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Mg Doping of $LiFePO_4$ by co-Precipitation for Lithium Ion Batteries

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A co-precipitation route was employed for Mg doping in $LiFePO_4$. The prepared samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic absorption spectrometry (AAS), energy dispersive spectroscopy (EDS) and electrochemical cycling measurement at different C-rates. It is found that a much smaller amount of Mg could be doped in $LiFePO_4$ via the co-precipitation route, but Mg doping leads to a more homogenous particle size distribution of $LiFePO_4$. The electrochemical performance measurement showed that the doped $LiFePO_4$ had a better rate performance than the undoped one. The results showed that the co-precipitate route is not a reliable method for Mg doping in $LiFePO_4$.

Keywords: Lithium ion batteries, $LiFePO_4$, Co-precipitation, cation doping, size effect

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]. To overcome these kinetic limitations, various strategies have been explored including conductive media coating [8-11], cation doping [5, 12-15], and particles size reduction [16, 17]. All these approaches can effectively enhance the rate capability of $LiFePO_4$. Since Chiang group initially reported that the electronic conductivity of $LiFePO_4$ could be increased by a factor of ~ 10^8 via a low-level supervalent metal ions doping [5], the method of cation doping has sparked intensive research works mainly focusing on doping metal ions screening and doping mechanism [18-20], which all based on the preparation of well doped $LiFePO_4$. To achieve uniform distribution of dopant into $LiFePO_4$, several groups have proposed a co-precipitation route to prepare cation doped $LiFePO_4$ [21, 22]. Among various metal ions, it is reported that Mg doped $LiFePO_4$ could be prepared by the co-precipitation route and showed enhanced rate performance [12].

In the present paper, we also employ the co-precipitation route to prepare Mg doped $LiFePO_4$ and properties of the resulting material were investigated. Although improved rate performance was observed in our doped sample, composition analysis surprisingly revealed that only negligible Mg was detected in the sample, which is clearly inconsistent with the results of the previous report [12]. Our results showed that the improved rate performance was attributed to the small particle size and the homogenous size distribution of the doped sample.

2. EXPERIMENTAL

Mg doped ferrous oxalate was synthesized using $FeSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 7H_2O$ and $H_2C_2O_4 \cdot 2H_2O$ by a co-precipitation method. $FeSO_4 \cdot 7H_2O$ and $MgSO_4 \cdot 7H_2O$ were dissolved into 200 ml deionized water in a 1-x: x (x=0, 0.01, 0.05) molar ratio to form a 0.5 M homogeneous solution. Then 240 ml 0.5 M $H_2C_2O_4 \cdot 2H_2O$ was slowly dropped into the above solution under stirring and heated to 80 °C. After the reaction, the obtained yellow deposit was centrifugally washed with deionized water and dried. Stoichiometric amounts of the dried deposit, Li_2CO_3 and $(NH_4)_2HPO_4$ were mixed with sucrose by ball-milling for 6 h in ethanol. After drying, the mixture was pretreated at 400 °C for 5h and then heated at 700 °C for 5 h under Ar atmosphere.

The crystalline phase of the products was identified by a powder X-ray diffraction (XRD). The morphology and particle size of the synthesized materials were observed by scanning electron microscopy (SEM). The composition of the samples was analyzed by energy dispersive spectroscopy (EDS) and atomic absorption spectrometry (AAS).

Electrochemical measurement was conducted by assembly of 2025 coin-type cell with a lithium metal anode. The cathode was constructed by mixing powders of the samples, Super P and polyvinylidene fluoride (PVDF) in an 8:1:1 weight ratio. The electrolyte was 1 M $LiPF_6$ in EC/DMC (1/1) solution. All cells were assembled in an Ar-filled glove box. Cells performance was evaluated between 2.5 and 4.2 V at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of undoped and 1 atom% Mg-doped ferrous oxalate. Both samples can be identified as a pure phase and no impurities were observed. The SEM images of them are showed in Fig. 2. It is seen that the doped sample had smaller particle size as compared to the undoped sample. This indicated that the presence of Mg in the solution leads to some extent suppress particle growth during the co-precipitation process.

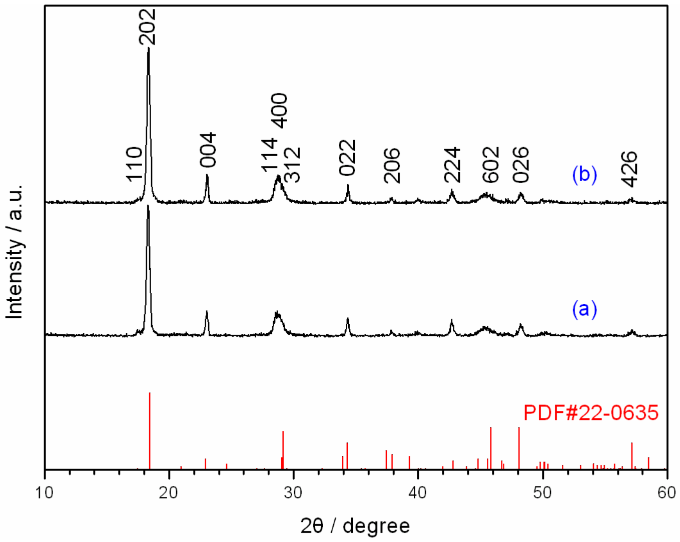

Figure 1. XRD patterns of (a) undoped and (b) 1 atom% Mg-doped $FeC_2O_4 \cdot 2H_2O$

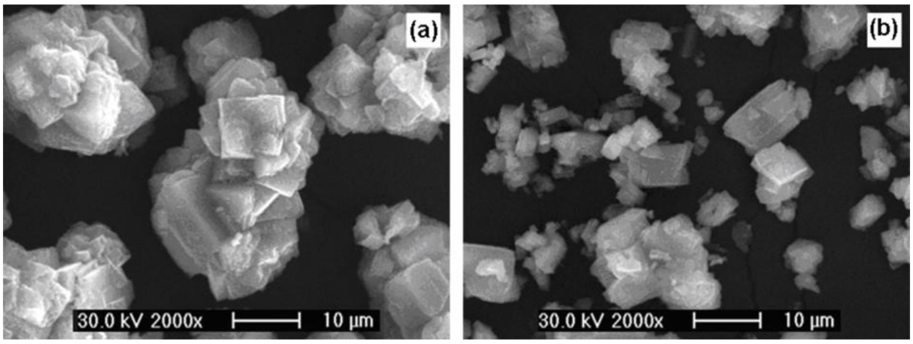

Figure 2. SEM images of (a) undoped and (b) 1 atom% Mg-doped $FeC_2O_4 \cdot 2H_2O$

Fig. 3 shows the XRD patterns of undoped and 1 atom% Mg-doped $LiFePO_4$. The two samples give very similar XRD patterns. All diffraction peaks of the two patterns can be fully indexed into an orthorhombic structure with a space group of *Pnma*, and no impurities were detected. Fig. 4a and b shows the SEM images of undoped and 1 atom% Mg-doped $LiFePO_4$. The undoped sample exhibits a broad particle size distribution as shown in Fig. 4a where large particles around 1 µm as well as small one around 100 nm are mainly observed, while the doped one has a homogenous distribution with the particle size centered around 100 nm as shown in Fig. 4b. This difference is thought to be associated with the different morphology of the undoped and 1% Mg-doped ferrous oxalate.

To get exact content of Mg in the doped $LiFePO_4$, the composition of the prepared samples was quantitatively analyzed by AAS. Surprisingly, it is found that only 0.032 wt.% of Mg was detected in the 1 atom% Mg-doped $LiFePO_4$ which is much smaller than the nominal percent (0.154 wt.%). Also, EDS (Fig. 4d) showed that no Mg peaks were observed in the spectrum of the doped $LiFePO_4$. This result further demonstrated that a very small amount of Mg was doped in $LiFePO_4$. Moreover, an elementary analysis of the Mg doped ferrous oxalate disclosed that there is also only little amount of Mg detected in the sample.

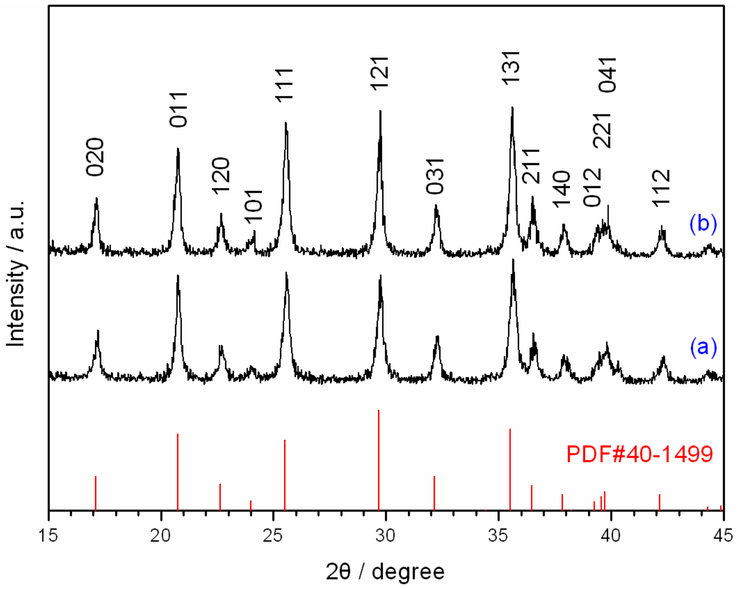

Figure 3. XRD patterns of (a) undoped and (b) 1 atom% Mg-doped $LiFePO_4$

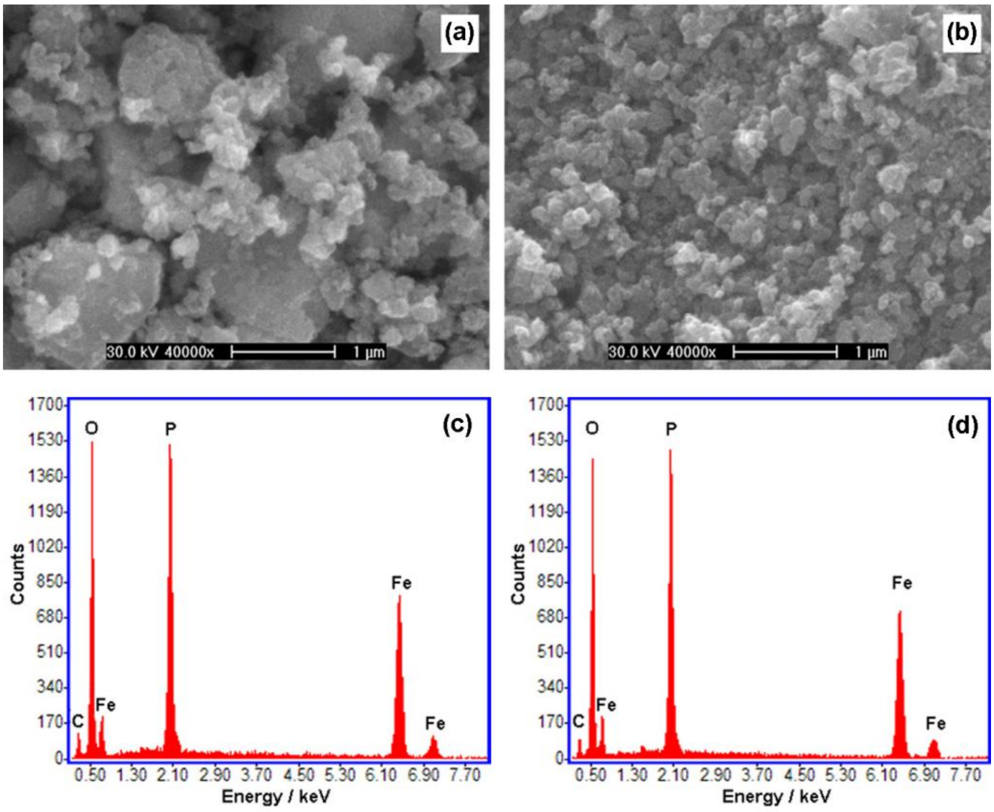

Figure 4. SEM images and EDS results of (a, c) undoped and (b, d) 1 atom% Mg-doped $LiFePO_4$

This result indicated that the co-precipitation process leads to dope a little amount of Mg into ferrous oxalate, which is clearly different from those reported in the available literature [12]. Such a result might be related to the fact that magnesium oxalate has a high solubility product (~10^{-5}) which is much larger than that of ferrous oxalate (~10^{-7}), and meanwhile the doped Mg concentration is in a quite low level (1 atom%). Under these conditions, even if the added Mg was initially co-precipitated with the iron as oxalate(s) from the solution, it would highly dissolve again in the water by the subsequent repeated washing. In fact, our additional experiment showed that there is still only small amount of Mg (0.094 wt.%) detected in the prepared sample even though the doping level increases up to 5 atom% (viz 0.778 wt.%).

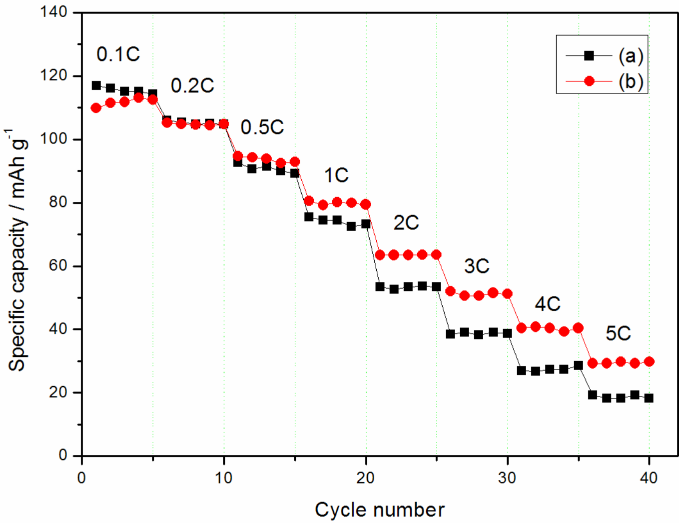

Figure 5. Rate performance of (a) undoped and (b) 1 atom% Mg-doped $LiFePO_4$. (0.1 C corresponds to 17 mA g^{-1}).

To evaluate the rate performance of undoped and 1 atom% Mg-doped $LiFePO_4$, the cells were charged at a constant rate of 0.1 C to 4.2 V and then discharged at various rates to 2.5 V (0.1 C corresponds to 17 mA g^{-1}). As shown in Fig. 5, it is seen that the two samples delivered a similar capacity at low rates (0.1 and 0.2C) and the discharge capacity decreased with increasing discharge rate, but the discharge capacity of the doped sample decreased much slower as compared to that of the undoped one. Obviously, the observed rate performance improvement of the doped $LiFePO_4$ should not be mainly ascribed to the enhancement of the electronic conductivity of $LiFePO_4$ by Mg doping on the basis of the results of the AAS and EDS. Based on the SEM images as shown in Fig. 4, we propose that the smaller particles as well as the uniform size distribution should also largely account for the improved rate performance of the doped sample in the present work. As a matter of fact, the particle size reduction of the doped sample prepared by the co-precipitate route has been observed in the previous reports where the authors often concentrated on the doping effect on the electronic conductivity. Our results suggest that the improved electrochemical performance may not only always be due to the cation doping itself, but also the size effect may be a cause for the sample prepared via the co-precipitate route.

Therefore, our results illustrate that the co-precipitate route is not a reliable method for synthesis of Mg doped $LiFePO_4$ when the oxalic acid is used as a precipitant. Meanwhile, it should be noted that other low level metal ions doping may also encounter a similar circumstance for the co-precipitate route, since most oxalates often have relative high solubility.

4. CONCLUSIONS

Mg doping in $LiFePO_4$ via the co-precipitate route were reinvestigated. Although the results of AAS and EDS showed that Mg is hardly detected in the precursor and final product, the doped $LiFePO_4$ sample had a homogenous particle size distribution and better rate performance. We suggest that the size effect rather than cation doping itself might be mainly responsible for the improved electrochemical performance of the doped sample prepared via the co-precipitate route.

ACKNOWLEDGEMENTS

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