Electrochemical properties and structure of LiFePO$_4$/C with Co-doping in Fe-site and Li-site

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Abstract: *LiFePO$_4$/C compounds of co-doping in Li-site and Fe-site were synthesized with traditional solid state reaction. The electrochemical and physical properties of these samples were characterized by XRD, SEM and EA. The substitution in Li-site and Fe-site led to the modifications of the structure and electrochemical performance such as initial capacity, capacity fading and polarization. The lattice constants and electrochemical performance of Sr-doped sample were larger and poorer than these of other doping samples. The co-doping samples with 1% M (Mo^{6+} and Nd^{5+}) and 3% Mn^{2+} exhibited excellent electrochemical performance, especially in high rate. Moreover, the co-doping samples with 6% Mn^{2+} exhibited mild capacity fading. From these results, it was suggested that the appropriate co-doping in Li-site and Fe-site could improve both electronic and ionic conductivities of LiFePO$_4$, which may pose to some modifications of its electrochemical performance.*

1. INTRODUCTION

Along with the economic development, in the past a decade lithium-ion batteries have been of great potential for electric vehicles (EVs), hybrid electric vehicles (HEVs). Due to poor high rate performance and security, the applications of traditional lithium-ion batteries in these fields are constrained greatly. Since Goodenough and co-worker[1] reported that olivine LiFePO$_4$ could be applied to a cathode material for lithium-ion batteries, much attention has been paid to improve the performance of LiFePO$_4$. At present, LiFePO$_4$ is the most promising candidate for cathode material for power lithium-ion batteries.

The pure LiFePO$_4$ has two main defects of low electronic conductivity and low lithium-ion diffusivity. In order to overcome these defects, many researchers adopted different methods with carbon coating[2-4], different synthetic methods[5,6], particle size reduction[7,8] and ion doping technique[9-12]. However, the carbon coating cannot increase the intrinsic electronic or ionic conductivity of LiFePO$_4$. Therefore, some researchers try to introduce cation to improve the intrinsic electronic or ionic conductivity. It was generally thought that the modifications of doping LiFePO$_4$ performance were attributed to its improvement or deterioration of

intrinsic electronic and ionic conductivity[13].

Though many researches on doping of LiFePO$_4$ were reported, the investigation on co-doping of LiFePO$_4$ in Li-site and Fe-site was very little. In this article, we select Mn^{2+} as the substitution cation at Fe-site and M (Mo^{6+}, Nb^{5+} and Sr^{2+}) as the substitution cation at Li-site, and try to investigate the effect of LiFePO$_4$ with co-doping at Li-site and Fe-site on the structural and electrochemical properties.

2. EXPERIMENTAL

Li$_{1-x}$M$_x$Fe$_{1-y}$Mn$_y$PO$_4$/C samples, (M=Mo^{6+}, Nb^{5+} and Sr^{2+}), were prepared with traditional solid state reaction using Li$_2$CO$_3$ (Aldrich, 99.9%), FeC$_2$O$_4$·2H$_2$O (Aldrich, 99.5%), NH$_4$H$_2$PO$_4$ (Aldrich, 99.5%) as the reactant, glucose as the carbon source and (CH$_3$COO)$_2$Mn·2H$_2$O (Aldrich, 99.5%), MoO$_3$ (Aldrich), SrCO$_3$ (Aldrich) and Nb$_2$O$_5$ (Aldrich) as the starting material of doping cation. A mixture of reactant in stoichiometric ratio, a spot of glucose and doping raw materials were ground and mixed by ball-milling in ethanol for 6 h. After dried in oven at 80°C under atmosphere, the mixture was sintered in a tube furnace with flowing argon (97%) and H$_2$ (3%) at 400°C for 6h. After cooled down to room temperature, the samples were reground and sintered at 700°C for 10h.

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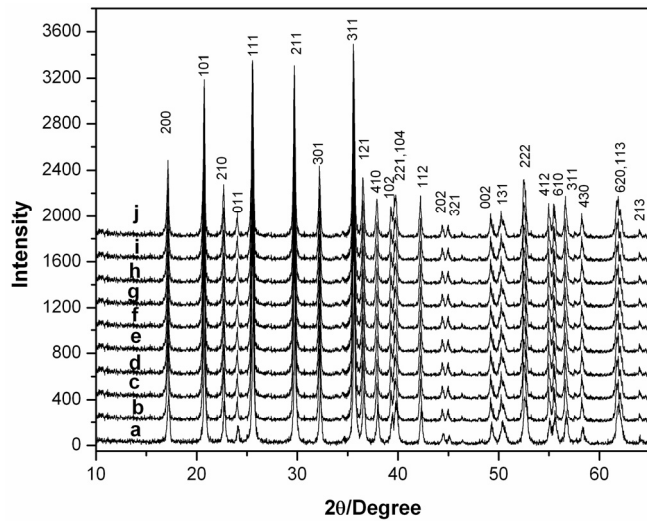Phone: +86-571-86835738, Fax: + 86-571-86835740

Figure 1. X-ray diffraction patterns of LiFePO$_4$/ C: (a) undoping, (b) 1%Sr^{2+},(c) 1%Mo^{6+}, (d) 1% Nd^{5+} , (e) 1%Sr^{2+} and 3%Mn^{2+} , (f) 1%Sr^{2+} and 6%Mn^{2+} , (g) 1%Mo^{6+} and 3%Mn^{2+}, (h) 1%Mo^{6+} and 6%Mn^{2+}, (i) 1% Nd^{5+} and 3%Mn^{2+} , (j) 1% Nd^{5+} and 6%Mn^{2+}

The structure of samples was characterized by X-ray diffraction (XRD) with Cu K$_\alpha$ (λ=0.15406nm) radiation (Rigaku B/MAX-2400) at speed of 1°/min. The diffraction patterns were collected from 10° to 70° with 2θ angle and scan step size of 0.02°.

The morphology of all the samples was observed by a scanning electron microscopy (JSM-6360LA; JEOL Ltd., Japan).

The electrochemical properties of samples were examined using a CR2025 coin cell with lithium metal as the anode assembled in an argon-filled glove box. The working electrode slurry was composed of 80 wt% LiFePO$_4$/C, 10 wt% acetylene black, and 10 wt% polyvinylidenefluoride (PVDF) binder. *N*-methyl-2-pyrrolidinon (NMP) was used as solvent. The slurry was cast onto the thin aluminum foil current collector. The electrode was then dried overnight under vacuum at 120 °C. The separator was cellgard 2400 microporous membrane, and the electrolyte was a 1M LiPF$_6$-propylene carbonate (PC)/dimethyl carbonate (DMC) (1:1 by volume). The cells were galvanostatically charged and discharged between 2.2 and 4.2 V at room temperature (25°C) with LAND test system (Wuhan, China) at different rates.

3. RESULTS AND DISCUSSION

3.1. XRD

Fig.1 exhibits the X-ray diffraction patterns of different LiFePO$_4$/ C samples. The results indicate that the diffraction peaks of all samples are well consistent with PDF (40-1499) of olivine structure LiFePO$_4$. However, some researchers' results suggested that when sintered at 700 °C, some impurities such as Fe$_2$P and Li$_3$PO$_4$ were detected by XRD in LiFePO$_4$/C powder[14].

In order to explore the effect of doping cation on lattice structure of LiFePO$_4$, we further study the XRD patterns and find that with the doping level increasing and variety of cation varying, the lattice parameter *a*, *b*, *c* of LiFePO$_4$/ C, and the crystal cell volume *V* also change continuously because the different cation and concentration occupies the Li$^+$ or Fe^{2+} site in the crystal, which induce the shrinkage or expanding of the crystal cell. The detailed cell parameters of different doping samples were listed in the table 1.

Table 1 reveals that after doping, the cell parameters of LiFePO$_4$ shrink or expand, which may be closely related to doping ionic radius. On the whole, the cell parameters of co-doping samples rather than Sr-doped are almost as large as that of the undoping samples, whereas the cell parameters of Sr-doped samples are much larger than that of other samples. To better understand the effect of cation radius on cell parameters, we also list the doping cation radius in the table 2.

3.2. SEM Morphologies

The SEM photos of three selected samples were taken. Fig.2 shows the SEM images of undoping and co-doping LiFePO$_4$ samples. To our surprise, though all the samples were sintered at the same temperature of 700°C, the particle morphologies and size were much different from each other. The particle size of undoping sample is about 0.5 μm, whereas that of both co-doping samples is more than 1μm. Moreover, for the sample with 6% Mn^{2+}, it seems to give birth to agglomeration. These results may imply that the cation Mn^{2+} can facilitate the growth of LiFePO$_4$ grain size.

3.3. Electrochemical Properties

Fig.3 shows the first electrochemical curves of the different LiFePO$_4$ samples. It is apparent that the capacity of Sr-doped and undoping samples was obviously lower than other samples, and in particular the capacity of co-doping sample with Mo^{6+} and Nd^{5+} plus 3% Mn^{2+} reach 146mAh/g, 10 mAh/g higher than that of the undoping sample.

In order to evaluate the rate performance, all the samples were

Table 1. Cell parameters of different LiFePO$_4$ samples.

sample	*a*/Å	*b*/ Å	*c*/ Å	*V*/ Å^3
LiFePO$_4$/ C	6.008	10.325	4.689	290.871
Li$_{0.99}$Sr$_{0.01}$FePO$_4$/ C	6.010	10.327	4.694	291.334
Li$_{0.99}$Mo$_{0.01}$FePO$_4$/ C	6.006	10.323	4.685	290.470
Li$_{0.99}$Nd$_{0.01}$FePO$_4$/ C	6.007	10.324	4.685	290.546
Li$_{0.99}$Sr$_{0.01}$Fe$_{0.97}$Mn$_{0.03}$PO$_4$/ C	6.015	10.330	4.695	291.724
Li$_{0.99}$Sr$_{0.01}$Fe$_{0.94}$Mn$_{0.06}$PO$_4$/ C	6.018	10.335	4.701	292.384
Li$_{0.99}$Mo$_{0.01}$Fe$_{0.97}$Mn$_{0.03}$PO$_4$/ C	6.007	10.325	4.687	290.698
Li$_{0.99}$Mo$_{0.01}$Fe$_{0.94}$Mn$_{0.06}$PO$_4$/ C	6.009	10.327	4.688	290.914
Li$_{0.99}$Nd$_{0.01}$Fe$_{0.97}$Mn$_{0.03}$PO$_4$/ C	6.008	10.326	4.689	290.899
Li$_{0.99}$Nd$_{0.01}$Fe$_{0.94}$Mn$_{0.06}$PO$_4$/ C	6.009	10.329	4.688	290.970

Table 2. The doping ionic radius.

Ionic radius on Li-site/Å	Li$^+$	0.76
	Sr^{2+}	1.12
	Mo^{6+}	0.65
	Nd^{5+}	0.69
Ionic radius on Fe-site/Å	Fe^{2+}	0.74
	Mn^{2+}	0.83

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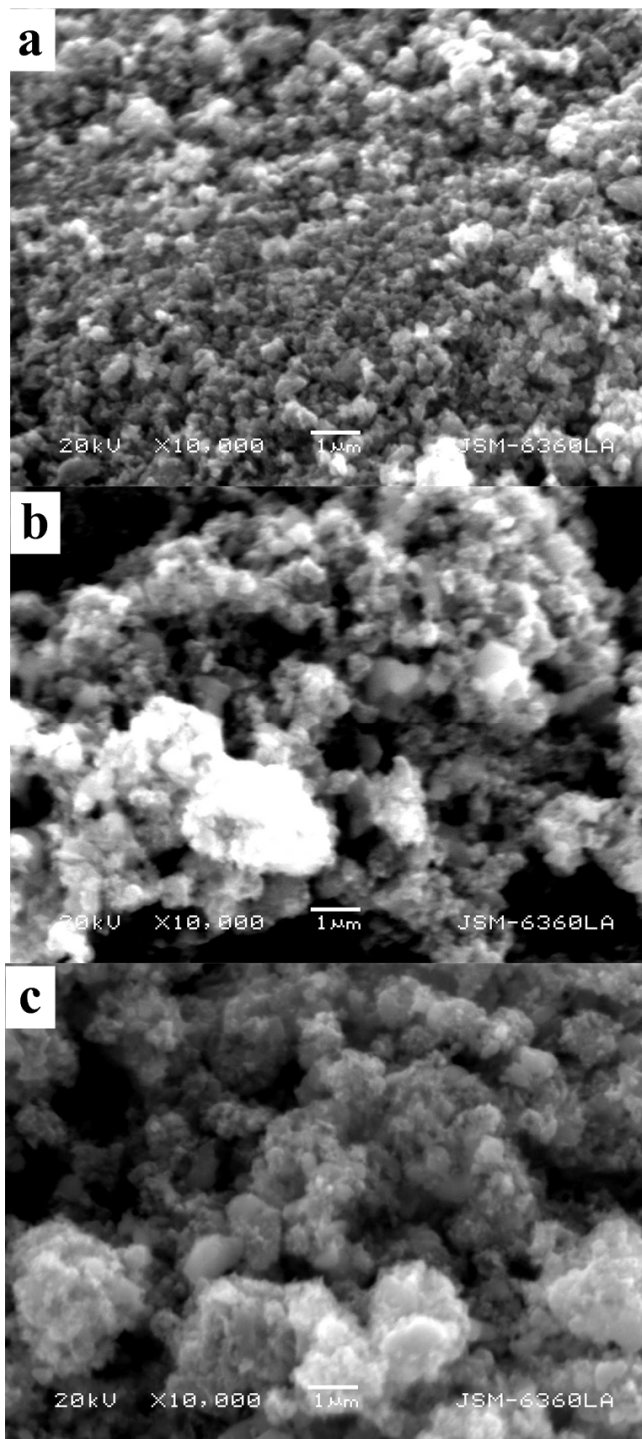*/ J. New Mat. Electrochem. Systems*

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Figure 2. SEM of images of LiFePO$_4$/C with different doping concentration: (a) undoping; (b) doping sample with 1% Mo^{6+} and 3% Mn^{2+}; (c) doping sample with 1% Mo^{6+} and 6% Mn^{2+}

charged under 1C and discharged under at rate of 1C, 2C, 5C, respectively. Here we give only the discharge curves at rate of 1C and 5C in Fig.4, Fig.5 respectively. The tested results indicate that the discharge capacity decreases and the electrochemical polariza-
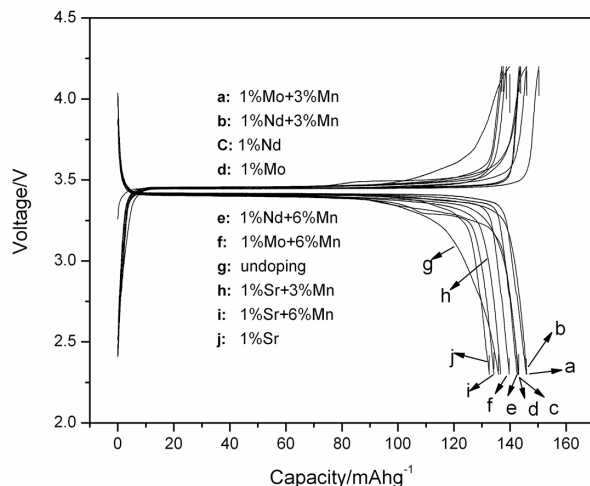

Figure 3. The charge and discharge curves of the first cycle of different LiFePO4 samples under 0.1C

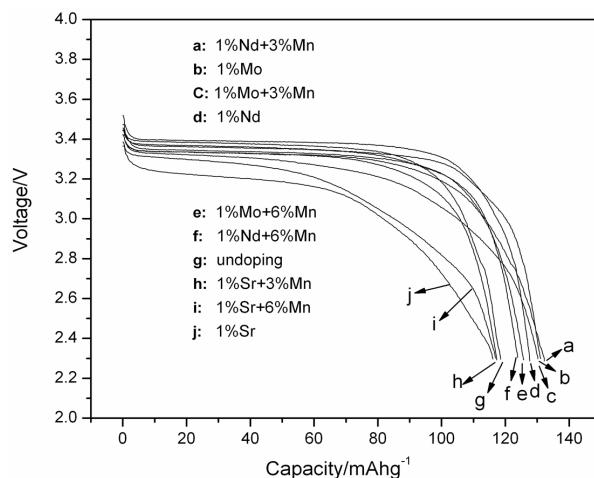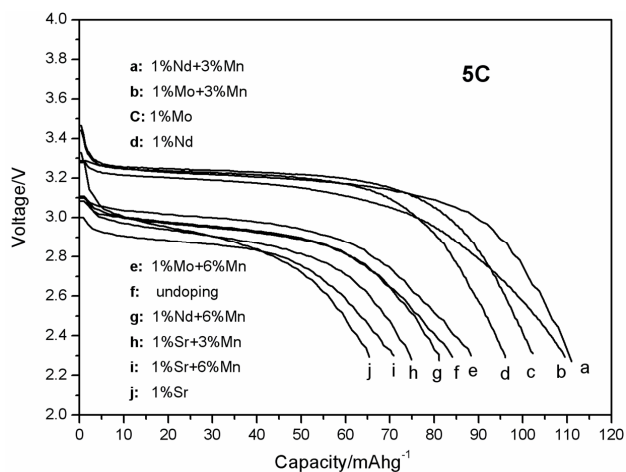Figure 4. The discharge curves of the first cycle of different LiFePO4 samples under 1C

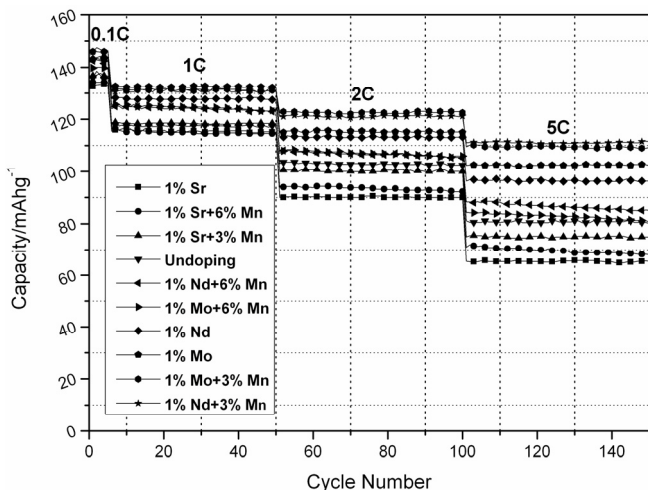Figure 5. The discharge curves of the first cycle of different LiFePO4 samples under 5C

Figure 6. Results of the capacity fading with various nC rates (n=0.1, 1, 2, 5) for the different doping samples

tion become serous as the discharge rate rises. The electrochemical performance of samples under high rate is similar to that under low rate (0.1C) and the capacity of the Sr-doped and undoping samples was lower than co-doping sample with Mo^{6+} and Nd^{5+} plus 3% Mn^{2+}, in particular at the rate of 5C. Furthermore, the electrochemical polarization of the Sr-doped and undoping samples was more serous than other doping samples, in particular under 5C.

As for the capacity fading of different doping samples, the tested result is shown in Fig.6, and it is found that the initial specific discharge capacity decreases with increasing C rate. Aside from mild capacity fading of samples with 6% Mn^{2+}, all the samples exhibit excellent specific capacity retention after 150 cycles under different rate. Moreover, the Sr dopant seems not to affect the capacity retention of Sr-doped samples, which is different from the fact that addition of Sr dopant decreases the specific capacity under different rate.

The tested results reveal that the doped or co-doped $LiFePO_4$ samples, in addition to Sr-doped samples, exhibit better electrochemical properties, and the co-doped samples with 1% M (Mo^{6+} and Nd^{5+}) and 3% Mn^{2+} show the best electrochemical performance, which can be interpreted as the improvement of electronic or ionic conductivity with ion doping. According to the mechanism proposed by Chung et al.[9] and extensively discussed by Wang et al.[11], the M (Mo^{6+}, Nb^{5+} and Sr^{2+}) ion dopant mainly substitute for Li ion, which leads to the coexistence of Fe^{2+} and Fe^{3+} in single phase and thus improves crystal electronic conductivity apparently. However, due to the one-dimensional diffusion channel of $LiFePO_4$ olivine structure, the addition of dopant may deteriorate ionic conductivity. The ionic radius of Sr^{2+} is much larger than that of other ion on Li-site, so the degradation of electrochemical performance for Sr-doped samples may result from the fact that the ion of Sr^{2+} blocks the diffusion channel. As for the mild capacity fading of samples with 6% Mn^{2+}, it may be posed by Jahn-Teller effect[15,16].

4. CONCLUSION

$Li_{1-x}M_xFe_{1-y}Mn_yPO_4$/C samples were prepared with traditional solid state reaction. The co-doping samples with 1% M (Mo^{6+} and Nd^{5+}) and 3% Mn^{2+} exhibited the excellent electrochemical performance, especially in high rate performance, whereas the electrochemical performance of Sr-doped samples tends to deteriorate. Moreover, too much addition of Mn^{2+} (beyond 6% Mn^{2+}) may cause capacity fading resulting from Jahn-Teller distortion. So the appropriate ionic types and concentration of co-doping samples in Li-site and Fe-site may improve both electronic and ionic conductivities of $LiFePO_4$/C and further increase the electrochemical performance.

5. ACKNOWLEDGEMENTS

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