



Poly(3-butylthiophene)-based positive-temperature-coefficient electrodes for safer lithium-ion batteries



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ABSTRACT

A new positive temperature coefficient (PTC) electrode is prepared simply by coating a thin layer of redox-active poly(3-butylthiophene) (P3BT) in between the electroactive $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ [523] layer and the Al foil substrate to improve the safety of lithium-ion batteries. The experimental results demonstrate that the electrical conductivity of the PF_6^- -doped P3BT decreases sharply at 120–150 °C, showing a remarkable PTC effect. As for the P3BT-523 composite electrodes, a rate capacity nearly reaching the reference electrode is obtained at less than 1C rate, while the rate discharge capacities increase obviously with the decrease of the P3BT solution concentration. Moreover, after being exposed to 150 °C for 5 min, the P3BT-523 composite electrodes are hardly discharged and the discharge voltage of the composite electrodes drop drastically below the cut-off voltage at a current density of 3C, suggesting an effective thermal shutdown switch for lithium-ion batteries.

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1. Introduction

Due to the intrinsic advantages of high energy density and long cycle life [1–3], lithium-ion batteries (LIBs) have been considered as the most competitive power source for high-rate and high-capacity applications such as electric vehicles (EVs) and large-scale energy storage systems (ESSs) [4,5]. However, higher capacity and energy density LIBs required by such applications are severely frustrated by their safety issues [6–8]. Apart from the fact that LIBs are comprised of highly oxidative cathode and reductive anode, the use of flammable organic electrolytes make the safety risk of LIBs unavoidable to some extent. Once LIBs are subjected to abuse, such as overcharge, internal or external short-circuit and high temperature impact, a number of exothermic side reactions inside the cell may be triggered, including the thermal decomposition of the solid electrolyte interphase (SEI), organic electrolyte and the cathode material. These reactions generate excessive heat and flammable gas, which may cause a sharp increase in the internal temperature, probably resulting in cell cracking, firing or even explosion [9–12].

For this reason, a number of strategies have been already applied to overcome the safety issues of LIBs. For example, commercial LIBs are usually designed with PTC devices, pressure

valves and thermal shutdown separators [13]. However, the former two external protective devices are slow to sense the temperature changes of the interior of the battery and may fail to response simultaneously when the hazardous reaction occurs in a very high rate [14]. Although the internal shutdown separators can cut off the electrochemical reactions between electrodes at a certain temperature, they can't retain their mechanical integrity and may lead to an internal short-circuit when the temperature is much higher than their melting point [15]. To seek for a better safety control, a great deal of new safety strategies for LIBs are developed recently. However, mechanisms reported for overcharge protection, such as redox shuttles [16,17], polymerizable monomers [18,19], potential-sensitive separators [20,21], can only be actuated at the high potential of positive electrodes. While, strategies, including high-temperature separator [22], material coating [23], can only improve the thermal stable ability of LIBs to some extent, but can not prevent LIBs from thermal runaway. In comparison, PTC electrodes [24–27], whose resistances increase dramatically with the temperature increase of LIBs at certain temperature ranges, thus providing a self-current-limiting capability to reduce the heat from battery reactions so as to prevent thermal runaway, seems to be a more attractive safety mechanism for LIBs.

Based on their strong PTC effect, four kind of plastics-carbon composite materials, namely polyethylene-carbon composite [24], epoxy-carbon composite [25], poly(methyl methacrylate)-Super P composite [26], polyethylene oxide-ethylene vinyl acetate-acetylene black composite [27], have already been employed as PTC

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materials to fabricate PTC electrodes. Those PTC electrodes all successfully restrain the reaction current in a certain temperature range, suggesting an effective self-actuating thermal cut-off protection mechanism for LIBs. However, the above mentioned PTC materials are all prepared by incorporating conductive particles into polymer matrix and this kind of PTC materials may lose their current cut-off protection because of negative temperature coefficient (NTC) effect caused by agglomeration of conductive particles when the temperature is much higher than the melting points of their matrices.

In this paper, a new kind of PTC material, based on the doping/thermal-dedoping behavior of electroactive polymers [28], without NTC effects, is studied and a simple processing method of the new PTC electrodes is reported. Furthermore, the discharge properties and thermal behaviors of the as-prepared PTC electrodes are all described in detail.

2. Experimental

3-Butylthiophene (purity $\geq 98\%$, Henan Wanxiang Chemical Industry Co., Ltd., Zhengzhou, China) was used as received without further purification. The electrolyte used in this study was 1 M LiPF_6 in a 1:1:1 (by vol.) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl-methyl carbonate (EMC) purchased from Guotai-Huarong New Chemical Materials Co., Ltd. (Zhangjiagang, China). The separator used in this study was polypropylene (PP) based with ceramic coating (SH224D14, Shenzhen Senior Technology Material Co., China). The test batteries used in this study were $\text{Li}/\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coin cells. The cathode electroactive layer comprised 80 wt.% $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, 10 wt.% Super-P, and 10 wt.% poly vinylidene fluoride (PVDF) as a binder. The cells were assembled in an argon-filled glove box.

P3BT used in this study was synthesized by chemically oxidative polymerization of 3-butylthiophene monomer in chloroform with FeCl_3 as an oxidant in the same way as described in our previous paper [29]. The as-prepared P3BT was washed with methanol for at least three times and then added into a mixture of chloroform and monohydrate under magnetic stirring at 60°C for de-doping. Finally, the de-doped P3BT was re-precipitated out by pouring the organic layer of chloroform solution into methanol and extracted with methanol in a Soxhlet extractor for purification.

The thus-prepared electroactive polymer of P3BT was first dissolved in chloroform to form a homogeneous solution with a certain concentration of 0.5 wt.%, 0.75 wt.%. Then a thin coating layer of the polymer on the aluminum foil was obtained through spraying to fabricate $\text{Al}/\text{P3BT}/523$ (P3BT-523) composite electrodes.

The charge-discharge measurements were conducted at a potential range of 4.30–2.5 V with a programmable computer-controlled battery charger (CT2001A Land Battery Testing System, Wuhan, China). The cyclic voltammetry measurements were measured using a two-electrode cell with a large lithium sheet as both counter electrode and reference electrode on a CHI 1140 electrochemical workstation (Chenhua Instrument Co., Shanghai, China) at a scan rate of 0.02 mVs^{-1} . AC impedance measurements were performed on a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research, USA) in the frequency range of 100 kHz–100 mHz at an amplitude of 5 mV. The cross section images of the composite electrode were examined using a S-4800 Scanning Electron Microscope (Hitachi, Japan).

The PF_6^- -doped P3BT was prepared by electrochemical oxidation. The P3BT polymer was first dissolved in chloroform, and then deposited directly on the shells of the coin cell to form a thin polymer film, which was applied as the cathode to fabricate a $\text{Li}/\text{P3BT}$ coin-type cell. The $\text{Li}/\text{P3BT}$ cell was charged at 4.0 V for

more than 48 h, and then the PF_6^- -doped P3BT film was obtained. The PF_6^- -doped P3BT film was sandwiched between two parallel Ni plates and its resistivity-temperature dependences were measured directly by a digital multimeter from ambient temperature (ca. 30°C) to 180°C .

3. Results and discussion

With a wide range of promising applications in organic electronics, poly(3-alkylthiophene)s (P3ATs) have been studied extensively as p-type semiconductors in the past two decades [30]. However, few interests have been focused on the huge decrease in electrical conductivity of this kind of polymers. The working mechanism of this polymer used for thermal cut-off protection is based on its intrinsic nature that it can transform from a conductive state to an insulating state upon thermal de-doping [28]. At normal operating temperature, the polymer coating layer is electrical conductive and allows the current to pass through form the Al foil substrate to the electroactive layer. However, when the cell is subjected to abuse and the internal temperature of the cell reach to a critical temperature, the polymer layer will convert to an insulating state and cut off the charging/discharging process so as to protect the cell from thermal runaway.

Fig. 1 gives the relationship between electrical conductivity and temperature of PF_6^- -doped P3BT. As shown in the figure, the conductivity of PF_6^- -doped P3BT is about $10^{-3.5}\text{ S cm}^{-1}$ at room temperature and decreases sharply by a factor of at least ca. 10^2 at $120\text{--}150^\circ\text{C}$, showing a remarkable PTC effect. In general, thermal runaway of large format prismatic lithium ion battery happens mainly due to massive internal short circuit caused by severely shrinking of separators and now the polyolefin separator coated with ceramic materials will not lose its integrity until about 250°C [31]. Therefore, it is possible for the P3BT polymer PTC layer to cut off the electrochemical reaction in advance and thus provide a self-actuating thermal cut-off protection for safety control of rechargeable lithium-ion batteries.

Besides, the electrochemical behavior of P3BT polymer in lithium-ion battery environment is another critical factor for industrial application. So the $\text{Li}/\text{P3BT}$ coin-type cells with a $2\text{ }\mu\text{m}$ -thick P3BT film as the cathode prepared by directly coating the polymer on current collector without any binder or conductive carbon were assembled and tested. The charge-discharge (doping/dedoping) curves of the thus-prepared cell is depicted in Fig. 2. As can be seen in Fig. 2, the initial charge/discharge curves of P3BT are somewhat different from the rest. The first charge specific capacity of the cell is about 118 mAh g^{-1} , however, the corresponding discharge capacity is 62 mAh g^{-1} , indicating that the polymer is partly doped and convert to a conductive state after the first cycle [32]. Moreover, the charge-discharge curves become reproducible

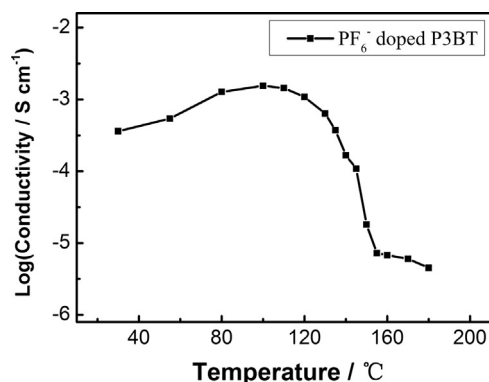


Fig. 1. Temperature dependence of conductivity for the PF_6^- -doped P3BT.

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