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Enhanced cycling performance and high energy density of LiFePO₄ based lithium ion batteries

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Abstract

LiFePO₄ attracts a lot of attention as cathode materials for the next generation of lithium ion batteries. However, LiFePO₄ has a poor rate capability attributed to low electronic conductivity and low density. There is seldom data reported on lithium ion batteries with LiFePO₄ as cathode and graphite as anode. According to our experimental results, the capacity fading on cycling is surprisingly negligible at 1664 cycles for the cell type 042040. It delivers a capacity of 1170 mAh for 18650 cell type at 4.5C discharge rate. It is confirmed that lithium ion batteries with LiFePO₄ as cathode are suitable for electric vehicle application.

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Keywords: LiFePO₄; Cathode materials; Capacity fading; 18650 cell type; Electronic materials; Electrical properties

1. Introduction

The demand for high energy rechargeable batteries for electric vehicle application has accelerated the development of lithium ion battery materials. The important factors governing their applications are low price, long cycle life, environment friendliness, safety, and high specific energy density. Orthorhombic LiFePO₄ which has an ordered olivine structure has attracted particular interest because it is environmentally benign, inexpensive and abundant in its raw materials [1]. However, LiFePO₄ has a poor rate capability attributed to low electronic conductivity which has hampered its applications as cathode materials in lithium ion batteries. Many efforts have been put in to solve the problems [2–5]. But, there is seldom a report on lithium ion batteries with LiFePO₄ as cathode

materials and the battery hasn't been successfully used in electric vehicle applications up to now due to poor rate capability and low energy density. This work shows that lithium ion batteries with LiFePO₄ as cathode are suitable for electric vehicle applications.

2. Experimental

LiFePO₄ sample was prepared by a solid state reaction. Li₂CO₃, Fe(C₂O₄)₂ and NH₄H₂PO₄ were dispersed into acetone and then thoroughly mixed and reground by energy ball-milling. After the evaporation of acetone, the powders were calcined at 700 °C for 24 h in a nitrogen atmosphere. The molar ratio for Li:Fe:P was 0.98:1:1 for the LiFePO₄ sample.

X-ray diffraction patterns of the calcined powder were collected for structural analysis. The XRD data were obtained over an angular 2θ range from 10 to 70° with a step size of 0.02° and a constant counting time of 1 s per step. X-ray Rietveld refinements were performed using GSAS. Powder morphologies were observed by SEM.

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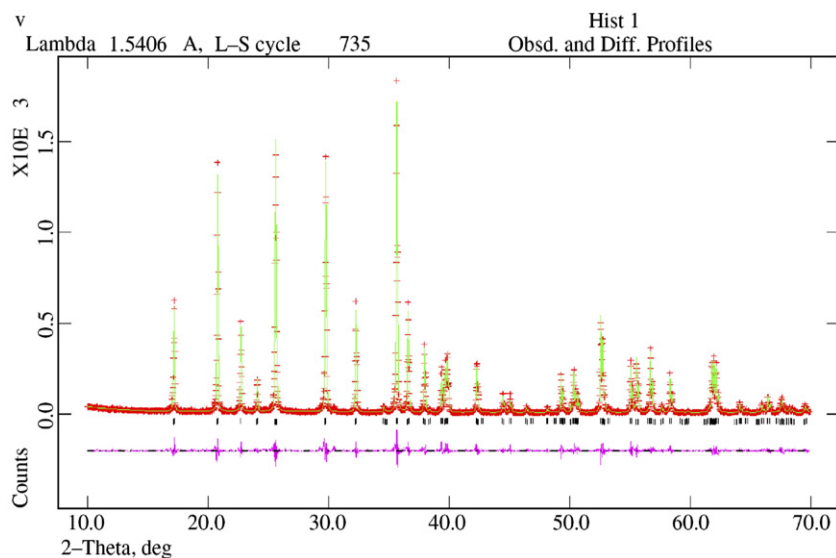


Fig. 1. The Rietveld refinement results of XRD for LiFePO₄ based on Pnma.

LiFePO₄ powder, super-P conducting additive, PVDF binder and NMP organic solvent were blend together in a high-speed mixer. The viscous slurry was then coated onto an aluminum foil current-collector and dried at 120 °C under vacuum for 24 h. The resulting electrode was used as a cathode. The cell was assembled using the above mentioned cathode, the anode consisting of natural graphite and PVDF binder, and Celgard 2400 microporous membrane as separator with 1.2 M LiPF₆ in a mixture of EC, PC and DMC electrolyte.

3. Results and discussion

Fig. 1 shows the XRD pattern of the LiFePO₄ powder and its Rietveld refinement as an olivine-tape single phase. The pattern could be indexed using Rietveld refinement with unit cell parameters of $a=10.323(0)$ Å, $b=6.004(3)$ Å and $c=4.691(6)$ Å. The value of R_p is 9.79% and R_{wp} is 13.68%. The morphology of obtained powder observed by SEM is shown in Fig. 2. The particle size of the powder is about 2 μm.

Fig. 3(a) shows the charge/discharge cycle properties of cell type 042040 with LiFePO₄ as cathode and natural graphite as anode at 0.8C. The capacity fading on cycling is surprisingly negligible at 1664 cycles. The cell has excellent cycling performance as compared to that

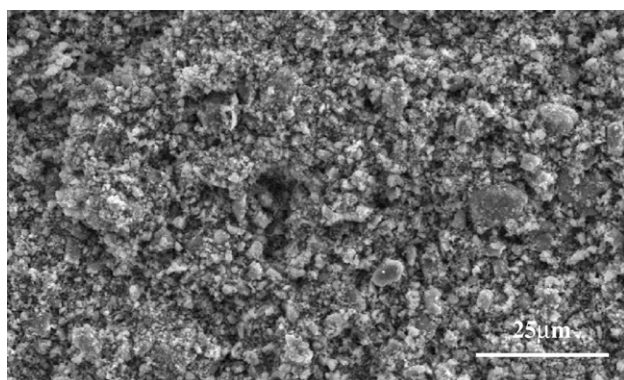


Fig. 2. SEM image of LiFePO₄ powder.

reported in the literature, e.g., Zaghbi [6] reported the capacity retention of 80% of its initial capacity at the 180th cycle and Shim [7] reported the capacity retention of 50% of its initial capacity for their

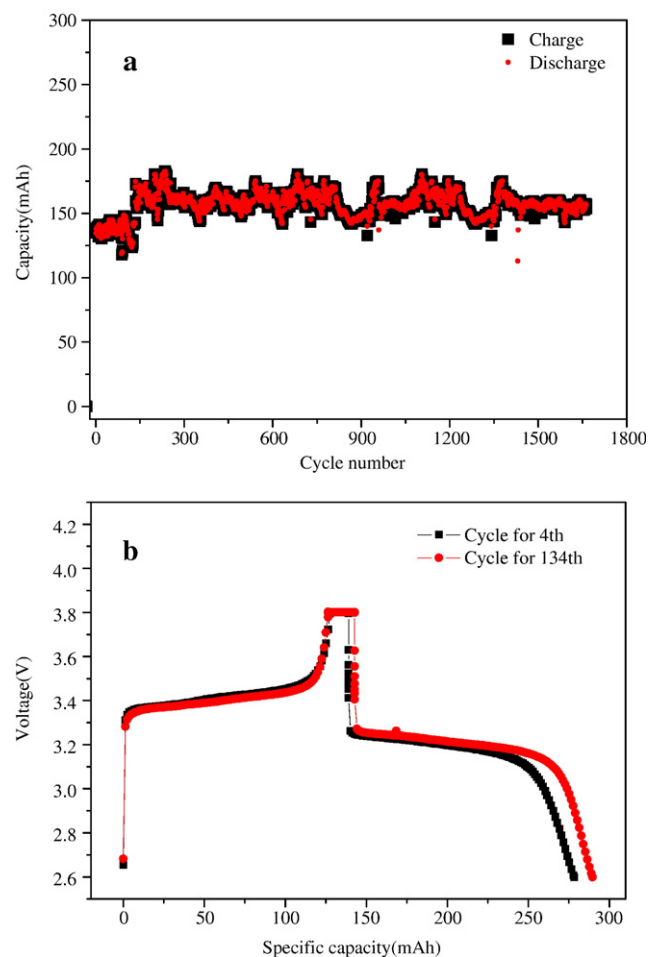


Fig. 3. (a) Charge/discharge cycle properties of LiFePO₄, the scan rate was 150 mA, the type of battery is 042040 and (b) voltage profiles at 4th cycles and 134th cycles for 042040 battery.

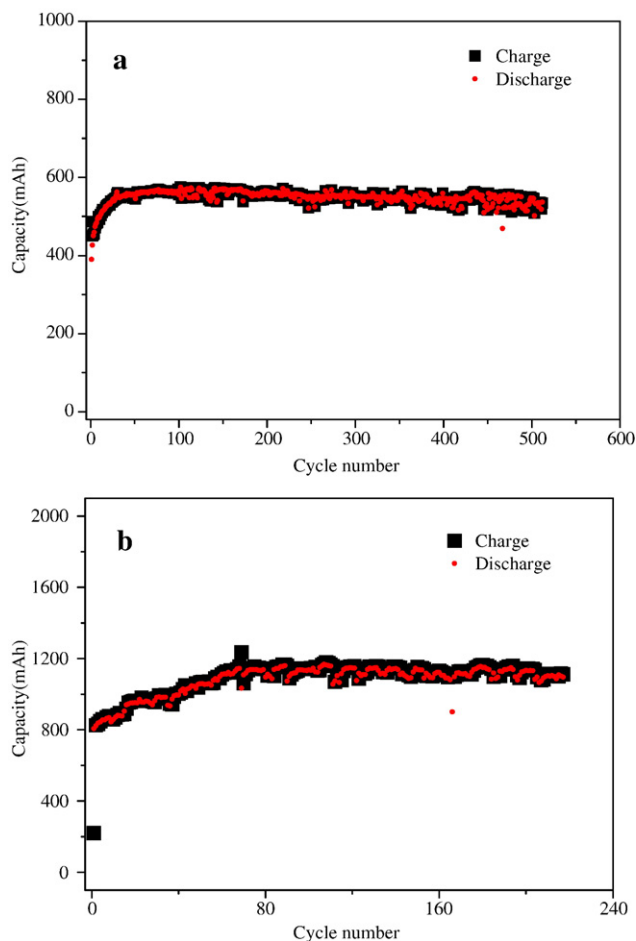


Fig. 4. (a) Charge/discharge cycle properties of LiFePO_4 , the scan rate was 250 mA, the type of battery is 063048 and (b) charge/discharge cycle properties of LiFePO_4 , the charge scan rate was 1000 mA, the discharge scan rate was 5000 mA, the type of battery is 18650.

cells. Fig. 3(b) shows the charge and discharge curves of the 4th cycle and 134th cycle. The voltage range of 2.6–3.8 V was used. A flat charge–discharge profile over a large range indicates that the redox reaction of LiFePO_4 proceeds as a two-phase reaction. The length of the plateau extended when the cycle number was increased.

The cycle properties of cell type 063048 are illustrated in Fig. 4(a). The charge/discharge current was 250 mA. The cycle properties of cell type 18650 are illustrated in Fig. 4(b). The charge current was 1000 mA, and the discharge current was 5000 mA. The performance of cell types 042040, 063048 and 18650 was summarized in Table 1. High energy density of 226.9 W h/L was obtained for the cell type 18650 at a high discharge rate of 4.5C.

Table 1

The properties of battery types 042040, 063048 and 18650

Battery type	042040 (0.8C)	063048 (0.45C)	18650 (4.5C)
Battery volume (L)	0.0032	0.00864	0.0165
Energy density (W h/L)	179.9	210.4	226.9

It has been reported that the battery with LiFePO_4 as cathode has a good performance in the temperature range of -20 – 100 °C and excellent safety characteristics against abuse conditions [8]. Our work shows the excellent performance of batteries with LiFePO_4 as cathode materials. The LiFePO_4 based lithium ion battery has a potential for electric vehicle application.

4. Conclusion

An excellent cycle life (the capacity fading on cycling is surprisingly negligible at 1664 cycles) and a high energy density make LiFePO_4 based lithium ion battery an excellent candidate for electric vehicle applications.

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