

Cracking causing cyclic instability of LiFePO_4 cathode material

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Received 4 June 2004; accepted 21 June 2004

Available online 2 September 2004

Abstract

The capacity of pure LiFePO_4 faded gradually from initial 149 mAh g^{-1} – 117 mAh g^{-1} under current density of 30 mA g^{-1} at room temperature after 60 cycles. Some obvious cracks are observed in LiFePO_4 particles after cycling. The formation of cracks would lead to poor electric contact and capacity fading. A possible mechanism is proposed for the appearance of the cracks.

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Keywords: Cracks; LiFePO_4

1. Introduction

The ever-increasing demand for electric vehicles promotes the development of advanced lithium ion batteries with high safety, energy density, power density, long cyclic life and low cost. LiFePO_4 is one of attractive cathode material to meet all these demands. Olivine is regarded as a stable structure for Li-insertion/extraction and should show a good cyclic stability. However, gradual fading of the capacity of pure LiFePO_4 has been observed in references without detailed explanation [1–4]. In this paper, we observe the formation of cracks during cycling, which should be one of the reasons of capacity fading for pure LiFePO_4 .

2. Experimental

LiFePO_4 was prepared by a solid-state reaction. Stoichiometric amount of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99%), $\text{NH}_4\text{H}_2\text{PO}_4$ (Beijing Chemicals, 99.5%) and LiF (Beijing Chemicals, 99%) were mixed and ground by ball milling for 3 h. The mixture was sintered in a tube furnace with flowing Ar-H_2 (92:8, v/v) at 400°C for 8 h. After cooled down to room tem-

perature, the sample was reground and maintained at 600°C for 24 h under the same atmosphere.

A LiFePO_4 electrode is composed of LiFePO_4 , carbon black, and polyvinylidene fluoride (PVDF) with a weight ratio of 75:15:10. Metallic lithium is used as the anode. Electrolyte is 1 mol L^{-1} LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1, v/v). Celgard® 2340 is used as the separator. The cells were assembled in a glove box filled with pure argon and cycled between 2.0 and 4.5 V under the current density of 30 mA g^{-1} on a Land automatic batteries tester (China).

The X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (Rigaku B/MAX-2400) is used to characterize the structure. The surface morphology of electrodes was investigated on Philips XL30S-F1G field emission scanning electron microscope (FMSEM). The transmission electron microscope (TEM) analysis was done on the Hitachi H9000 NF electron microscope. Elemental compositions of the sample (Li, Fe, P) were detected by ICP (inductively coupled plasma).

3. Results and discussion

Fig. 1 shows the XRD pattern of the prepared sample. Compared with the criterion, the prepared sample shows a pure LiFePO_4 phase with an olivine structure indexed in

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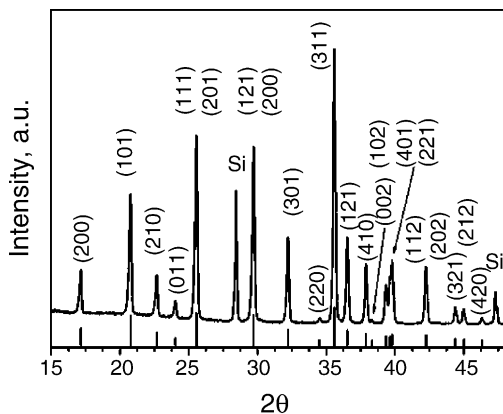


Fig. 1. The XRD patterns of prepared sample and criterion.

Pnmb. The amount of Li, Fe, P is 4.38, 35.3, and 19.6 wt.% according to ICP result, corresponding to 0.997:0.998:1.00, respectively, at a molar ratio. Above results indicate that the prepared sample is pure LiFePO_4 without any impurity, such as Fe_2P and Li_3PO_4 [5–9].

Fig. 2 shows the charge–discharge curves of the prepared LiFePO_4 . The plateau around 3.4 V corresponding to the reaction of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ is shortened during cycling, and becomes a slope feature after 60 cycles. The polarization is increased upon cycling. The capacity of LiFePO_4 decreases seriously, from 149 mAh g^{-1} of the first cycle to 117 mAh g^{-1} in the 60th cycle (78.5% of the initial capacity). Capacity fading of LiFePO_4 can be seen clearly in the inset of Fig. 2.

The XRD patterns of electrodes before cycling and after 10, 30, and 60 cycles are compared carefully in Fig. 3. The variations of peak position, peak shape and relative intensity are not distinguishable. It indicates that the capacity fading is not related to structure collapse.

Fig. 4 shows the morphology of the as-prepared LiFePO_4 sample, test electrodes before and after cycling. The particles of as-prepared LiFePO_4 are in the range of 300–600 nm with a smooth surface (Fig. 4a). Fig. 4b shows the morphology of a test electrode before cycling. This image shows that LiFePO_4

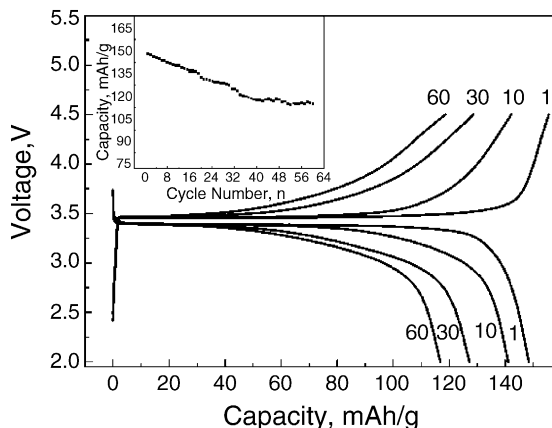


Fig. 2. Charge–discharge curves of LiFePO_4 in different cycles. The inset shows cyclic performance of LiFePO_4 .

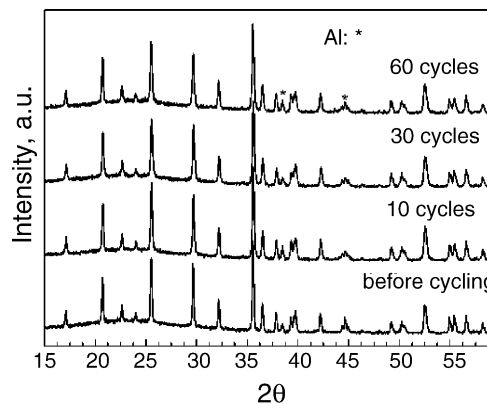


Fig. 3. The XRD pattern of electrodes in different cycles.

particles are surrounded by small carbon black particles of 30–50 nm. After 10 cycles, flaws can be observed in some LiFePO_4 particles (Fig. 4c). Fig. 4d shows a particle with a crevice in an electrode after 30 cycles. With further cycling to 60th, the cracks in the particles are more obvious. Fig. 4e shows part of the electrode after 60 cycles. Particle 1 and 2 is zoomed out in Fig. 4f and g. Both two particles were severed into three parts, especially the gap width in particle 2 are 13.5 and 33 nm, respectively.

The cracks in LiFePO_4 particles after 60 cycles also are found with TEM (Fig. 5a). The observed particle has severed into two parts. Their SAED images indicate that both parts are twin crystal, shown in Fig. 5b and c, respectively.

LiFePO_4 possesses an olivine structure with three-dimensional network. The lattice constants of LiFePO_4 are $a = 10.33 \text{ \AA}$, $b = 6.01 \text{ \AA}$, $c = 4.69 \text{ \AA}$, $V = 291.2 \text{ \AA}^3$ and the lattice constants of FePO_4 are $a = 9.81 \text{ \AA}$, $b = 5.79 \text{ \AA}$, $c = 4.78 \text{ \AA}$, $V = 271.5 \text{ \AA}^3$, respectively [11]. The volume change of this phase transformation is 6.77%. The volume change is not so large. Therefore the structure should be stable during Li-ion insertion/extraction. The formation of cracks should be a result from internal high strain during lithium extraction/insertion process in the particles. It is supposed that a grain of single phase LiFePO_4 turns to two-phase structure of $\text{LiFePO}_4/\text{FePO}_4$ with a sharp interface during lithium extraction/insertion process [10]. According to the calculation of Cedar et al. [12] and Ouyang et al. [13], transport of Li ions in LiFePO_4 occurs preferably along the axis b due to low activation energy. Accordingly, the movement of the two-phase interface of $\text{LiFePO}_4/\text{FePO}_4$ is along b -axis, and the interface is parallel to a – c plane. The stress from volumetric change (shrinking 5.03% along axis a , and elongating 1.92% in axis c during lithium extraction) may exert on the interface. Upon successive cycles, flaws may appear in the local place firstly and develop into a crack later on. Inhomogeneous change may cause cracking at grain boundaries, at twin crystal boundaries, or on grains.

It is reasonable that the formation of the cracks will lead to poor electric contact between active particles and carbon black particles or aluminum foil current collector.

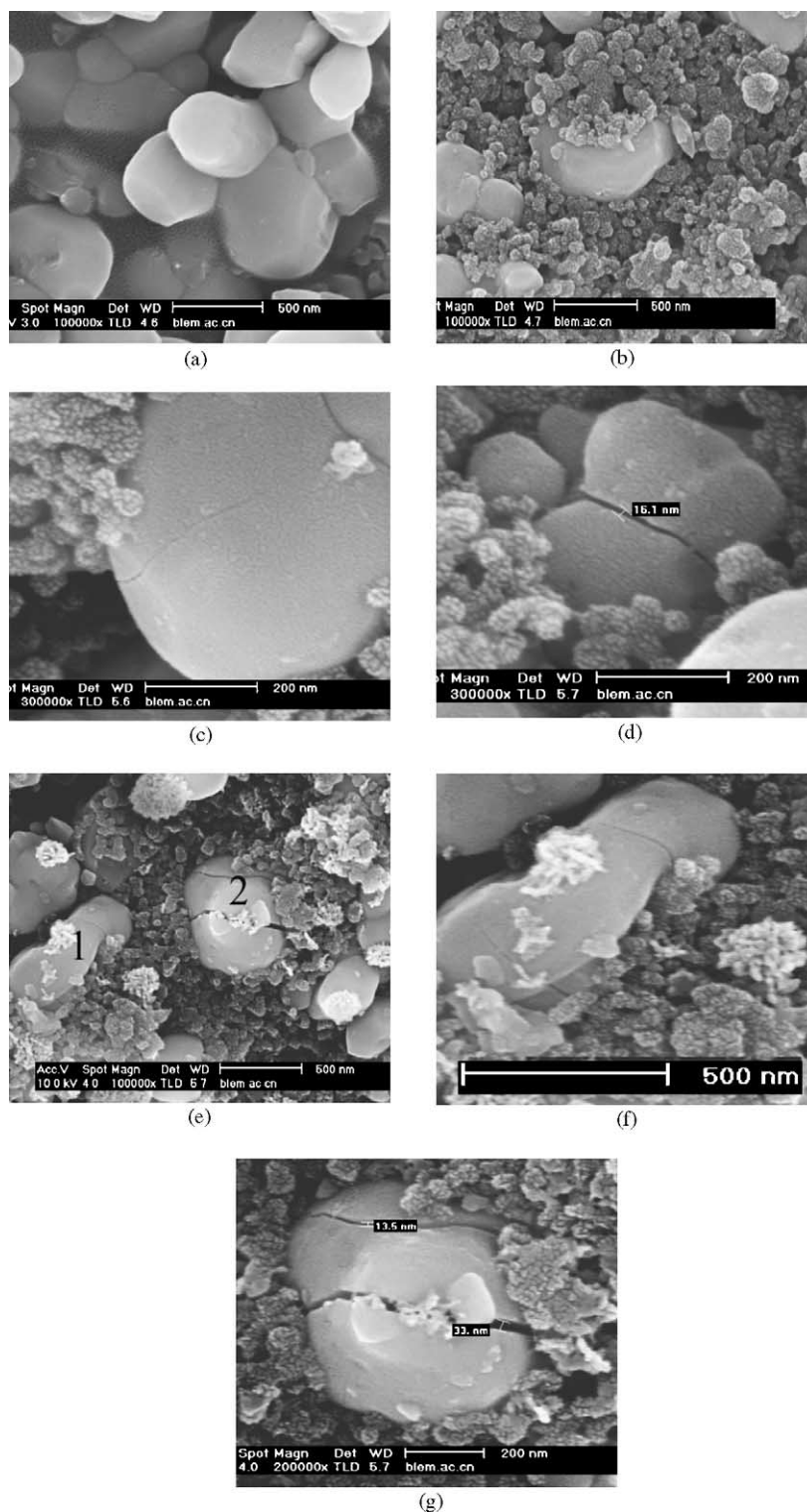


Fig. 4. The SEM images of LiFePO_4 . (a) The prepared sample; (b) the electrode before cycling; (c) the electrode after 10 cycles; (d) the electrode after 30 cycles; (e) the electrode after 60 cycles; (f) particle 1 in the image (e); and (g) particle 2 in the image (e).

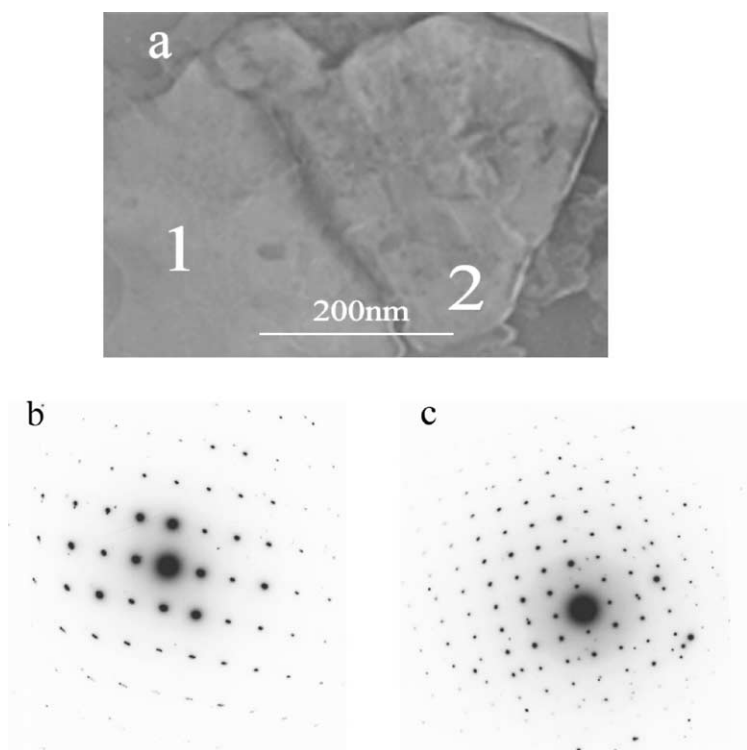


Fig. 5. (a) The TEM image of LiFePO₄ after 60 cycles; (b) the SAED image of area 1 in (a); and (c) the SAED image of area 2 in (a).

Consequently, high polarization is induced as shown in Fig. 2. This should be at least one of the reasons for capacity fading.

4. Conclusion

Some of the LiFePO₄ particles are cracked during cycling with a current density of 30 mA g⁻¹. The cracks may be caused by high internal strain along *b*-axis upon Li-extraction/insertion. The formation of cracks will lead to increased polarization of electrode and poor electric contact between active particles and conductive additives or aluminum foil current collector. This should be one of the reasons for capacity fading for pure LiFePO₄. The formation mechanism and possible strategies for overcoming this problem, such as surface coating and doping, will be further investigated.

Acknowledgments

Authors are much obliged to Dr. Hong Li of helpful discussion. This work was supported by the National 973 Program (Contract No. 2002CB211802).

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