

Shorting Effects of LiFePO₄ Cathode in Lithium Ion Batteries

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Abstract: Lithium ion battery is being widely developed with increasing interest on hybrid vehicles and electrical vehicles. The shorting effects of LiFePO₄ cathode in lithium ion battery were studied in this paper. Amorphous phase on LiFePO₄ can be formed during shorting tests. There is almost no capacity after shorting tests with 5 hours or 10 hours charging at C/20, which is because the amorphous phase is so thick that it can block the Li⁺ move in or out of the LiFePO₄ particle. However, after shorting test with 15 hours charging at C/20, the specific capacity is about 10mAh/g, although it is still very low. With fully charging at C/20, the specific capacity can reach to 85mAh/g. Therefore, it is suggested that amorphous phase on LiFePO₄ cathode is thicker after shorting tests with two phases including LiFePO₄ and FePO₄. From the shorting effects, lithium ion battery with LiFePO₄ as the cathode material should be fully charged or not be charged at all. These shorting effects are permanent, which cannot be recovered by cycle tests, polishing or heat treatment.

Keywords: Lithium ion batteries, LiFePO₄, shorting, charging, discharging

1. INTRODUCTION

Lithium-ion batteries have been widely researched and developed since Sony commercially released the first generation in 1991. Lithium-ion batteries are currently systems of choice, offering high energy density, flexible and lightweight design, and long lifespan in comparison to competing battery technologies [1, 2]. Several cathode materials, including LiCoO₂, LiMn₂O₄ and LiFePO₄, are being successfully used in the commercial lithium ion battery. Olivine LiFePO₄ has received widely interests because of its high capacity (170mAh/g), low cost and low toxicity since it was first proposed by Padhi, et al in 1997 [3-20]. LiFePO₄ does not include noble elements such as cobalt, the price of raw material is lower and both phosphorus and iron are abundant on Earth which lowers raw material availability issues.

With the development of portable electronic devices, hybrid car and electrical car, huge amounts of lithium ion battery will be used. The rechargeable secondary lithium ion battery market was approximately \$4.6 billion in 2006 but should grow to more than \$6.3 billion by 2012. Therefore, dead and shorted lithium ion batteries need to be widely recycled in the near future. As we know, shorting is very harmful to any battery. Lithium ion battery can explode when shorting. However, to our knowledge, no research has been done on the shorting effects of LiFePO₄ cathode in the

lithium ion battery. In this work, we try to study the shorting effects and mechanism of LiFePO₄ cathode materials in lithium ion battery. Also we hope that this study can provide the guidance of proper use and recycle in lithium ion battery industry.

2. EXPERIMENTAL DETAILS

Structure analysis: X-ray patterns of the LiFePO₄ cathode was obtained using a PANalytical X'Pert with Cu K α radiation, with a scan rate of 200 sec/step over a 2 θ range from 25° to 50°. The XRD data was analyzed using Jade 9.0.

Electron microscopy: Scanning electron imaging was done using a Philips XL30 FEG ESEM scanning electron microscope operating at 15kV accelerating voltage at 5000 magnification.

Electrochemical Tests: Electrode was made by mixing LiFePO₄ (80wt%), carbon (super P, 10%) and binder (polyethylenetetrafluoride (PTFE), 10%). The particle size of LiFePO₄ is about 50nm. Swagelok type cells used Li metal foil as the counter electrode, two layers of microporous polymer (Celgard 2500) as the separator and liquid electrolyte mixtures containing 1:1 by mole ethylene carbonate: dimethyl carbonate (EC: DMC), and 1 M LiPF₆ as the conductive salt. For the electrochemical tests, biological instrument was used. Electrochemical cells were galvanostatically charged and discharged at C/20 with 2.0-4.2V voltage range at room temperature. The impedance measurements were performed at open circuit potential before and after charging

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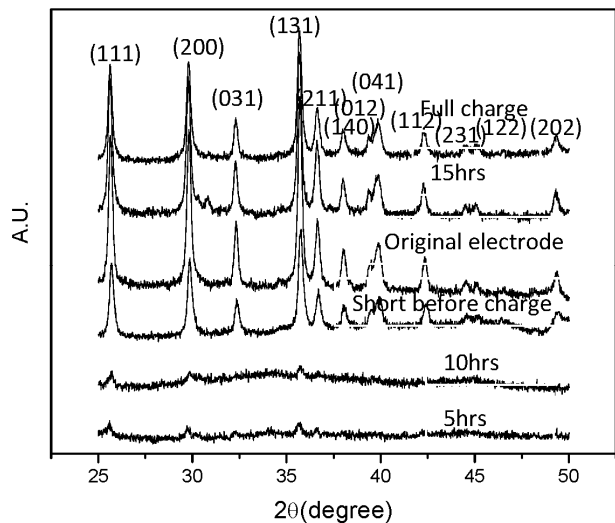


Figure 1. X-ray diffraction patterns of LiFePO_4 electrode before and after shorting

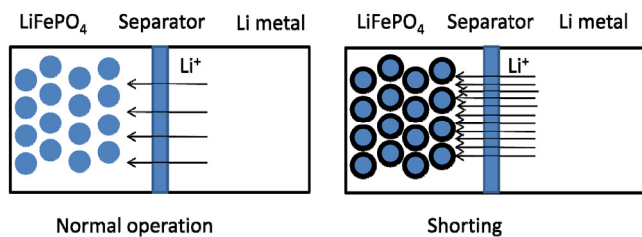


Figure 2. Comparison of LiFePO_4 electrode between normal operation and shorting

and the perturbation amplitude was 10mV at the range of 0.1Hz to 1MHz. Before the shorting tests, the cells were cycled twice. In the shorting tests, the cells were charged 5 hours, 10 hours, 15 hours or fully at C/20. Then LiFePO_4 electrode touched the lithium metal directly for 1 hour.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD)

Fig.1 presents the XRD analysis for LiFePO_4 electrode before and after shorting at the different charging state. The LiFePO_4 became amorphous phase after shorting tests with 5 hours and 10 hours charging. However, when charging 15 hours, fully or without charging, LiFePO_4 still have good crystallization after shorting tests. Therefore, one phase (either LiFePO_4 or FePO_4) is more stable than two phases in the shorting tests. In the normal operation of the lithium ion battery, Li^+ diffuses to LiFePO_4 particle from electrolyte when discharging. However, when the LiFePO_4 electrode is shorted with lithium metal, large amount of Li^+ will diffuse to LiFePO_4 very fast. These Li^+ have no time to diffuse into the grain of LiFePO_4 and accumulate onto the FePO_4 or LiFePO_4 surface. The structure on the surface of FePO_4 or LiFePO_4 changed to amorphous phase. The mechanism is shown in Fig.2. Also we believe that amorphous can also formed after shorting tests for charging 15

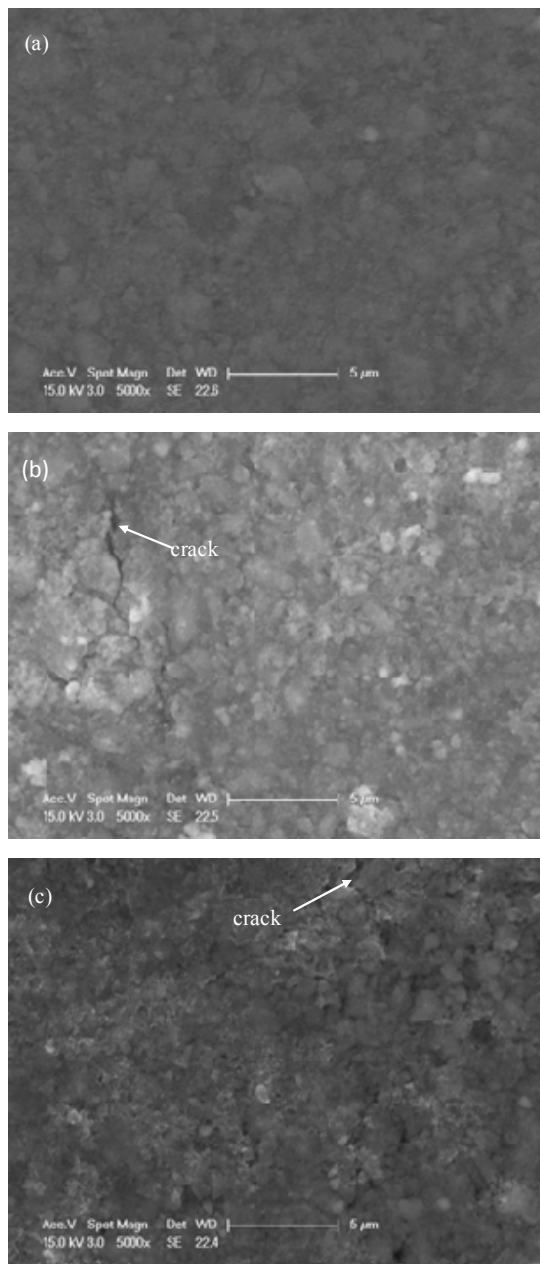


Figure 3. SEM examination for LiFePO_4 electrode before and after shorting tests, (a) original electrode, (b) shorting after 5 hour charging, (c) shorting after fully charging

hours and fully. However, the amorphous layer is thinner than that formed after 5 hours and 10 hours charging. So x-ray can still penetrate through the LiFePO_4 amorphous layer.

3.2. Scanning electron microscopy (SEM) examination

Fig.3 shows us the surface appearance before and after shorting tests. Based on the figures, we cannot see apparent difference for these electrodes before and after shorting tests. However, there are some cracks after the charging and discharging tests. After shorting

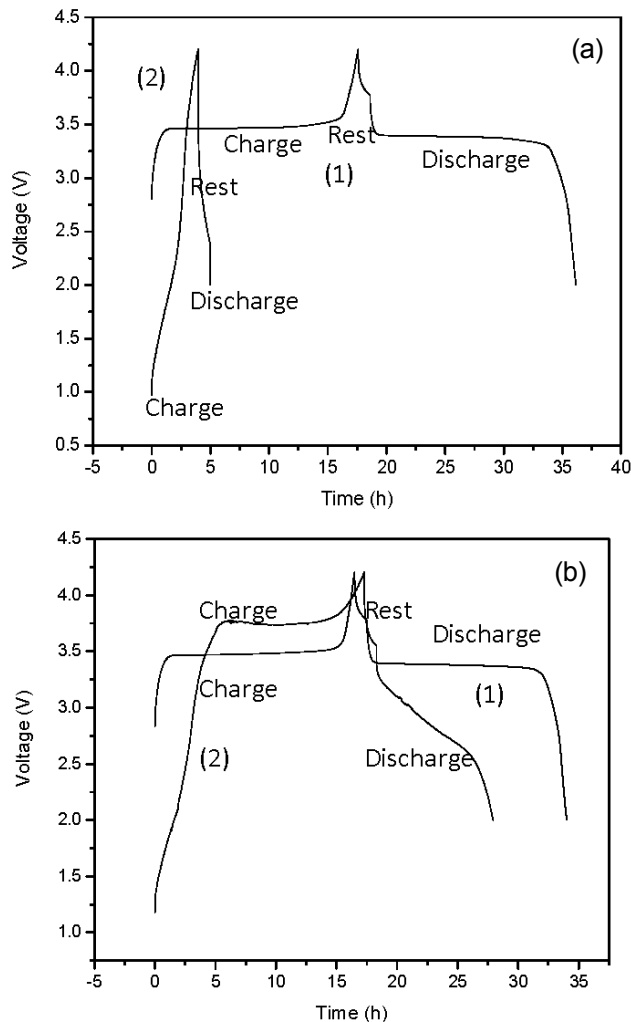


Figure 4. Charge and discharge tests for LiFePO₄ electrode before and after shorting tests, (a) short after 5 hours charging, (b) short after fully charging

Note: (1) charge and discharge curve before shorting tests, (2) charge and discharge curve after shorting tests

tests, the electrodes become rigid and it is easy to have cracks.

3.3. Charging and discharging tests

The discharge capacity of LiFePO₄ electrode after shorting tests at different charge state was shown in Table.1. The specific capacity for the LiFePO₄ electrodes is normally about 160mAh/g at C/20 charge and discharge. From the table, we can see that there is no capacity after shorting tests with 5 hours and 10 hours charging. The amorphous phase on the LiFePO₄ surface blocks the Li⁺ to

Table 1. Discharge capacity of LiFePO₄ electrode after shorting tests

Charge time (h)	0	5	10	15	full
Specific capacity (mAh/g)	101.4	0.07	0.02	5.1	81.4

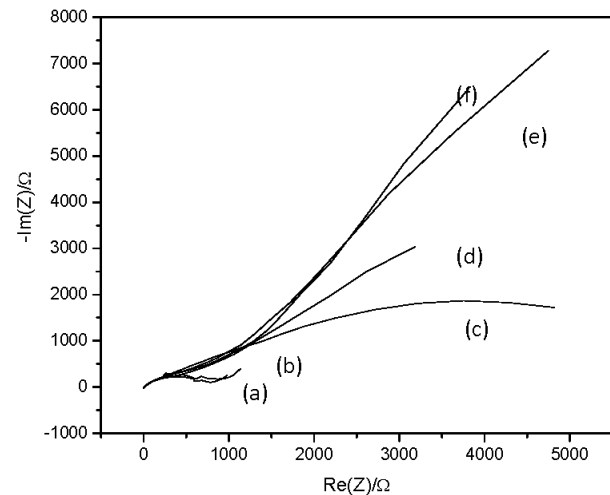


Figure 5. Electrochemical impedance tests before and after shorting, (a) charge state (no shorting), (b) discharge state (no shorting), (c) charge state (shorting after fully charging), (d) discharge state (shorting after fully charging), (e) charge state (shorting after 5 hour charging), (f) discharge state (shorting after 5 hour charging)

move in and out. After 15 hours charging, the capacity is still very low. For the electrodes with no charging and full charging, the specific capacity is about half of the theoretical capacity. The amorphous phase on these electrodes is relatively thin and Li⁺ can still move into or out of the grain of LiFePO₄. From the Fig.4(a), after shorting tests with 5 hours charging, there is no charge and discharge plateau. Although there is charge and discharge plateau after shorting tests with full charging, the charge voltage is higher and the discharge voltage is lower. This suggests that the cell has a higher resistance after shorting tests. It needs a higher energy for Li⁺ to diffuse into or out of the grain. Also I believe that particle size can significantly affect the electrode characteristics after shorting tests. Smaller particle size can have a much bigger portion of amorphous surface layer after the shorting tests. Most likely the capacity is higher for larger particle size after shorting tests and further experiments need to be done to prove it.

We also found an interesting phenomenon. If the LiFePO₄ electrodes do not cycle, the discharge capacity is only about 10mAh/g after shorting tests if fully charged. The LiFePO₄ electrodes cannot be fully charged and discharged in the first cycle. LiFePO₄ electrode still has two phases even if the cell was charged to the cut off voltage in the first cycle. Therefore, from the perspective of shorting effects, lithium ion battery with LiFePO₄ electrode should be charged and discharged for two cycles in order to be activated. Even for LiFePO₄ electrodes without full charging or charging, if the shorting time is long enough, for example, several hours or several days, there is no capacity for these electrodes. The thickness of the amorphous layer is increasing with the increasing of the shorting time.

3.4. Electrochemical impedance tests

Impedance spectroscopy was done in order to further analyze the reason why the capacity is lower after shorting tests. From the im-

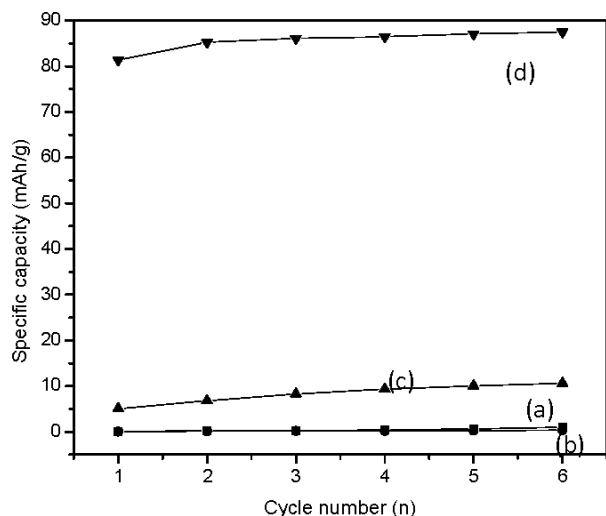


Figure 6. Cycle tests for LiFePO₄ electrode after shorting tests at C/20 (a) short after charging 5 hours, (b) short after charging 10 hours, (c) short after charging 15 hours, (d) short after fully charging

pedance curve, we can see that the impedance is almost the same at high frequency. Also the charge transfer resistance is similar. However, the impedance shows much difference at low frequency range, which is because of the Li⁺ diffusion in the particle. These results are consistent with the XRD analysis and capacity tests.

3.5. Cycle tests

Fig.6 shows us the cycle test at C/20 charging and discharging results for the electrodes after 1 hour shorting. The capacity is only slightly increased in these cycles and cycle tests cannot recover the capacity loss for LiFePO₄ electrodes. Therefore the shorting effects for LiFePO₄ electrodes are permanent. In order to recover the capacity loss, the amorphous layer on LiFePO₄ must be removed by some ways. Rate capability tests are not necessary since the shorted electrodes have a very low capacity.

Heat treatment at 500°C, polishing and cycle tests have been tried in order to recover the capacity loss. However, none of them works. Also we know that the shorting affect the whole electrode, not just the surface of the electrode. Therefore, shorting is detrimental to the LiFePO₄ electrode, which is permanent, even if it is a short time like 1 hour.

4. CONCLUSIONS

The shorting effects of LiFePO₄ electrode has been studied in this paper. After shorting tests, amorphous phase can be formed on the LiFePO₄ surface, which can block the diffusion of Li⁺ in the LiFePO₄ grain. When LiFePO₄ has two phases including LiFePO₄ and FePO₄, the amorphous phase is thicker after shorting tests. This can be proved by the charging and discharging curve, XRD analysis and impedance spectroscopy. When LiFePO₄ electrode was charged for 5 hours or 10 hours at C/20, there is almost no capacity after shorting tests. From the perspective of the shorting effects for

lithium ion battery with LiFePO₄ electrode, the battery should be activated twice before shipping to customer. Also the battery should be in full charge or discharge state in order to minimize the shorting effects. The shorting effects for LiFePO₄ electrode are permanent, which cannot be recovered by simply polishing, cycle tests or heat treatment.

It will become more important to recycle the lithium ion battery considering the high price of lithium ion battery when large amount of lithium ion batteries will be used. However, the proper recycle method will be very important in order to proper use the natural resources on the earth. For LiFePO₄ electrode, we cannot simply recycle the materials because the structure is already changed and the proper way is to decompose the material and get the necessary elements, for example, Li⁺. Then LiFePO₄ can be remade based on these elements.

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