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RESEARCH ARTICLE

CURRENT DEVELOPEMENTS ABOUT $LiFePO_4$ BATTERY FOR STATIONARY ENERGY STORAGE IN AFRICA

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Abstract

Stationary energy storage is one of current and major challenge in the world. $LiFePO_4$(LFP) batteries have been used more and more for several applications, stationary energy storage specifically.This technology of batteries is one of promising candidates for power lithium ion batteries due to their flat voltage profile, environmental benignity, cycling stability, and high theoretical capacity. However, the poor electronic conductivity and a low lithium ion diffusion coefficient of $LiFePO_4$ cathode materials are the mains disadvantage which make the researchers to investigate on doping materials. This review summarize the main research which allow to improve electrochemical performance of the $LiFePO_4$ batteries in context of stationary energy storage. The improvement of $LiFePO_4$ batteries is mainly due to the cathode. Li-site doped with particular elements increase the width of the one-dimensional diffusion channels of lithium ions and decrease the charge transfer resistance, which resulted in a good electrochemical performance of doped $LiFePO_4$. Fe-site doping enhance the electronic conductivity of $LiFePO_4$ while O-site doped with proper ion improve the intrinsic conductivity and promote the redox potential of $LiFePO_4$. Furthermore, multi-elements co-doping enhance the electrochemical performances of$LiFePO_4$cathodes.The more interesting doping are:
$LiFe_{0.975}Zn_{0.025}PO_4$,$LiV_{0.069}Ti_{0.025}Fe_{0.905}PO_4$and
$Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4$

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Introduction:-

During the last decade, renewable energy sources have been widely used for the electrification of isolated sites, especially in tropical Africa. According to the International Renewable Energy Agency, annual electricity consumption in West Africa could quadruple by 2030, reaching 219 TWh per year, against only 52.5 TWh in 2015 (1). The operation of an electrical system from renewable energies, such as wind or solar energy, is often limited by the variable and intermittent nature of these energies. As the main renewables (wind, solar) are intermittent, the operation of power systems with a high proportion of renewables will only be possible if the electricity can be stored efficiently. To ensure continuity in the production of energy, it is therefore necessary to use energy storage systems (2). One of the most proven and efficient solutions for the storage of electrical energy is the use accumulation

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batteries (3). Indeed, if several electrical storage technologies coexist, with different characteristics more or less adapted to the different applications, the battery is today the new technology leader both technically and economically for the majority of applications including stationary storage.

Several comparative studies between the different battery technologies used for stationary storage of electricity, have nowadays raised $LiFePO_4$(LFP) battery technology to the top rank (4).For about two decades, these LFP batteries have gradually replaced the lead-acid batteries which have known a remarkable failure for stationary electricity storage. LFP batteries is one of competitive candidate of lithium ion batteries technology for stationary electricity storage. But its poor electronic conductivity and low lithium ion diffusion coefficient limited its further application. Many efforts have been devoted to improve electrochemical performance of the LiFePO4 cathode. This review summarizes the main research about LFPbatteries.

General description of lithium batteries:-

Lithium battery technology was born in the 1960s. This technology is based on the interesting properties of lithium. Indeed, lithium is a silver-white alkali metal, with symbol Li and atomic number 3. It has the following advantages:

- Lithium (Li) is the metal with the lowest atomic weight (a molar mass equal to 6.941 g/mol) in the periodic table of chemical elements. Its density is the lowest of metals ($0{,}534\ g/cm^3$ at $20°C$).
- As an electrochemical energy storage material, lithium at a specific capacity is very high (about 3.8 Ah/g).
- Lithium has the lowest electrode potential. Its standard potential (Li/Li^+) equal to -3.045 V, which gives it a very pronounced reducing character. By associating lithium with an oxidant, we can have an electromotive force greater than that created by most electrochemical couples.

All these advantages have made lithium batteries, the subject of several researches. This has led to the successive implementation of several lithium battery technologies, which we present in the following...

From lithium metal batteries to lithium ion batteries:

Early lithium batteries used metallic lithium as a negative electrode material. This idea of using metallic lithium was born thanks to the development of intercalation electrode batteries. This gave birth, in the 1970s, to the first lithium metal batteries. These batteries have:

- a negative electrode made of metallic lithium,
- a positive electrode into an insertion compound such that MoS_2
- an organic electrolyte containing a lithium salt.

However, this technology very quickly revealed security issues. Indeed, over time, during the cyclic operation of charging and discharging lithium metal batteries, lithium filaments called dendrites are formed at the level of the negative electrode. These dendrites eventually touch the positive electrode, causing a short circuit and in some cases, the explosion of the battery.Faced with this problem, two main solutions for safety were developed: lithium-polymer (Li-Po) technology and Li-ion technology.

Li-Po batteries are virtually identical to lithium metal batteries. Indeed, the electrodes do not change and the metal anode is preserved. The liquid electrolyte is replaced by a polymer electrolyte that strongly limits the formation of dendrites but has the disadvantage of limiting the mobility of lithium ions from one electrode to another and therefore the specific energy of the battery.

Li-ion technology, on the other hand, consists of replacing metallic lithium with a material whose structure allows the insertion and disintegration of lithium ions. (4)

Principe of operation of a Li-ion battery:

Figure 1 shows the main constituents of a Li-ion cell and circulation of electrons and lithium ions during discharge. There are two electrodes, one positive and the other negative. These electrodes have an overall potential difference that is a function of the chemical nature of the two electrode materials. Each electrode has a support serving as a metal current collector, most often an aluminum collector for the positive electrode and a copper collector for the negative electrode. The electrode is composed of active ingredients (> 80%), an electronic percolate (carbon black) and a polymer binder. Metal collectors are connected to an external circuit, their role being to ensure the circulation of electrons. It should be noted that a separator is arranged between the two electrodes in order to avoid an internal short circuit. It is a porous membrane; whose role is to allow the passage of ions between the two electrodes without allowing electronic conduction. Both electrodes are bathed in an electrolyte whose ionic conductivity is high to facilitate the movement of Li^+ions.

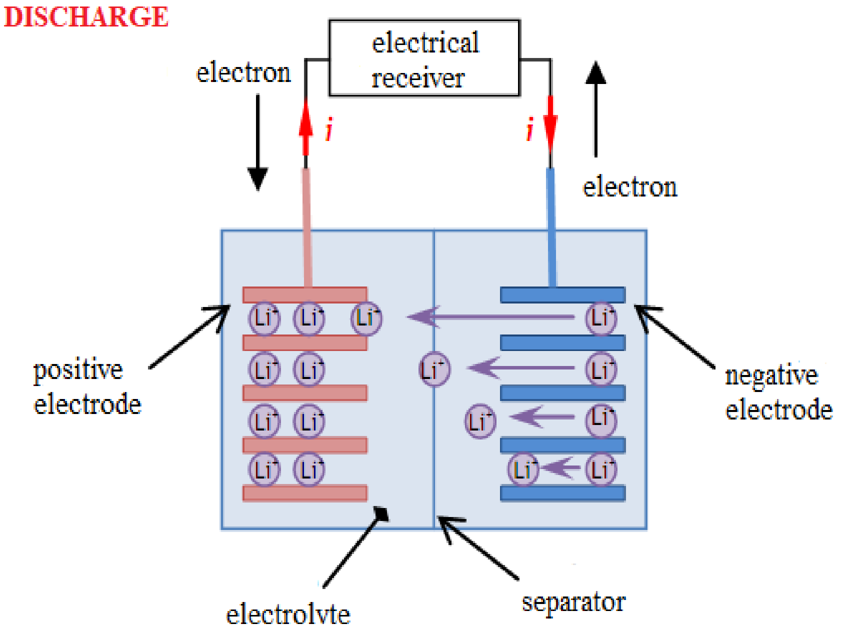

Figure 1:- Constitution of a Li-ion cell and circulation of electrons and lithium ions during discharge

The functioning of the Li-ion cell is based on two different reactions:

- electrochemical redox reactions that take place at the level of the active ingredients of the electrodes
- the solid chemistry reaction, called insertion/disintegration, in which ions with a very small diameter take place in the host crystal structure of the two electrodes. Li^+

During the discharge of the Li-ion battery, the ion leaves the negative electrode which also releases an electron to ensure its electrical neutrality. This electron will be captured by the aluminum collector of the positive electrode after circulating in the external circuit containing the electrical charges or receivers to be powered. As for the ion, it migrates into the electrolyte, passes through the separator and reaches the surface of the positive electrode where it diffuses to insert itself into a vacant active site in the host structure. It will then be recombined with an electron that has successively passed through the copper collector of the negative electrode, the external circuit and the aluminum collector of the positive electrode. Li^+

While the Li-ion battery is charging, the process reverses. The battery has an external electromotive force. This requires displacement of the ion that Li^+leaves the positive electrode to the negative electrode. The positive electrode also releases an electron to ensure its electrical neutrality. This electron will be captured by the copper collector of the negative electrode after circulating in the external circuit. As for the ion it migrates into the electrolyte, passes through the separator and reaches the surface of the negative electrode where it diffuses to insert itself on a vacant active site in the host structure. It will then recombise with an electron that has successively passed through the aluminum collector of the positive electrode, the external circuit and the copper collector of the negative electrode. The redox reactions corresponding to these different processes are:

$$\mathrm{Li}_{1-y}\mathrm{M} + y\mathrm{Li}^+ + ye^- \underset{\textbf{charge}}{\overset{\textbf{discharge}}{\rightleftarrows}} \mathrm{LiM} \qquad \text{(1) on the positive electrode (cathode)}$$

$$\mathrm{LiC}_6 \underset{\textbf{charge}}{\overset{\textbf{discharge}}{\rightleftarrows}} \mathrm{Li}_{1-x}\mathrm{C}_6 + x\mathrm{Li}^+ + xe^- \qquad \text{(2) on the negative electrode (anode), usually}$$

In case of LFP batteries, M is FePO_4

Diffferent lithium–ion battery technologies

In order to improve the performance of Li-ion batteries, in terms of power, stored energy, lifespan, cost, and safety/reliability of use, a multitude of research works have been conducted and are continuing. The majority of research follows two main parallel axes. On the one hand, it is the development of the insertion materials that go into the battery (the negative electrode, the positive electrode, the electrolyte and the separator) and on the other hand, the optimization and choice of the most appropriate combinations to improve the performance of Li-ion batteries.

The development of li-ion battery insertion materials to increase the potential difference between the positive and negative electrodes is in order to increase energy. Many research projects aim to optimize these insertion materials. The majority of this work focuses on positive electrode materials, due on the one hand to the small contribution of the standard (carbon-based) negative electrode material to the total cost of cell design, and on the other hand to the significant influence of positive electrode materials on the life and performance of Li-ion batteries(5). It should be noted, however, that new work is trying to give a future to the negative lithium metal electrode for the development of rechargeable batteries (6).

Negative electrode insertion materials:

To overcome the safety problems encountered in lithium metal batteries, one of the solutions was to replace lithium metal with other insertion materials at the negative electrode. Thus, these materials have a standard potential as close as possible to that of lithium. Robert et al .(7) on the one hand, and Badin(8) on the other, reflected on the issue. They tested different materials for the replacement of lithium metal at the negative electrode. The following Table 1 summarizethe results achieved:

Table 1:- Negative electrode insertion materials(7) (8)

Material	Difference between the standard potential of the material and that of Lithium (V)	Theoretical specific capacity (mAh/g)
Metallic Li	0	3800
LiC_6 (Graphite)	0.02 to 0.3	372
$Li_{0.05}C_6$ (coke)	0.2 to 1.3	185
Li-Al	0.2	800
$Li_4Ti_5O_{12}$ (LTO)	1.5	175
$LiWO_2$	0.3 to 1.4	120
$LiMoO_2$	0.8 to 1.4	199
$LiTiS_2$	1.5 to 2.7	226

These results from Badin et al. make it possible to raise graphite to the highest rank for the choice of substitute materials for lithium metal to the negative electrode. However, the theoretical specific capacity of graphite is slightly lower. In addition to having a standard potential as close as possible to that of lithium, the insertion materials of the negative electrode must allow lithiation and disintegration with the smallest change in volume. Three different materials were tested for the replacement of lithium metal at the negative electrode. The following Table 2 summarizes the results obtained.

Table 2:-Change in volume of the negative electrode(9)

Material	Percentage of volume change during a full battery charge
Si	270 %
LiC_6 (graphite)	10 %
$Li_4Ti_5O_{12}$ (LTO)	0,2 %

Positive electrode insertion materials:

Several research projects have been devoted to the development of new insertion material at the positive electrode of Li-ion batteries. The insertion materials developed for the positive electrode can be arranged in four groups according to their crystal structure. The doping modification is classified into Li-site doping, Fe-site doping, O-site doping, and multi-elements co-doping. Each kind of doping method effects on the rate capability and cyclic performance of $LiFePO_4$ cathodes are presented.

Li-site doping

Researcher have substituted Li-site by ions with small ionic radius. This substitution or doping would increase the width of the one dimensional diffusion channels of lithium ions and decrease the charge transfer resistance, which in turn enhance the electrochemical performance of $LiFePO_4$ cathodes. The mains research about Li-site doping of $LiFePO_4$ cathodes are summarized in table 3.

Table 3:-Li-site doping of $LiFePO_4$ cathodes.

Compound	Specific capacity ($\mathbf{mAh.g^{-1}}$) - current rate	Synthesis methods	Main conclusions
$Li_{0.97}Na_{0.03}FePO_4$ (10)	158 – (0.1 C) (10)	restriction–carbonthermal reduction method	• Na doping improve the electronic conductive property and ionic transport feature of $LiFePO_4$ • Na doping decrease the charge transfer resistance of $LiFePO_4$, improve its lithium diffusion coefficients,the kinetic and electrochemical performance of $LiFePO_4$. (10) (11)
$Li_{0.95}Na_{0.05}FePO_4$ (11)	164.2 – (0.2 C) (11) 151.5 – (1 C) (11) 130.5 – (2 C) (11)	co-precipitation method	
$Li_{0.99}Nb_{0.01}FePO_4$ (12)	139.3 – (1 C) (12)	mechanochemical activation	Nb doping in the Li-site enhance the electronic conductivity of $LiFePO_4$ and discharge capacity (22.4mAh.g^{-1} higher than un-doped samples)(12)
$Li_{0.97}Al_{0.01}FePO_4$(13)	95 – (0.2 C) (13)	neutron diffraction method	• Al doping decrease slightly the discharge capacity (13) • Al-doping induce gap states in $LiFePO_4$ and create the lithium vacancy upon lithium extraction. (14) (15) • Al particle size affect negatively the electrochemical performance of $LiFePO_4$.
$Li_{0.97}K_{0.03}FePO_4$ (16)	154 – (0.1 C) (16) 142 – (1 C) (16) 131 – (2 C) (16) 90 – (5 C) (16)	sol–gel method	K in the Li-site doping increase the lithium ion diffusion coefficient and decrease the charge transfer resistance. (16)
$Li_{0.99}Nd_{0.01}FePO_4$ (17)	161 – (0.1 C) (17)	novel solid-state reaction method	• Nd-doping increase the lithium vacancies and favor the deintercalation of interior lithium ions, thus enhancing the intrinsic electronic conductivity of $LiFePO_4$. • Nd doping improve discharge capacity, cycling performance and electrode impedance of $LiFePO_4$ cathodes. (17)

Fe-site doping :

Theoretically, doping alkali metal ion in Fe-site facilitate the diffusion of lithium ions along the 1D pathway, and increase both the electronic and ionic conductivity of the $LiFePO_4$ cathodes. All the Fe-site doping modifications contribute to optimize the electrochemical performance of $LiFePO_4$ cathodes. The mains research about Fe-site doping of $LiFePO_4$ cathodes are summarized in table4.

Table 4:- Fe-site doping of $LiFePO_4$ cathodes.

Compound	Specific capacity ($\mathbf{mAh.g^{-1}}$) – current rate	Synthesis methods	Main conclusions
$LiFe_{0.99}La_{0.01}PO_4$ (18)	156 – (0.2 C) (18)	high temperature solid state method	La-doping in the Fe-site did not affect the structure of $LiFePO_4$, but considerably improved its capacity performance and cyclic stability. (18) (19)
$LiFe_{0.995}La_{0.005}PO_4$ (19)	167.7– (0.1 C) (19)		
$LiFe_{1-x}Cu_xPO_4$ (20)	102– (0.2C) (20)	Sol-gel method	• Cu doping induce gap states in $LiFePO_4$,

			improve the discharge capacity, cyclic and rate performance of $LiFePO_4$ • Cu doping is an effective way to improve the electro chemical performance of $LiFePO_4$ and $LiFePO_4$ showed a promising material for use as cathode material in lithium ion battery. (20)
$LiFe_{0.98}Y_{0.02}PO_4$ (21)	166.7– (0.2 C) (21) 155.8– (0.5 C) (21) 148.2– (1 C) (21) 139.8– (2 C) (21) 121.1– (5 C) (21)	high temperature solid state method	Y doping maintain the microstructure of $LiFePO_4$, modify the particle morphology, decrease the charge transfer resistance, enhance the exchange current density and the electrochemical performance of the $LiFePO_4$ (21)
$LiFe_{0.97}V_{0.03}PO_4$ (22)	140.2– (5 C) (23) 120.4– (10 C) (23) 105.8– (20 C) (23)	quasi-sol-gel method	• V-doping refine $LiFePO_4$ particle size, induce the lattice distortion to weak the Li-O bonds, and improve the electronic conductivity and the electrochemical performance of the $LiFePO_4$ (23) • V-doped $LiFePO_4$ have an enhanced electrochemical performance especially at high rates. (22) (23) • The improvement of the reaction kinetics in V-doped $LiFePO_4$ cathodes is due to the decreasing of the electrochemical capacity after some cycle. (22)
$LiFe_{(1-x)}Mn_xPO_4$ (24)	131.4– (0.1 C) (24)	Liquid solution combined with solid-state method	• Mn-doping have no direct contribution to the electrochemical reaction of $LiFePO_4$ cathode, but improve both the electronic and ionic conductivities. • Mn-doping held a stable cycling performance • Mn-doped $LiFePO_4$ did not work completely at a higher discharge rate due to electrical conductivity and a serious Jahn-Teller effect of Mn^{2+} ions(24)
$LiFe_{0.96}Mg_{0.04}PO_4$ (25)	155– (0.2 C) (25) 148– (0.5 C) (25) 140– (1 C) (25) 137– (2 C) (25)	Reaction extrusion method	• Mg doping improve highly lithium ion conductivity and electronic conductivity • Mg doping in the Fe-site reduce the electrode polarization effectively without any serious effects on material structure and morphology (25)
$LiFe_{0.94}Bi_{0.04}PO_4$ (26)	149.6 – (0.1 C)(26)	sol-gel method	Bi-doping can dramatically decrease the charge transfer resistance of $LiFePO_4$/C(26)
$LiFe_{0.75}Co_{0.25}PO_4$ (27)	170 – (0.1 C) (27)	Sol-carbothermal method	Co-doping in the Fe-site did not have a favorable effect on the electrochemical performance of $LiFePO_4$ cathode materials (27)
$LiFe_{0.99}Co_{0.01}PO_4$ (28)	154.5 – (0.5 C) (28) 114.8– (10 C) (28) 104.2 – (20 C) (28)	Sol-carbothermal method	Co-doping increase the intrinsic defect of $LiFePO_4$ (28)
$LiFe_{0.96}Pt_{0.04}PO_4$ (29)	168– (0.1 C) (29) 162– (0.2 C) (29) 135– (1 C) (29) 120– (5 C) (29) 102– (10 C) (29)	Hydrothermal method	Pt-doping in the Fe-site stabilize the structure and enhance the lithium ion conductivity of $LiFePO_4$ abd the specifiy capacity (29)

$LiFe_{0.96}Pd_{0.04}PO_4$ (30)	107– (0.2 C) (30) 79– (1 C) (30) 58- (5 C) (30) 42– (10 C) (30)	Sol-gel method	• Pd-doping affect the specific capacity of $LiFePO_4$(30) • Pd-doping enhance the electrochemical performance of $LiFePO_4$ and improve the electrical conductivity and electrochemical performance of $LiFePO_4$ (30)
$LiFe_{0.95}Ni_{0.05}PO_4$ (31)	155– (0.2 C) (31)	sol-gel-assisted carbothermal reduction method	• Ni-doping improve the electrical conductivity and diffusion coefficient of lithium ions. • Ni-doped $LiFePO_4$/C has an excellent high-rate charge, discharge capability, and long-term cyclability(31)
$LiFe_{0.975}Zn_{0.025}PO_4$ (32)	177– (0.02 C) (32)	Solid-statehigh temperature reaction	Zn-doped $LiFePO_4$ exhibited great electrochemical performance higherthan the un-doped sample . (32)
$LiFe_{(1-3x)}Mo_xPO_4$ (33)	162– (0.5 C) (33)	microwave-assisted method	Mo-doping wide the lithium ion migration channels,and shows enhanced capacity retention compared to that of undoped LiFePO4/C. Moreover, the electrode exhibits excellent rate capability, with an associated high discharge capacity and good electrochemical reversibility(33)
$LiFe_{0.97}Cr_{0.03}PO_4$ (34)	151.5 – (0.1 C) (34) 120 – (10 C) (34)	mechanochemical process followed with a one-step heat-treatment	Cr-doping improve the rate performance which is attributed to the phase transformation between triphylite and heterosite during cycling(34)

O-site doping in

Theoretically, the conductivity of $LiFePO_4$ can be significantly enhanced by O-site doping. It is verified that the enhanced conductivity is due to the proper ions doping suppressed anti site defects in $LiFePO_4$, which facilitated the migration of lithium ions in the diffusion channels without blockage . The mains research about O-site doping of $LiFePO_4$ cathodes are summarized in table5.

Table 5:- O-site doping of $LiFePO_4$ cathodes.

Compound	Specific capacity $(mAh.g^{-1})$ - current rate	Synthesis methods	Main conclusions
$LiFe(PO_4)_{0.95}F_{0.15}$ (35)	162 – (0.1 C) (35) 113 – (10 C) (35) 78 - (40 C) (35)	carbothermal reduction route	F-doping improve the cycling performance, electrochemical performance and the discharge capacity (35) (36)
$LiFe(PO_4)_{1-x}Cl_x$ (37)	162– (0.1 C) (37) 90– (20 C) (37)	carbothermal reduction route	• Cl-doping optimize electrochemical reaction ,promote lithium ions diffusion in the bulk of LiFePO4 and enhanced discharge capacity and reversibility of LiFePO4(37) • Cl-doping facilitated the electrochemical reaction during cycling and thus improved the high-rate capability, which mainly resulted from the improvement of the Li+ ion diffusion in the bulk of the material. The optimized Li+ ion diffusion could be attributed to the introduction of Cl− into the lattice of olivine structure, which resulted in the weakness of Li–O bonds.

Multi-Elements Doping

Recently, multi-elements doping modification attracted much attention, which means doping with more than one kind of element. Research in this area can be divided into two groups : doping on different elements in the same site of $LiFePO_4$ and doping on different elements in different sites of $LiFePO_4$. The mains research about doping on different elements in the same site of $LiFePO_4$ summarized in table6.

Table 6:- Doping on different elements in the same site of $LiFePO_4$.

Compound	Specific capacity $(\boldsymbol{mAh.g^{-1}})$ - current rate	Synthesis methods	Main conclusions
$LiV_{0.069}Ti_{0.025}Fe_{0.905}PO_4$ (38)	144.1 – (10 C)(38) 124.8– (20 C)(38)	carbothermal reduction method	Ti and V co-doped on the Fe-site maintain the olivine structure, increase the electronic conductivity, improve the lithium ion diffusion coefficient, and thus lead to the enhanced electrochemical performance of $LiFePO_4$(38)
$LiFe_{0.95}Ni_{0.02}Mn_{0.03}PO_4$ (39)	145 – (1 C)(39)	high-temperature solid-state route	Ni and Mn co-doped on the Fe-site have a stable crystal structure, enhance the cycling and rate capability (39)
$LiFe_{0.97}(Ni_{0.98}Co_{0.01}Mn_{0.01})_{0.03}PO_4$ (40)	150.6– (1 C) (40) 116.5– (10 C) (40)	the spen electroless nickel plating solution	Ni, Co and Mn co-doped on the Fe-site modify the particle morphology, decrease the charge transfer resistance, improve the lithium ion diffusion coefficient, and in turn enhance the electrochemical properties of $LiFePO_4$(40)

The mains research about doping on different elements in different sites of $LiFePO_4$ are summarized in table7.

Table 7:- Doping on different elements in different sites of $LiFePO_4$

Compound	Specific capacity $(\boldsymbol{mAh.g^{-1}})$ - current rate	Synthesis methods	Main conclusions
$Li_{0.97}Na_{0.03}Fe_{0.97}Ti_{0.03}PO_4$ (41)	151 – (1 C) (41)	simple high-temperature solid-state method	Na doping on the Li-site and Ti doping on the Fe-site of the $LiFePO_4$/C, promote lithium ion diffusion, optimize its crystal microstructure, enhance electrical conductivity, modify the particle morphology, decrease charge transfer resistance, and thus in turn improve its electrochemical performance(41)
$Li_{0.97}Na_{0.03}Fe_{0.97}V_{0.03}PO_4$ (42)	156.5 – (0.1C) (42)	sol-gel method	Na doping on the Li-site and V doping on the Fe-site of the $LiFePO_4$ exhibited smaller particle size, smaller charge-transfer resistance, higher discharge capacity, more stable cycle performance and better rate capability (42)
$Li_{0.99}Nb_{0.01}Fe_{0.97}Ti_{0.03}PO_4$ (43)	163.3 – (0.1C) (43)	sol-gel method	Nb doping on the Li-site and Ti doping on the Fe-site of the $LiFePO_4$ increase the lithium ion conductivity, improve the reaction reversibility, decrease the

			charge transfer resistance, and thus in turn enhance the electrochemical performance of $LiFePO_4$ (43)
$Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4$ (44)	120.3– (1 C) (44) 85.4– (10 C) (44) 75.3– (20 C)(44) 56.6– (50 C)(44)	simple solution impregnation process using carbon aerogel	La doping on the Li-site and Mg doping on the Fe-site of the $LiFePO_4$ maintain the olivine structure and improve the electrochemical performance of the $LiFePO_4$ at low temperature and high rate (44)
$LiFe_{0.92}Mg_{0.08}(PO_4)_{0.99}F_{0.03}$ (45)	121– (0.1 C) (45) 109– (1 C) (45) 94– (2 C) (45) 74– (5 C) (45)	simple solid state reaction	• Mg doping on the Fe-site and F doping on the PO_4-site of the LiFePO enhance electrochemical performance of $LiFePO_4$/C • Carbon coating is not a major factor which influence the electrochemical performance of Mg and F co-doped $LiFePO_4$ (45)

Graphic synthesis of mains doping LiFePO4 cathode of LFP batteries: -

The various investigations of the researchers on the improvement of LFP batteries revealed that the improvement in the performance of this battery technology is mainly related to the cathode. The figure below summarizes the mains researches about doping $LiFePO_4$ cathode of LFP batteries.

This graphic allows to make a general comparison of the various researches on the development of the cathode of $LiFePO_4$ batteries. It also allows to study the current limits and to detect the possible combinations which can permits to exceed these limits.

Conclusion:-

In order to address the challenges of availability, price and environmental impacts, renewable energies (solar, wind, hydroelectric, etc.) are increasingly occupying the main place in the global energy mix. However, the intermittency of these energy sources presents a challenge of continuous energy supply, so an energy reservoir is needed to ensure a continuous supply of energy produced. Stationary energy storage has therefore become a global issue and a major challenge.

Among the technologies currently used for stationary energy storage, we find $LiFePO_4$batteries . This technology of batteries LiFePO4 have been considered as promising candidates for power lithium ion batteries due to their flat voltage profile, environmental benignity, cycling stability, and high theoretical capacity. However, the poor electronic conductivity and a low lithium ion diffusion coefficient of LiFePO4 cathode materials are the mains disadvantage which make the researchers to investigate on doping materials. The improvement of $LiFePO_4$ batteries is mainly due to the cathode. Li-site doped with particular elements would increase the width of the one-dimensional diffusion channels of lithium ions and decrease the charge transfer resistance, which resulted in a good electrochemical performance ofdoped $LiFePO_4$. Fe-site doping enhance the electronic conductivity of $LiFePO_4$. O-site doped with proper ion improve the intrinsic conductivity and promote the redox potential of $LiFePO_4$. Furthermore, multi-elements co-doping is a combination of these three kinds of mentioned doping methods, which is demonstrated to effectively enhance the electrochemical performances of LiFePO4 cathodes.

The more interesting doping are: $LiFe_{0.975}Zn_{0.025}PO_4$(32),$LiV_{0.069}Ti_{0.025}Fe_{0.905}PO_4$(38) and$Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4$(44).

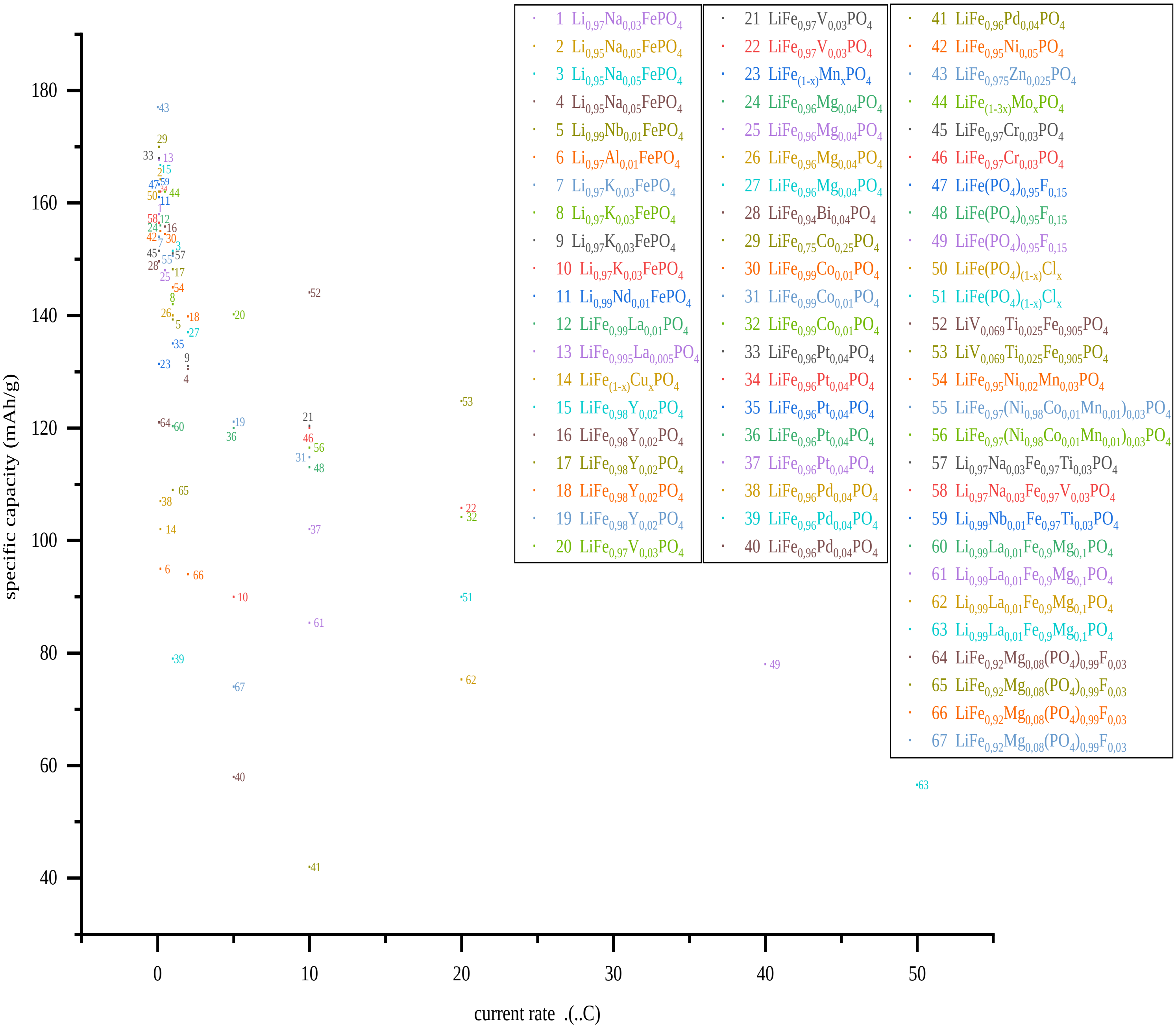

Figure 2:- Synthesis of main doping LiFePO4 cathode of LFP batteries.

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