



# Analysis of the relationship between vertical impurity distribution of conductive additive and electrochemical behaviors in lithium ion batteries

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## ABSTRACT

In this work, double layered LiFePO<sub>4</sub> materials with different content of conductive carbon black are proposed for evaluating systematically the influence of impurity distribution of conductive additive on the electrochemical behaviors of cathode material for lithium ion batteries. Their polarization effects and electrochemical performances were investigated and compared in detail. It was found that there exists a simple empirical rule correlating the distribution of the conductive additive and the depolarization effect under the premise that the total content of the conductive additive is kept constant. The electrochemical performance of LiFePO<sub>4</sub>/C electrode tends to get better with increasing the conductive additive loading in the lower layer. This can be attributed to that the more conductive additive content in the lower layer could provide more available paths for electronic transmission, and markedly decrease the interfacial impedance between LiFePO<sub>4</sub>/C cathode material and current collector, thus improving the ability of collecting electron and maintaining a reliable electron transport system, especially under high current densities. This finding can enlighten us to design a more rational optimization of the electrode by controlling the distribution of conductive additive in the cathode material for high performance lithium ion batteries.

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## 1. Introduction

Owing to the advantages of environmentally-friendly, sustainability, portability and potentially low cost, rechargeable lithium-ion batteries are getting more and more attention and appreciation in various portable electronic devices and electric vehicles [1,2]. The electric performance of batteries depends largely on the material components used in the batteries. Among them, the cathode material has been proved to be the core element of battery, and occupies an important position on the performance of lithium ion batteries. Among all the existing cathode materials, olivine-structured lithium iron phosphate (LiFePO<sub>4</sub>) is expected to be a highly promising cathode material due to its flat voltage profile, better environmental compatibility, long cycle life, high theoretical

capacity (170 mAh g<sup>-1</sup>) and high safety rating [3,4]. However, the slowest step of electrochemical kinetics in this material limits the electrochemical performance of the whole lithium ion battery by significant polarization effect, increasing charging voltage and decreasing discharge voltage. To break this bottleneck, LiFePO<sub>4</sub> has to surmount the barriers of poor electronic conductivity and slow lithium ion diffusion. There are indeed numerous common methods that have been utilized to enhance the electrochemical performance of LiFePO<sub>4</sub>, e.g. changing lattice parameters by doping with transition metals [5,6], coating conductive materials on the surface of cathode materials to reduce contact impedance [7], optimizing the acetylene black (AB) /PVDF ratios or moderate increase of binder contents to form a cohesive conductive carbon particle network [8–11], and controlling nanoparticles' granularity to shorten the lithium-ion diffusion length [12]. Although the electrochemical performance of cathode materials has been addressed to some degree through the above approaches, several potential problems may be raised at the same time, including

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capacity loss, higher cost and low tap density.

It has been well-known that the capacity density is more significant in evaluation of cathode materials, rather than specific capacity [4]. The nanosized  $\text{LiFePO}_4$  particles have unsatisfactory tap density (approximately  $0.8\text{--}1.2\text{ g cm}^{-3}$ ) and require much more content of conductive additive, which have been the major obstacles to obtain satisfactory capacity density. It is not a good judgement to merely control nanoparticles' granularity in terms of both capacity density and electrochemical performance. The deviation of voltage between practical and theoretical values (voltage drop of battery,  $\Delta U = I \times R$ ) is mainly determined by internal resistances, which consist of ohmic resistance and polarization resistance and the maximum resistance has a dominant influence on electrode reaction rate in the lithiation process. Previous works on the comparison of the rate performance of different  $\text{LiFePO}_4$  materials have pointed out that the electron transport efficiency between the particle surface of  $\text{LiFePO}_4$  material and the current collector plays a decisive role in the rate performance of the batteries, particularly at high current rate [4,13]. Therefore, higher conductive carbon loading and carbon coating would be more effective to improve the electrochemical performance of  $\text{LiFePO}_4$  when compared with cation doping and reducing of particle size. Using more conductive carbon could improve the electron transmission rate significantly, and may be the most simple and effective method to enhance the electrochemical performance of cathode materials. Highly conductive additives like carbon fibers, graphene and carbon nanotubes are usually used for accelerating the speed of electronic transmission between the cathode and current collector [14–16]. These previous studies mostly focus on the impact of content and properties of conductive additives [17–19], nevertheless, few researchers pay attention to the influence of their vertical imparity distribution on the electrochemical performance.

With these considerations, the cathode materials which are composed of double layers of  $\text{LiFePO}_4$  with various conducting carbon additive loadings are fabricated for systematically evaluating the influence of distribution of conductive additive on electrochemical performance of  $\text{LiFePO}_4$  cathode. By measuring and comparing the charge and discharge curves of different systems at different rates, we found that the more conductive additive loading in lower layer is capable of making the LFP/C cathode exhibit higher specific capacity and the better retention efficiency of capacity under the premise that the total content of conductive additive remains unchanged. Based on this finding, we believe that the rate capability of  $\text{LiFePO}_4$  cathode is strongly correlated to the interfacial impedances between the particle surface of  $\text{LiFePO}_4$  material and the current collector. Furthermore, the mechanism of the

experiment is discussed in detail in this work.

## 2. Experimental

### 2.1. Sample preparation

The  $\text{LiFePO}_4$  sample with 2.0 wt% carbon coating used in this work was obtained from Shenzhen Dynanonic Co., Ltd. and the average particle size was  $0.5\text{--}1.0\text{ }\mu\text{m}$ . The standard graphite used in full-cell was provided by Hunan Shanshan energy Polytron Technologies Inc. The battery slurry was obtained by mixing the dried Polyvinylidene fluoride (PVDF), conductive additive Super-P (SP) and  $\text{LiFePO}_4$  in N-methylpyrrolidone (NMP) suspension and vigorously stirring for 24 h. The content of PVDF in all the samples was all fixed to 10 wt%, while SP content was precisely controlled to be 1, 3, 5, 7 and 9 wt%, respectively. To make double layered  $\text{LiFePO}_4$  materials with different conductive additive loadings, firstly, the cathode slurries with 1, 3, 5, 7 and 9 wt% SP, were uniformly spread on aluminum foil (thickness:  $18\text{ }\mu\text{m}$ ) with final thickness of  $15\text{--}20\text{ }\mu\text{m}$  by an automatic coating machine (Ke Jing Materials Technology Co., Ltd., China.), and then dried in oven for  $30\text{--}40\text{ min}$  at  $60\text{ }^\circ\text{C}$ . As illustrated in Fig. 1, the cathode slurries (as upper layers) with 9, 7, 5, 3 and 1 wt% SP were uniformly spread on the cathode slurries (as lower layers) with 1, 3, 5, 7 and 9 wt% SP with  $15\text{--}20\text{ }\mu\text{m}$  final thickness, respectively. Cathode slurries were rolled assuming that the two layers are tightly joined together on the rolling machine after drying in oven. The thus-prepared double-layered  $\text{LiFePO}_4$  cathode materials are labeled hereafter as B-1, B-3, B-5, B-7 and B-9, respectively, i.e., SP contents in upper and lower layers are 9 and 1 wt%, respectively (B-1), 7 and 3 (B-3), 5 and 3 (B-5), 3 and 7 (B-7) and 1 and 9 (B-9).

### 2.2. Characterization

Electrochemical measurements were carried out by using 2032 coin-type test cells, which consisted of double-layered  $\text{LiFePO}_4$  cathode, lithium anode (counter electrode), separator (Celgard 2400) and electrolyte. The electrolyte consisted of 1.0 M  $\text{LiPF}_6$ , containing dimethyl carbonate (DMC)-ethylene carbonate (EC)-ethyl methyl carbonate (EMC) mixture (1:1:1 vol ratio). The cells were assembled in an argon-filled glovebox in which the content of  $\text{H}_2\text{O}$  and  $\text{O}_2$  was strictly controlled to be  $<0.1\text{ ppm}$  and  $<0.5\text{ ppm}$ . The electrochemical performance of cathode materials was recorded by a Land CT2001A charge–discharge instrument, China.

The morphology and structure of cathode materials were investigated by scanning electron microscopy (Hitachi S-4800

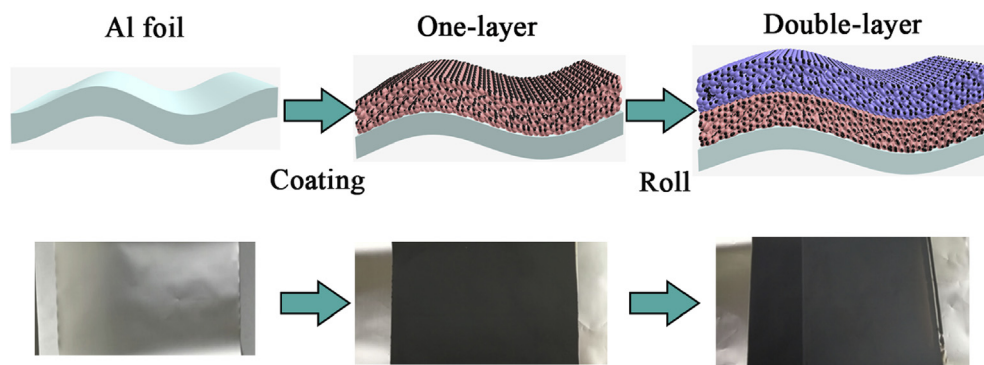


Fig. 1. Schematic diagram for the preparation of double-layered  $\text{LiFePO}_4$  cathodes on aluminum foil.

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