphology and size. Average crystal size of the particle between 400-600nm for undoped and doped LiFePO_4 . It is clear that the particle size became larger for higher Rh^{3+} doped LiFePO_4 .

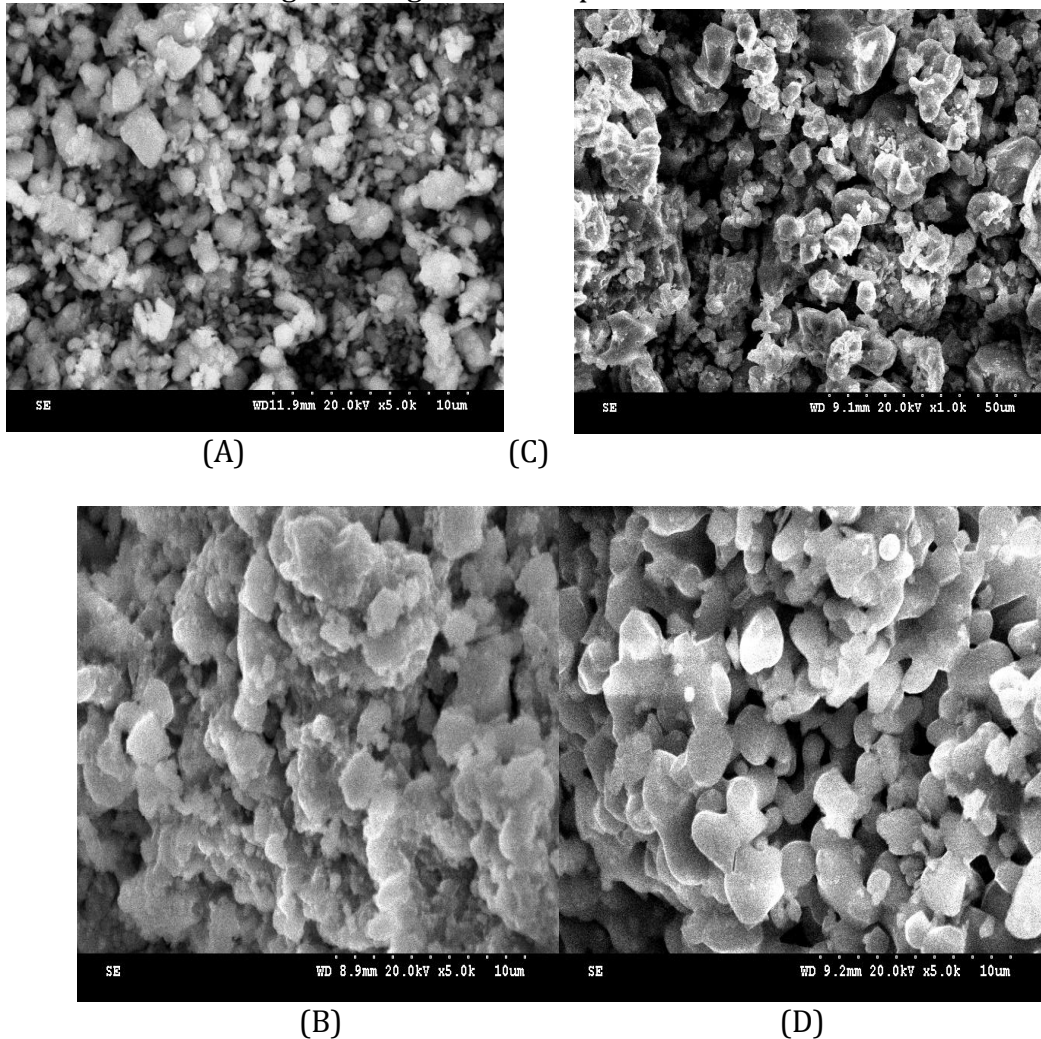


Figure 2: SEM images of (A) LiFePO_4 (B) $\text{LiRh}_{0.01}\text{Fe}_{0.99}\text{PO}_4$ (c) $\text{LiRh}_{0.02}\text{Fe}_{0.98}\text{PO}_4$ and (D) $\text{LiRh}_{0.03}\text{Fe}_{0.97}\text{PO}_4$

Fig. 3 shows the CV curves of the $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0.00 - 0.03$). The CV profile of Rh-doped LiFePO_4 shows sharper shape of the oxidation–reduction peaks than the undoped one does. The similar CV curve with pair of peak is evident single electron reaction mechanism. The shape of CV profile is become sharp for Rh doping. However, the higher content of Rh (0.03) possesses broad and lower peak height. The narrow voltage separation and symmetric CV curve is for better reversibility. Redox peak intensity of doped material is higher than undoped one. The details of the polarized potential and the peak current density of the reactions are presented in Table 2, which implies that the peak current densities were enlarged by Rh-doping, and the reversibility was also improved.

Table 2: Redox potential and peak current density of prepared cathodes

Compound	E_{Ox}	E_{Red}	$\Delta E(E_{\text{Ox}} - E_{\text{Red}})$	$I_p(\text{Ox})$	$I_p(\text{Red})$
$\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$	(V)	(V)	(V)	mA/g	mA/g
X= 0.00	3.650	3.490	0.160	0.243	0.210
X= 0.01	3.640	3.485	0.155	0.310	0.241
X= 0.02	3.663	3.570	0.093	0.352	0.254
X= 0.03	3.630	3.430	0.200	0.252	0.189

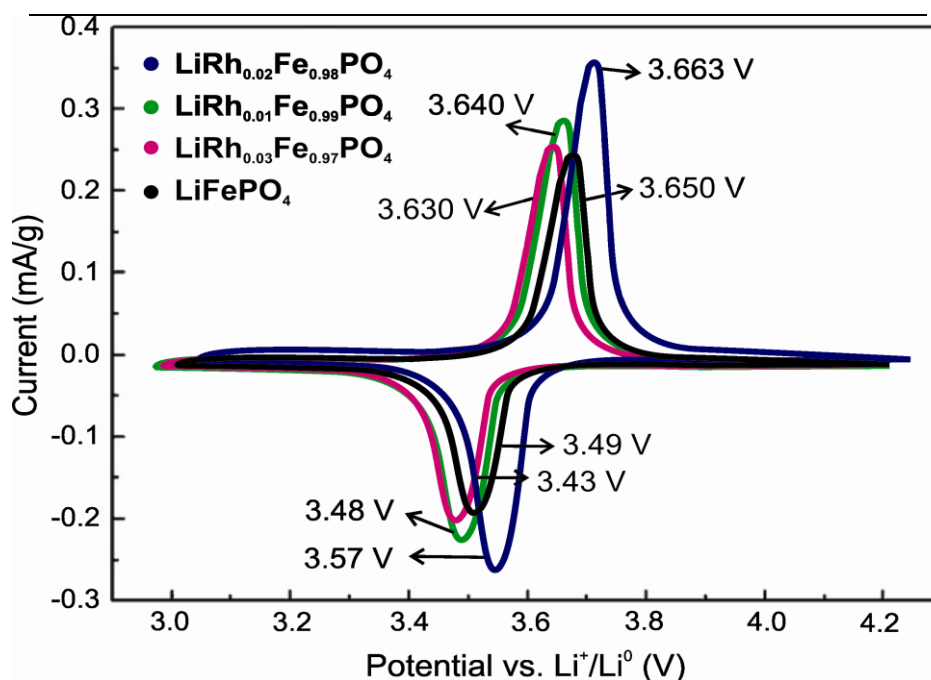


Figure 3: CVs showing the first cycle for the $\text{LiFe}_{1-x}\text{Rh}_x\text{PO}_4$ ($x = 0.00, 0.01, 0.02, 0.03$) samples at 0.1 mV/sec.

The galvanostatic charge/discharge test were carried out to understand the cycling performance of $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$ ($X = 0.00, 0.01, 0.02, 0.03$) cathodes at the first cycle, which were carried out at 0.1C (17mA/g) between 2.5 and 4.2V vs. Li^+/Li . The plateaus of the charge and discharge curve corresponds to Li intercalation and de intercalation reaction. From the Fig. 4 cut off voltage, polarization between charge and discharge plateaus is minimum for $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$ ($X=0.02$) posses better kinetic phenomena and has exhibits significantly better electrochemical performance with a specific capacity of 159.8mAhg^{-1} , which is 94% of its theoretical capacity in contrast, the undoped one exhibit only 139.5mAh g^{-1} .

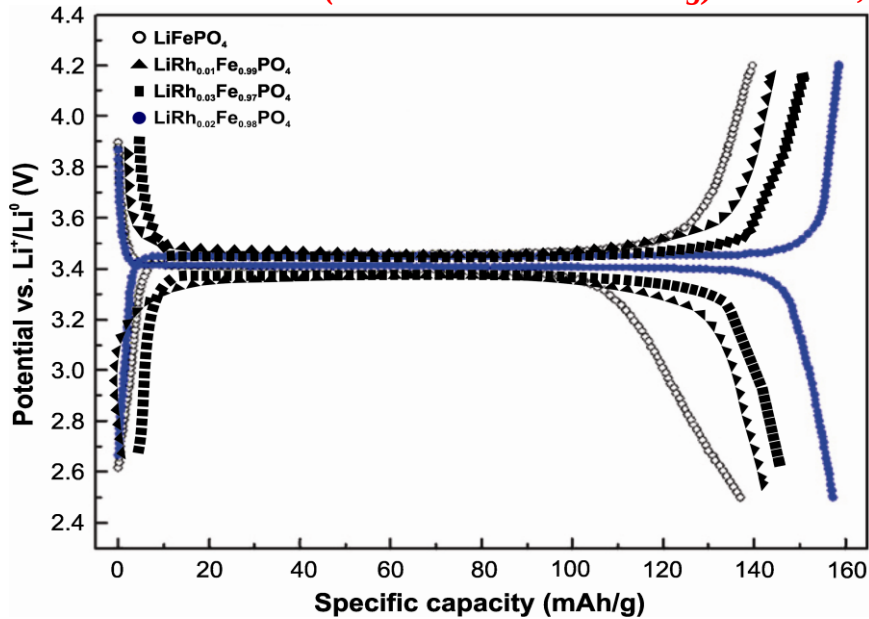


Figure 4: Initial charge/discharge curves of $\text{LiRh}_x\text{Fe}_{1-x}\text{PO}_4$ ($X=0.00, 0.01, 0.02, 0.03$.) cathodes at a current rate of 0.1C

The cycling behavior of prepared sample at 0.1C were compared with pure LiFePO_4 which shows no obvious capacity fade after 20 cycles. When the amount of Rh reaches 0.02, achieve better cycle performance with discharge capacity 159.0mAh/g after 50cycle has 0.5 % of capacity fade, is mainly attributed by enhancement of electronic conductivity and increases in lattice volume to facilitate the Li ion insertion- extraction process has better agreement with XRD results. However, higher concentration of Rhodium ($x=0.03$) shows poor electrochemical behavior due to higher charge transfer resistance. Thus the better doping concentration of Rhodium is fixed as 0.02.

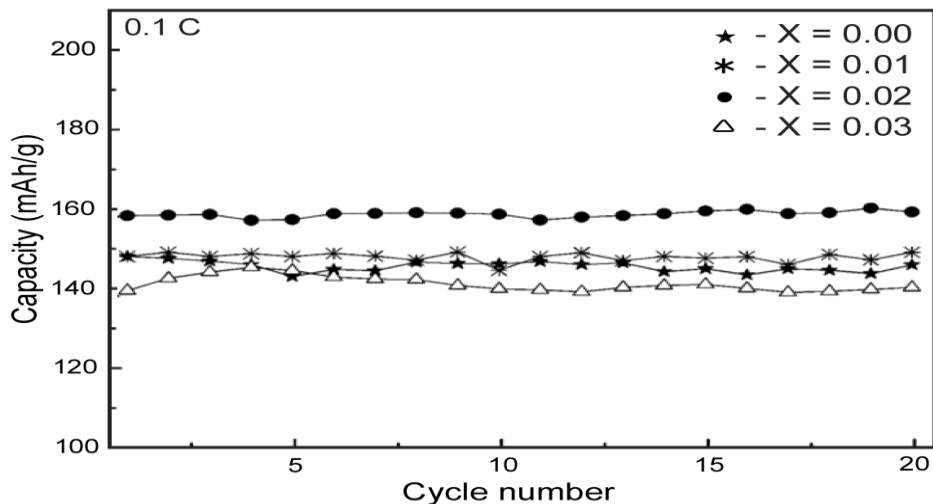


Figure 5: Cycling performance of $\text{LiFe}_{1-x}\text{Ru}_x\text{PO}_4$ ($X=0.01-0.03$) at 0.1C

The Nyquist Plots of $\text{Rh}_{0.02}\text{Fe}_{0.98}\text{PO}_4$ with various cycle numbers (1, 50, and 100) are shown in Fig.5. All the impedance profile shows a semicircle in the high frequency region and straight line at low frequency region. The diameter of semicircle on Z_{re} axis is approximately equal to R_{ct} (charge transfer resistance) (19, 23). It is observed that the resistance of the sample at first, 50th and 100th cycle are 125, 132, 141 ohm respectively. The diffusion of lithium ion in to the bulk of the electrode is evident from the straight

line in the low frequency region is called "Warburg diffusion". The diffusion coefficient and exchange current density which is inversely related with R_{ct} . It is observed that slope of low frequency region slightly down upon cycling.

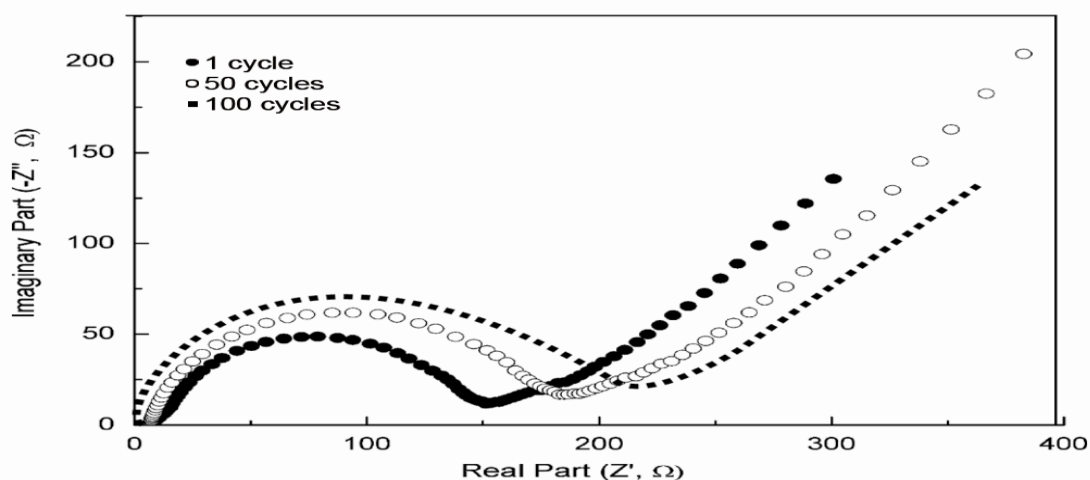


Figure 6: The Nyquist Plots of $Rh_{0.02}Fe_{0.98}PO_4$ with various cycle number

Conclusion:

The structure and electrochemical properties of $LiFePO_4$ and $LiRh_xFe_{1-x}PO_4$ were synthesized by microwave method are properly examined by physical and electrochemical methods. The Rh doped compound, $LiRh_{0.02}Fe_{0.98}PO_4$ was identified as better cathode than undoped material. This is mainly attributed the contraction of unit cell volume for parent compound during Li^+ extraction where Fe^{2+} is converted in to Fe^{3+} results low Li^+ diffusion, where as Rh doped $LiFePO_4$ contraction of unit cell volume has been compensated by Rh^{3+} which is higher radii than Fe^{3+} , stabilize the unit cell volume by means of pillar effect.

References:

1. K.Mizushima, P.C. Jones, P.J. Wiseman and J.B. Good enough *Muter Sci. Eng. B₃* (1980) 97.
2. C.Delmas, *Muter Sci. Eng. B₃* (1989) 97.
3. J.M. Taraswn, E.Wang, F.K.Shokouhi, W.R Mckinnon and S. Colsor, *J.Electrochem, Soc*, 138 2859 (1991)
4. M.M. Tlackoray, *J. Electrichom, Soc.*, 142, 355 (1955)
5. G.X Nang's Zhong, D.A. Bradhurst, S.X Dou and Hik Liu *solid state Iorics* 116, 271 (1999)
6. AR. Armstrong and P.G Brace, *Nature (London)* 381, 499 (96)
7. Z.P. Guo, S.Zrong G.x wang, G.Walter, H.K. Liu and S.X Dou, *J. Electrochem Soc.* 149, 792 (2002)
8. R.Kanno, T.Shirane, Y.Inaba and Y.Kawarnoto *J.Power sources* 68, 145 (1997).
9. T.Sakurai, H. Arai, S.Okada, and J. Yarnaki *J.Powersources* 68, 711 (1977).
10. T.Ohzuku, H.Noguchi, K.Yamamoto and M.Yostio *J.Ceram Soc. (Japan)* 102 (1994) 258.
11. A.K Padi, ks Nayuiduswamy and JB good enough *J. Electronical SOC*, 144 1188 (1997).
12. A.K padi k.S. Nayundaswamy, C.Masquelior, S.Okada *J.B. Good enough J.Electronical Soc*, 144, 1609 (1997).
13. M.M. Doeffer, Y.Hu, F.Mclarnon, R. Kostecki, *Electronical solid state left* 6 (2001) A 207.
14. PS.Herle, B. Ellis, N.Coobs, L.F Nazar *Nat.Mater* 3 (2004) 147.

15. S.Y chung Y.M. Chiang, Eletrochem, solide state left 6 (2003) A 278.
16. C.S. Sun Z.Zhou, Z.G.Xu, DG.Wang, J.P.wei. X.K.Bian, J.Yan, I power sources 193 (2009) 841-45
17. Lingjun Li, Xinlai Li,, Zlixing wang, Ling Wu, Jun chaozhang, Huajun Guo J.F Physics and electroing of soliodo 70 (2009) 238 242.
18. G.X Wang, S.Bowlay, S.A Needhan, J.Electroeham Soc. 153(1) A 23. A2 (2006).
19. Yourong wong, S.Bowlay, S.A Needham, J.Electrochem Soc.153 (1) A 23 A21 (2006)
Yourong wakq yifu yang, xin Hu Yanbo yang J.F alloaways and compounds 481 (2009) 540 -594.
20. N.Penazzi et.al., J. of the European ceramic society24 (2004) 1381 – 1384.
21. A tofy.Sheaouda, Hua K.Liu J.F alloys and compounds 477 (2009) 498 – 503.
22. Misashi Higchi, keiichi katuyama, J.F power sources 119 – 121 (2003) 258 – 261.
23. H.Liv, a.Cao, L.J, C.Li, Y.P. Wu, Electrochem. commu 8 (2006 / 1553.
24. Dan Li. Yudai Huang. et.al., Solid state Electrochem(2010) 14: 889-895.