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Safe positive temperature coefficient composite cathode for lithium ion battery

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HIGHLIGHTS

- ► The T_c of PTC material is about 90 °C, much lower than the previously reported.
- ► They can endow the electrode with a current limiting effect at around 90 °C.
- ► It will not impose any negative effect on its electrochemical property.
- ► PTC composite also can be used with $LiCoO_2$ or $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$, etc.

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ABSTRACT

Ethylene vinyl acetate (EVA) based positive temperature coefficient (PTC) material with a transition temperature (T_c) of 90 °C is proposed and successfully fabricated in this study. It is further introduced into $LiFePO_4$ cathode by directly mixing it with $LiFePO_4$ powder, binder and conductive carbon or sandwiching it between the current collector and $LiFePO_4$ electrode membrane. Thus obtained $LiFePO_4$/PTC composite electrodes both show a self-current-limiting effect at 90 °C. The electrochemical properties of the $LiFePO_4$/PTC composite electrodes are determined in terms of galvanostatic charging/discharging, cyclic voltammograms and electrochemical impedance spectroscopy measurements. Comparing with bare $LiFePO_4$ electrode, both $LiFePO_4$/PTC composite electrodes show no degradation in cycling stability, rate capability and electrochemical kinetic property at room temperature. The results indicate that the proposed $LiFePO_4$/PTC composite electrode with the suitable T_c of 90 °C can effectively prevent thermal runaway before the occurrence of side reactions and better protect lithium ion battery during the abnormal temperature increasing.

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1. Introduction

Lithium-ion batteries have revolutionized the portable electronics market since it was first proposed in 1990's, but even now, safety concerns associated with the electrode reaction and solid-electrolyte interphase (SEI) instability still hinder the development of lithium ion battery and its wider application. Because of the using of highly flammable organic solvents and the highly reactive electrode material in lithium ion battery, safety risk seems unavoidable in some degree, especially when being used under abusive conditions, lithium-ion batteries may undergo thermal runaway that generates a sharp rise in temperature and then results in serious hazards of fire and explosion. Therefore, it becomes very important to find an effective approach to retard the fire and explosion. A number of strategies have been implemented to improve the safety of lithium-ion batteries, including the addition of safety protection agent and the adoption of the safety technique, such as fire retardant additive [1], overcharge protector [2], lithium salt [3], and safety vents [4], internal or external PTC devices [5–7], shutdown separators [8], coatings [9], and so on.

Generally, thermal stability of the battery components is a decisive factor in the safety property. Any abuse, including disposing in fire, overcharging, external short circuiting or crushing, can trigger spontaneous heat evolving reactions, which can lead to fire and explosion [10]. And usually, temperature increase is the first abnormal signal that can be detected. Basing on this point, PTC devices such as PTC resistor near the top of the crimped seal header [7], have already been widely used in commercial lithium ion battery. PTC behaviour is characterized by a drastic rise in volume resistivity as temperature approaches the melting point of the matrix resin. The phenomenon is believed to be closely related with localized disaggregation and re-aggregation of conductive fillers as hydrodynamic conditions permit [11]. When PTC device is embedded into lithium ion battery, its sensitivity to temperature increasing can help to introduce a temperature activated switch feature.

However, the distance between the external PTC devices and the SEI, where the thermal runaway most likely starts, can cause some

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hysteresis in PTC's response to temperature. It means that even when the internal cell temperature is above Curie temperature of PTC, the skin temperature of the cell may still not be high enough to activate the external PTC device, and then the effect of PTC device is weakened. The consequence of this hysteresis can be more serious when thermal runaway proceeds quickly and thus more chain reactions may be initiated before the external PTC takes effect. In fact, in the power lithium ion battery, fast charging may cause inhomogeneous polarization and which can further leads to some local temperature increasing within the electrode or in SEI layer and thus the response of the external PTC can be greatly delayed even not able to hinder the electrode reaction before thermal runaways happens.

Reducing the distance between the PTC device and the electrode can be an effective strategy to make PTC device function better, and basing on this, Kise and his coworker proposed a new cathode [5] containing the PTC component, it showed an sharp and nonlinear increase in the electrode resistivity at 130–140 °C due to the expansion of polyethylene at its melting point. Yang reported a new PTC contained cathode [6], in which the PTC layer is sandwiched between the common electrode and the current collector. The result showed that a resistance increasing initiated at around 100 °C, but a complete current-limiting effect required a higher temperature of 130 °C. However, previous work also indicated that at around 100 °C, solvent evaporation, oxidation reaction between the cathode and the electrolyte, or decomposition of SEI already starts [12]. Additionally, it has to be noted that most commercial lithium-ion batteries use Polypropylene/Polyethylene/Polypropylene(PP/PE/PP) separators with a lower melting temperature of 130 °C and the melting of the PE layer at around 130 °C can break the circuit [13]. So, a more effective PTC with lower transition temperature (T_c) is required to better protect the battery before the occurrence of side reaction at 100 °C.

Here we report our recent work on safe electrode containing PTC component, a new EVA-based PTC [14] component was introduced into $LiFePO_4$ electrode through two approaches, the one is manufacturing the cathode by directly mixing the PTC material with other reagents such as active material, conductive carbon and binder (see Fig. 1a), the other is constructing a sandwich-type electrode by applying a PTC layer between the current collector and the common electrode (see Fig. 1b). Our results show that they both can endow the electrode with a current limiting effect at around 90 °C. It has been further proved that the incorporation of the PTC component into $LiFePO_4$ electrode will not impose any negative effect on its electrochemical property, even under a high current rate. Therefore, it is believed that this new PTC/$LiFePO_4$ composite electrode is a promising technology for lithium ion batteries with improved safety characteristic.

2. Experimental

The PTC material used in this study is the mixture of polyethylene oxide (PEO), EVA and acetylene black with the mass concentration range of 1–7%, 50%–85% and 10%–30% respectively, and the typical mixture contained 20 or 24 wt.% acetylene black, depending on how PTC component was introduced into the electrode. Firstly, the above reagents were mixed in a reflex condenser in petroleum ether medium, after 5 h reflux under 105 °C, a well dispersed slurry can be obtained. Thus obtained PTC material is stored into petroleum ether medium for a further use.

The PTC/$LiFePO_4$ electrodes were prepared by two methods, one is to mix the above PTC slurry with polytetrafluoroethylene (PTFE) binder, $LiFePO_4$ powder and acetylene black in the weight ratio of 7.5: 5: 67.5: 20; the other is to construct a sandwich-type electrode by applying a PTC layer between the current collector and the $LiFePO_4$ electrode membrane, in which the $LiFePO_4$ electrode contains 75% $LiFePO_4$ powder, 20% acetylene black and 5% PTFE by weight. A bare $LiFePO_4$ electrode with the same composition was also made by pressing the above mixture onto the Al foil current collector as a reference. No matter what kind of electrode was used, the size of the electrode is 8×8 mm^2 and the typical loading of $LiFePO_4$ was 6 mg. The electrode were vacuum dried at 70 °C and then the 2016 cell was fabricated in an argon filled glove box (MECABOX80-1"s", Switzerland) with the above cathodes, lithium anode, 1 M $LiPF_6$ in 1:1 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte, and Celgard 2300 separator.

The charging/discharging tests were conducted on Land battery cycler (Land Co. Ltd., China). Unless specified, the cells were cycled between 2.0 and 4.0 V at C/2 under room temperature (1C = 150 mAg^{-1}).

Cyclic voltammetry (CV) measurements were carried out on CHI660A Electrochemical Workstation with a scan rate of 0.1 mV s^{-1}. A three electrode cell was used, in which the working electrode has the same composition as being described above, both the counter and the reference electrodes were lithium metal.

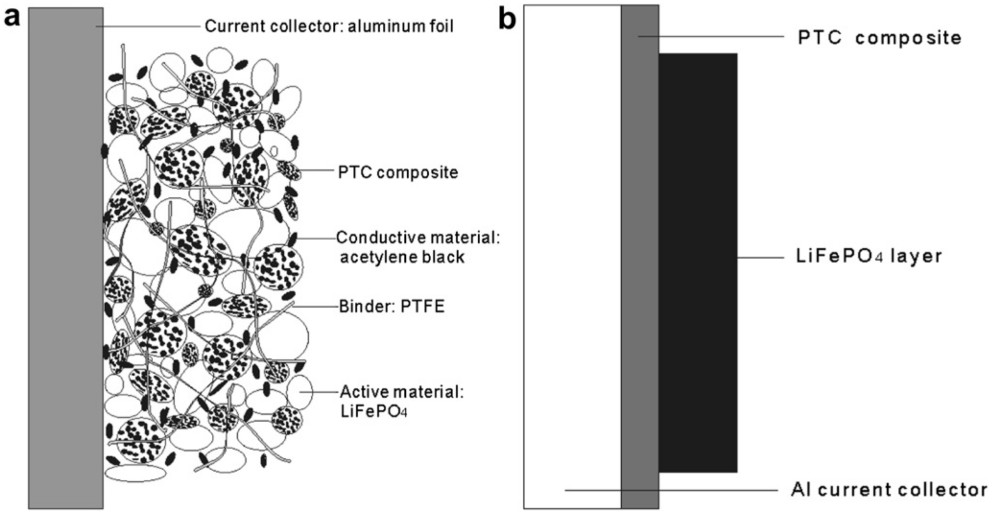

Fig. 1. A schematic illustration of the $LiFePO_4$/PTC composite electrode, directly mixture electrode (a) and sandwich-type electrode (b).

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