Short communication

A poly(3-decyl thiophene)-modified separator with self-actuating overcharge protection mechanism for LiFePO$_4$-based lithium ion battery

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ABSTRACT

A voltage-sensitive separator is prepared simply by impregnating electroactive poly(3-decylthiophene) (P3DT) polymer into a commercial porous separator and tested for a self-actuating control of overcharge voltage of LiFePO$_4$/C lithium-ion batteries. The experimental results demonstrate that this type of separator can be reversibly p-doped and dedoped to maintain the cell's voltage at a safe value of $\leq$4 V even at high rate overcharge of 3 C current, effectively protecting the batteries from voltage runaway. Since this P3DT-modified separator has no obvious negative impact on the normal charge–discharge performance of the batteries, it may be adopted for practical application in commercial lithium ion batteries.

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1. Introduction

Safety is a primary concern for commercial development of high-rate and high capacity lithium ion batteries for hybrid electric vehicles (HEV) and electric vehicles (EV) [1,2]. Since present lithium ion batteries use volatile and flammable organic electrolytes, irreversible decomposition of the electrolyte may occur to produce combustible organic gases at high overcharge voltage and the small gaseous molecules cannot recombine again into their parent molecules. Thus, the organic electrolyte is incapable to provide an internal voltage control during overcharging. As a result, the overcharge voltage may go up immoderately and therefore induce a series of hazardous exothermic reactions, which eventually leads to a thermal runaway, causing cell cracking, firing or even explosion [3–8].

In pursuit of safety and reliability, great efforts have been focused in recent years on developments of internal and self-actuating overcharge protection mechanisms for lithium ion batteries. Various types of electrolyte additives, such as redox shuttles [9–13] and polymerizable monomers [14–18], have been proposed as safety electrolyte additives to prevent the lithium ion batteries from overcharging. But until now, most of the reported shuttle molecules cannot meet the requirements for practical battery applications due to either their poor stability at oxidized state or their poor solubility in commonly used organic electrolytes [11].

While the polymerizable monomers, such as biphenyl [15] and xylene [17], can function as a shutdown additive to increase the cell's overcharge tolerance to some extent [14–17]. Comparatively, use of electroactive membranes that modified with electroactive polymers with appropriate oxidation potential seems to be a more attractive means to clamp down the overcharging voltage of lithium ion batteries, because this type of separator can provide not only reversible electrochemical on–off for the charge reaction, but also sufficiently high shunting currents for the overcharged batteries [19–23].

In this paper, we report the preparation method of a poly(3-decyl thiophene) (P3DT)-modified separator and describe the applications and overcharge protection behaviors of this separator in the commercial LiFePO$_4$-based lithium ion batteries.

2. Experimental

3-Decylthiophene (3DT) (purity $\geq$98%, Henan Wanxiang Chemical Industry Co., Ltd., Zhengzhou, China) was used as received without further purification. The electrolyte used in this study was 1 mol L^{-1} LiPF$_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 test batteries used in this study were prismatic LiFePO$_4$/graphite batteries with a nominal capacity of 450 mAh, friendlily donated by Fenghua Lithium Battery Co., Ltd. (Zhaoqing, China).

P3DT used in this study was synthesized by chemically oxidative polymerization of 3-decylthiophene monomer in chloroform

using FeCl$_3$ as a catalyst according to the method described in literature [24]. A typical experimental procedure is to add 8.68 g FeCl$_3$ oxidant into a three-necked 250 ml flask containing 50 ml chloroform under magnetic stirring, and then slowly drop 100 ml of a chloroform solution containing 4 g monomer into the reaction solution at a dropping rate of $\sim$1 ml min^{-1}. The oxidative polymerization of P3DT usually lasts twenty more hours in the solution under aerating of nitrogen. After completion of the polymerization reaction, the reaction mixture was poured into methanol for precipitating out the polymer. This polymer was then washed several times with methanol and then added into a mixture solvent of chloroform and monohydrate hydrazine under magnetic stirring for de-doping. Finally, the de-doped polymer was extracted with methanol in a Soxhlet extractor for removing the residual oxidant and oligomers. All the chemicals used in this synthesis process were obtained commercially and used as received without further purification.

The electroactive polymer of P3DT was first dissolved in chloroform to form a homogeneous polymer solution of 2 wt.% P3DT. The P3DT-modified separator was then prepared simply by immersing a commercial porous PP/PE/PP membrane (UBE UP3074, 20 μm thick, 50% porosity) into the polymer solution for 10 min, and then, evaporating the solvents off to leave a modified separator with a thickness of 22 μm.

The surface morphologies of the separators before and after incorporation of P3DT were examined using a Quanta 200 Scanning Electron Microscope (FEI Company, Netherlands). The electrochemical behavior of P3DT synthesized from chemically oxidative polymerization of 3-decylthiophene monomer was studied with cyclic voltammetry (CV). The working electrode used in this study is a P3DT-coated Pt microelectrode, which was prepared by dipping a Pt microelectrode (diameter = 100 μm) in a chloroform solution of P3DT, and then taking out for evaporating the solvents off to leave a P3DT coating film on the Pt microelectrode. The voltammograms were recorded on a two-electrode cell using P3DT-coated Pt microelectrode as working electrode and a large lithium sheet as both counter electrode and reference electrode on a CHI 600c electrochemical workstation (Shanghai, China). The charge and discharge measurements of the prismatic LiFePO$_4$/C batteries using P3DT-modified separator were performed using a programmable computer-controlled battery charger (Land Battery Testing System, Wuhan, China).

3. Results and discussion

As an electroactive material working for overcharge protection, the electroactive polymer should have appropriate oxidation potential, which is required to be slightly higher than the terminating potential of the completely charged cathode and considerably lower than the decomposition potential of the electrolyte. For LiFePO$_4$-based lithium ion batteries, the potential of fully charged cathode is ca. 3.6 V.

Fig. 1 gives the CV curves of P3DT in 1 mol L^{-1} LiPF$_6$/EC + DMC + EMC electrolyte. It can be found that the anodic current, representing the oxidative p-doping process of P3DT, arises at the onset potential of 3.7 V, which is at least 250 mV positive than the charging voltage plateau of LiFePO$_4$. On the cathodic scans, the electrochemical reduction, corresponding to the de-doping process of the oxidized P3DT, almost completes at 3.5 V, at which the cathodic reaction of the oxidized LiFePO$_4$ just starts to occur. This comparison implies that the electro-oxidation of P3DT polymer can occurs only after the complete oxidation of LiFePO$_4$ and the electrochemical reduction of P3DT polymer takes place before the cathodic discharge of LiFePO$_4$ electrode. These results indicate that the P3DT polymer can be suitably
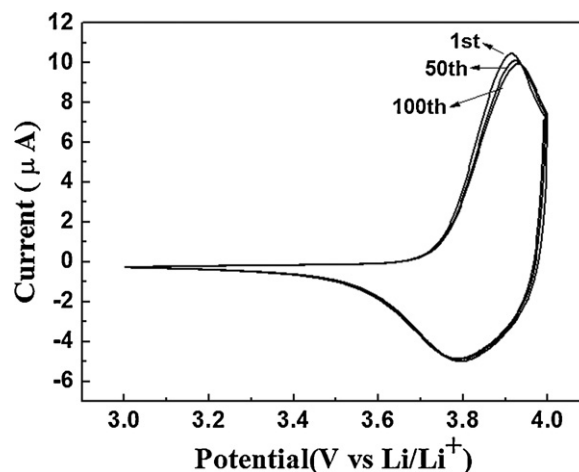

Fig. 1. The CV curves obtained from a P3DT-coated Pt microelectrode in 1 mol L^{-1} LiPF$_6$/EC + DMC + EMC electrolyte. Scan rate: 10 mV s^{-1}.

used for controlling the charging voltage of LiFePO$_4$-based lithium ion batteries, and that the use of P3DT-modified membrane as separator may not interfere the normal charge–discharge reactions of the batteries. In addition, the anodic and cathodic current peaks of P3DT are very symmetric and have only a slight decay during successive 100 scans, suggesting a very reversible and fast electrochemical kinetics of the electroactive polymer. The reversible electrochemical p-doping/dedoping process of P3DT with simultaneous intercalation and deintercalation of PF$_6^-$ anions can be formulated as follows:

$$\text{P3DT} + n\text{PF}_6^- \underset{+ne \text{ p-doping}}{\overset{-ne \text{ p-doping}}{\rightleftarrows}} \text{P3DT}^{n+}(\text{PF}_6^-)_n$$
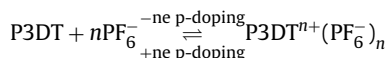
Fig. 2 compares the SEM images of the microporous separator before and after P3DT modification. It can be found in Fig. 2a that the commercial porous separator has a clear and highly uniform pore distribution. In contrast, the P3DT-modified separator (Fig. 2b) shows a smooth surface and partially blocked pore structure, suggesting that the P3DT polymer has been successfully filled into partial pores of the separator. Since the pores of the separator substrate are only partially filled with P3DT polymer and have plenty of remaining void pores, it is expected that the modified separator thus prepared can not only act as a normal separator allowing electrolyte to pass through at normal cell operating voltage, but also function as an internal self-actuating potential-sensitive membrane at overcharge state to prevent cell from voltage runaway.

Fig. 3 shows the charge–discharge curves of the prismatic LiFePO$_4$/C batteries using P3DT-modified separator at a charging rate of 1.0 C. It is clearly shown that at normal charge region, the charging voltage profiles display a typical charging plateau at about 3.45 V, indicating that the P3DT-modified separator has no discernible impact on the normal charge behavior of the test cell. Once overcharged, the charging voltages of the cells climb up steeply at first and then gradually drop to produce a voltage plateau at $\sim$3.7 V, showing an effective control of the charging voltage. In the following discharge, the test cell can deliver a capacity of 450 mAh even subjected to a 50% overcharge of its nominal capacity, showing no negative impact of the P3DT-modified separator on the discharge performance of the batteries. After 100 cycles of overcharge testing, the overcharging voltage plateau is only slightly elevated and can still be well controlled at a safe value less than 3.8 V, indicating a very reversible and effective overcharge protection for the test cells by the P3DT-modified separator.

As aforementioned in our previous publication [19], the sustainable charge and discharge current of the modified separator is
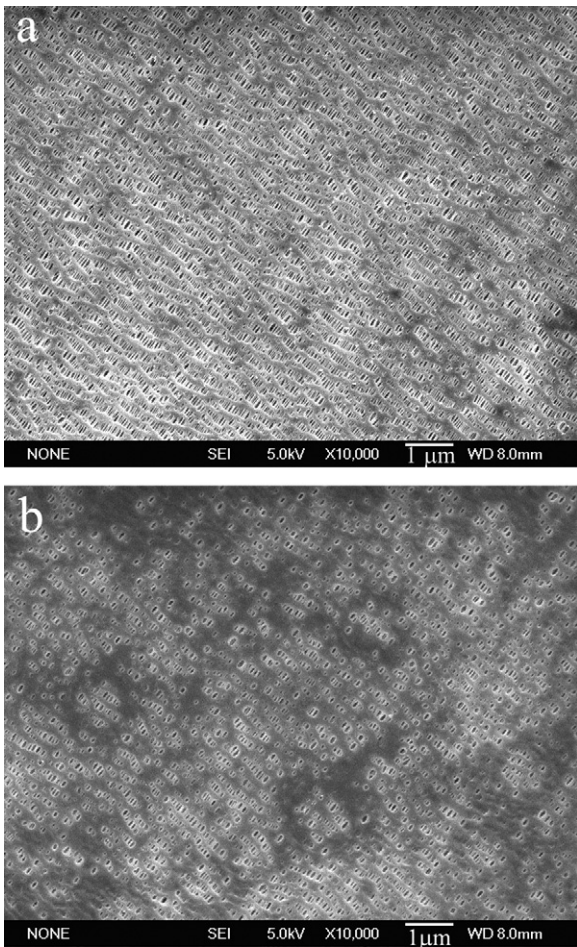
Fig. 2. SEM photographs of separator before (a) and after (b) P3DT modification.

Fig. 4. Charge–discharge curves of prismatic $LiFePO_4/C$ batteries using a P3DT-modified separator at various rates.

Fig. 5. The cycling performance of prismatic $LiFePO_4/C$ battery using a P3DT-modified separator at normal voltage interval of 2.0–3.6 V at 0.5 C rate.

an important factor for its practical application in lithium ion batteries. Fig. 4 shows the charge–discharge curves of the prismatic $LiFePO_4/C$ batteries using a P3DT-modified separator at various current rates. As it can be seen, the overcharge voltage plateaus of the test cell increase only slightly and still remain below 4 V, although the charging rates are heightened from 0.5 C to 3 C. Even at a very high current rate of 3 C, the test cells can still deliver a capacity of 415 mAh, showing a good overcharging shunting capability and an excellent high rate charge–discharge capability.
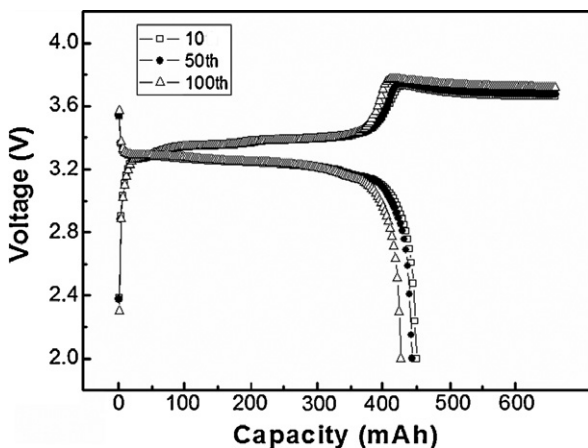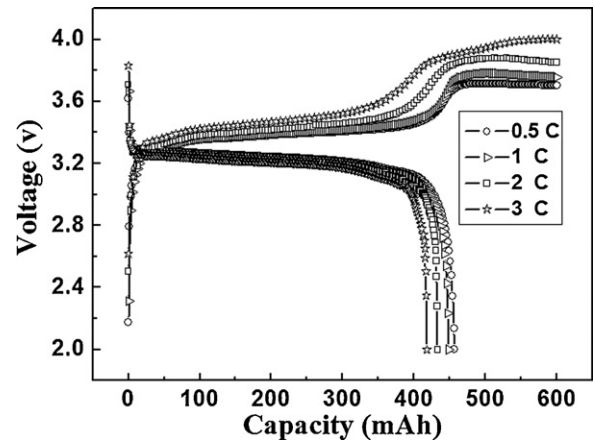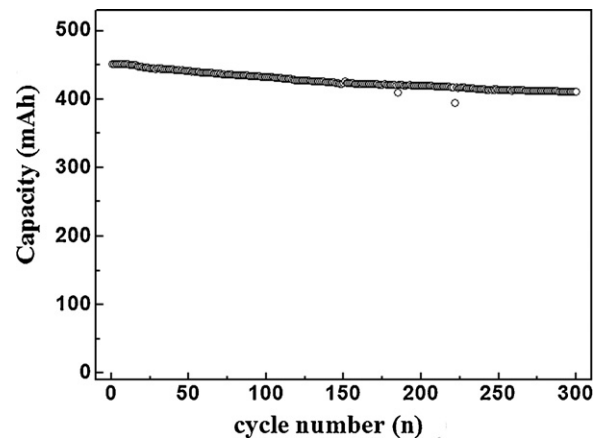
As a separator feasible for practical applications, it is very required not only to provide an effective voltage control at overcharge, but also have no negative impacts on the normal charge–discharge performances of the batteries. In order to evaluate the influence of P3DT-modified separator on the normal cycling performance of the batteries, the prismatic $LiFePO_4/C$ batteries using the P3DT separator are cycled at voltage interval of 2.0–3.6 V at 0.5 C rate. The typical cycling performance of these batteries is shown in Fig. 5. It can be seen that the discharge capacity of the battery is still kept at 410 mAh after 300 cycles, showing a very similar capacity retention as the commercial batteries of the same type.

The influence of the P3DT-modified separator on self-discharge rate of $LiFePO_4/C$ batteries is also investigated. The batteries are fully charged and then discharged at 0.2 C rate after stored at room temperature for 30 days. The self-discharge rate is calculated by comparing the discharge capacity of the batteries before and after storage. The self-discharge rate of the batteries using P3DT-modified separator is only 3.7% after 30 days storage, which is almost the same as that of the batteries with commercial separator.

4. Conclusion

In summary, a P3DT-modified separator was prepared and adopted for practical $LiFePO_4/C$ lithium ion batteries. The experimental results demonstrated that, as a self-actuating overcharge protection separator, this separator could transform from an electronically insulating state to a conductive state at overcharged

Fig. 3. Overcharge cycling curves of the prismatic $LiFePO_4/C$ batteries using a P3DT-modified separator at 1 C rate.

voltage, leading to an internal short-circuit to prevent the cells from voltage run-away. In addition, this separator works reversibly and has no significant impact on the normal charge–discharge performance of the batteries, showing a great prospect for practical application in $LiFePO_4$-based lithium ion batteries.

Acknowledgments

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