

## Effect of Mg and Co co-doping on electrochemical properties of $\text{LiFePO}_4$

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**Abstract:**  $\text{LiFePO}_4$  co-doped with  $\text{Mg}^{2+}$  and  $\text{Co}^{4+}$  ions was synthesized by a solid state reaction method. The structure and electrochemical properties of the prepared  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  were investigated by X-ray diffraction (XRD), galvanostatic charge-discharge experiment and cyclic voltammograms (CV). Specific discharge capacity of  $\text{LiFePO}_4$  co-doped with Mg and Co ions reach 147.2 mA·h/g at 0.1C and 133.3 mA·h/g at 1C. The results of CV show that the reversibility of lithium extraction/insertion in  $\text{LiFePO}_4$  can be promoted by ( $\text{Mg}^{2+}$ ,  $\text{Co}^{4+}$ ) multiple-ion doping.

**Key words:**  $\text{LiFePO}_4$ ; multiple-ion doping; Fe-site doping; solid state reaction; electrochemical performance

### 1 Introduction

Since they are first reported by the SONY corporation in the early 1990s, lithium-ion batteries have rapidly taken over the high-performance rechargeable battery market due to their high energy and power densities [1–3]. The improvement of the performance and cost of cathode materials is an important task in the lithium-ion batteries study. Recently, olivine-structured  $\text{LiFePO}_4$  was investigated intensively as a potential cathode material for rechargeable Li-ion batteries because of its low cost and improved safety [4–6]. The main disadvantage of  $\text{LiFePO}_4$  is its low electronic conductivity and diffusion coefficient of lithium ions which lead to its poor rate capability and hinder its commercialization as cathode material for lithium ion batteries.

The electronic and ionic transport limitations were overcome by doping with metal atoms [7,8], reducing the particle sizes [9] or coating electrically conductive agents [10,11]. Among them, heterogeneous doping at Li-site was widely adopted for optimization of electrochemical performance. HU et al [12] reported that  $\text{LiFePO}_4$  turned into a good P-type semiconductor material and its electric conductivity was promoted by metal ion doping at Li-site. However, there are fewer reports on the study

of  $\text{LiFePO}_4$  doped by low-level aliovalent cation in Fe-sites [13,14]. Fe-site doped samples  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  were prepared by a solid-state reaction method using oxalate as precursor. And the effect of Mg and Co co-doping on electrochemical properties of  $\text{LiFePO}_4$  was studied. This is the first report of  $\text{LiFePO}_4$  doping with multiple-ion at Fe-sites. This method may open up new avenues for application of  $\text{LiFePO}_4$  in high-performance lithium-ion batteries.

### 2 Experimental

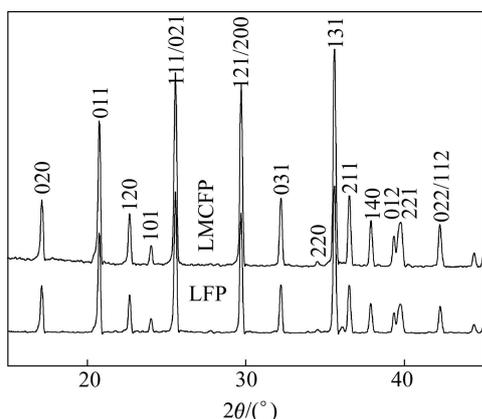
$\text{LiFePO}_4$  (LFP) was prepared by a solid-state reaction method. A mixture of  $\text{Li}_2\text{CO}_3$ ,  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  with mole ratio of 0.5:1:1 was ground and mixed by ball-milling for 5 h. The mixture was calcinated in a tube furnace at 350 °C for 10 h with flowing high-pure nitrogen gas. After being cooled down to room temperature, the sample was pressed to flake product and sintered at 700 °C for 24 h in the tube furnace under a protective atmosphere. The sample of  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  (LMCFP) was prepared following the same procedures.  $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Co}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  were used as precursors for doping samples.

X-ray diffraction (XRD) measurements were carried out with a Bruker D8 using filtered Cu  $K_\alpha$  radiation.

The electrochemical experiments were performed using two-electrode coin-type cells. The working electrode composed of active materials, carbon black and poly (vinyl difluoride) (PVdF) with mass ratio of 80:10:10 was pasted on Nickel foam. The metallic lithium foil was used as the counter electrode, 1 mol/L  $\text{LiPF}_6$  was dissolved in ethylene carbonate/dimethyl carbonate with volume ratio of 1:1 as electrolyte, and Celgard<sup>®</sup> 2400 as separator. Test cells were assembled in an argon-filled glove box with less than  $1 \times 10^{-6}$  of oxygen, water and nitrogen contents. The discharge and charge measurements were carried out under an identical electrochemical condition on a Neware battery tester. Cyclic voltammograms (CV) were performed on a PARSTAT 2273 at a slow sweep rate of 0.1 mV/s and voltage between 2.7 and 4.3 V.

### 3 Results and discussion

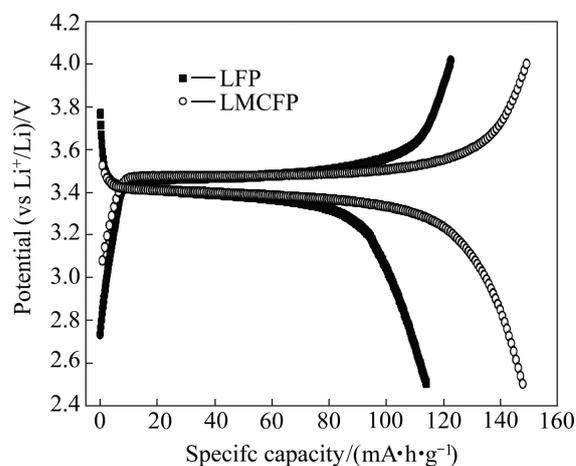
XRD patterns of the prepared  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  are shown in Fig.1. XRD patterns for the samples indicate that pure phases with an ordered olivine structure indexed in orthorhombic  $Pnmb$  are exclusively formed [15].  $\text{LiFePO}_4$  is chemically stable in the presence of  $\text{Mg}^{2+}$  and  $\text{Co}^{4+}$  doping. No extra diffraction peaks from related secondary phases or impurities are found. It is obvious that multiple-ion doping with a low amount does not affect the structure of the samples.



**Fig. 1** XRD patterns of  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  samples

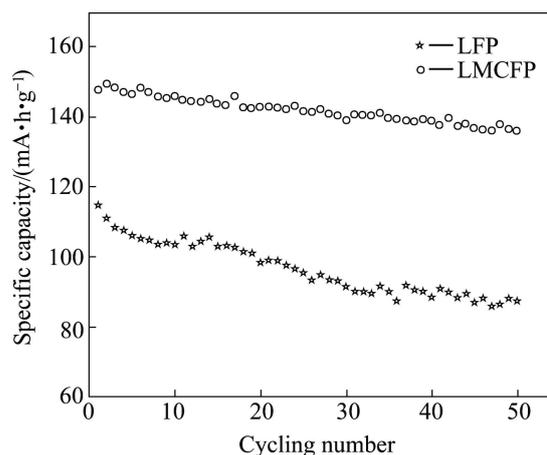
Figure 2 displays the charge-discharge curves of  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  samples with cutoff voltages of 2.5–4.0 V (vs  $\text{Li}^+/\text{Li}$ ) at a current density of 0.1C. As can be seen from the figure, the cells show very smooth and monotonous charge-discharge curves. The initial discharge capacity of raw  $\text{LiFePO}_4$  is 114.8 mA·h/g with a discharge efficiency of 93.1%. For doped samples, the initial discharge capacity and discharge efficiency increase to 147.2 mA·h/g and 97.8%,

respectively.  $\text{Mg}^{2+}$  has approximately the same size as  $\text{Fe}^{3+}$ , but is larger than  $\text{Fe}^{2+}$ . So, Mg-doping causes lattice defect in  $\text{LiFePO}_4$ . The lattice defects promote the spread of lithium ions, and then improve the electrical conductivity of the  $\text{LiFePO}_4$  [13,14]. Furthermore, Co doping makes the Li-O interaction weakened, which leads to high ionic mobility and diffusion coefficient [13]. This is probably the main reason for the dramatic increase of the initial discharge capacity from raw  $\text{LiFePO}_4$  to doping samples.



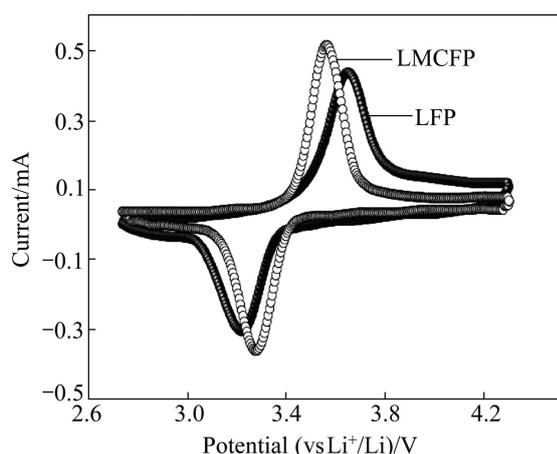
**Fig. 2** Charge-discharge curves of  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  samples

The cycling performance of raw and co-doping  $\text{LiFePO}_4$  is shown in Fig. 3. The raw  $\text{LiFePO}_4$  shows a poor cycling performance, with capacity fading of more than 22% after 50 cycles at the current density of 0.1C. One possible reason for this rapid capacity fade is the constantly generated inactive material causes by the structure collapse during  $\text{Li}^+$  insertion and extraction [16,17]. In the case of doping materials LMCFP, the discharge capacities at the 50th cycle hold at 136.5 mA·h/g with capacity retention rate of 92.3%. This indicates that the structural stability of  $\text{LiFePO}_4$  is improved by Mg and Co co-doping.



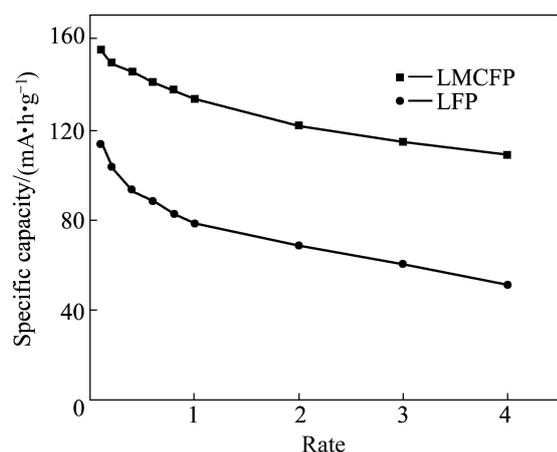
**Fig. 3** Cycling performance of raw and co-doping  $\text{LiFePO}_4$

Figure 4 shows the cyclic voltammograms of raw and doped  $\text{LiFePO}_4$  measured at a sweep rate of 0.1 mV/s at room temperature and voltage between 2.7 and 4.3 V (vs  $\text{Li/Li}^+$ ). Anodic and cathodic peaks appear at about 3.6 and 3.3 V, which correspond to the two phase charge-discharge reaction of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple [18]. The potential separation of doped  $\text{LiFePO}_4$  between anodic and cathodic peaks is 0.29 V, whereas that of the virginal  $\text{LiFePO}_4$  is 0.45 V. Furthermore, the shape of anodic/cathodic peaks of doped  $\text{LiFePO}_4$  is more symmetrical and sharper than that of pure  $\text{LiFePO}_4$ , which indicates that the reversibility of lithium extraction/insertion in  $\text{LiFePO}_4$  can be promoted by ( $\text{Mg}^{2+}$  and  $\text{Co}^{4+}$ ) multiple-ion doping.



**Fig. 4** Cyclic voltammetry profiles of undoped LFP and LMCFP

The rate capabilities of undoped  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$  were measured at different discharge current densities. By increasing the discharge rate, utilization of the active material is decreased, which causes the decrease of discharge capacity [19]. As shown in Fig.5, pure  $\text{LiFePO}_4$  has the discharge specific capacities of 78.4, 68.4, 60.1 and 51.2  $\text{mA}\cdot\text{h/g}$  at 1, 2, 3



**Fig. 5** Rate capability of undoped  $\text{LiFePO}_4$  and  $\text{LiFe}_{0.99}\text{Mg}_{0.005}\text{Co}_{0.005}\text{PO}_4$

and 4C, respectively. Doping samples show good rate capability compared with raw  $\text{LiFePO}_4$ , and the discharge specific capacities increase to 133.3, 121.4, 114.3 and 108.7  $\text{mA}\cdot\text{h/g}$  at the same discharge current density.

## 4 Conclusions

1) Mg-doping causes lattice defect in  $\text{LiFePO}_4$ , and Co-doping makes the Li-O interaction weakened, which leads to high ionic mobility and diffusion coefficient.

2) The initial discharge capacity and discharge efficiency of doping samples increase to 147.2  $\text{mA}\cdot\text{h/g}$  and 97.8% compared to pure  $\text{LiFePO}_4$ . The discharge capacities of LMCFP at the 50th cycle also hold at 136.5  $\text{mA}\cdot\text{h/g}$  with capacity retention rate of 92.3%.

3) Discharge specific capacity of doped  $\text{LiFePO}_4$  increases to 133.3, 121.4, 114.3 and 108.7  $\text{mA}\cdot\text{h/g}$  at 1, 2, 3 and 4C, respectively. And cycling performance and rate capability of  $\text{LiFePO}_4$  are improved by Mg and Co co-doping.

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## Mg-Co 复合掺杂对 $LiFePO_4$ 电化学性能的影响

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**摘要:** 通过固相反应制备了  $Mg^{2+}$  和  $Co^{4+}$  复合掺杂的  $LiFePO_4$  电极材料。采用 X 射线衍射、恒电流充放电和循环伏安研究复合掺杂对  $LiFePO_4$  结构和电化学性能的影响。结果表明: 复合掺杂能够提高  $LiFePO_4$  的首次放电比容量, 0.1C 和 1C 的放电容量分别达到 147.2 mA·h/g 和 133.3 mA·h/g。循环伏安测试结果表明: 复合掺杂改善了  $LiFePO_4$  的导电性能, 增强了  $Li^+$  的脱嵌可逆性。

**关键词:**  $LiFePO_4$ ; 复合离子掺杂; Fe 位掺杂; 固相法; 电化学性能

(Edited by LI Yan-hong)