

Polytriphenylamine used as an electroactive separator material for overcharge protection of rechargeable lithium battery

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Abstract

An electroactive polytriphenylamine (PTPAn) was synthesized and used as separator material for providing a self-activating overcharge protection of rechargeable lithium batteries. The experimental results from the Li–LiFePO₄ cells demonstrated that the electroactive separator could transform from an electronically isolating state to a conductive state at overcharge, producing an resistive internal short circuit to maintain the cell's voltage at the safety value of ~3.75 V. In addition, the electroactive PTPAn separator works reversibly and has no negative influences on the normal charge–discharge behaviors of the Li–LiFePO₄ cells.

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1. Introduction

Large capacity Li-ion batteries are greatly needed for a number of applications such as electric vehicles and electric storages. However, commercial development and applications of these batteries are primarily due to safety concerns. In general, the safety hazards were mostly found in the overcharged states of the batteries because a number of highly exothermic reactions would take place in the strongly oxidized cathodes, leading to thermal runaway [1–3]. Commercial small batteries are usually protected with external electronic monitoring and charge interrupting devices, however, these devices are not applicable for large capacity battery stacks. In recent years, great efforts have been devoted on the development of internal self-actuating overcharge protection mechanisms for rechargeable lithium batteries. Various types of electrolyte additives, such as redox shuttles [4–12] and polymerizable monomers [13,14], have been proposed to protect the batteries from overcharging, but these additives can not provide sufficient shunting current at high rate charge or cause irreversible damages to batteries. In compari-

son, the use of electroactive polymer separator to control the charging voltage seems to be a more attractive method for overcharge protection because the polymer can be selected to switch between conductive and insulating states reversibly at required overcharging potentials and sustain sufficient high charging current [15–20].

The first electroactive polymer membrane was made of poly(3-butylthiophene) with an oxidation potential about 3.2 V (versus Li⁺/Li), which is quite low than the charging voltage required for controlling most of the currently used Li-ion batteries [15–18]. Subsequently, Chen et al. [20] and Xiao et al. [19] reported different types of bilayer electroactive polymer separators with extended high oxidation potential limits, but the bilayer configuration seems to be much more complicate for preparation and battery applications.

In this work, we report a simple electroactive polymer, polytriphenylamine (PTPAn) and used this polymer as separator material for overcharging protection of rechargeable Li–LiFePO₄ cells. Since this polymer can be oxidized to a conductive state at quite high potential of +3.75 V (versus Li⁺/Li) and is stable toward lithium, it is convenient to use this polymer simply as a single electroactive material to incorporate into a commercial membrane separator, or as a substrate material for making a single layer membrane.

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2. Experimental

2.1. Preparation of polytriphenylamine

PTPAN was prepared in a similar method as reported [21]. A typical experimental procedure is to add 100 ml of a mixed solution of 0.25 M triphenylamine (TPAn, 0.25 M) in CHCl_3 into a three-necked 250 ml flask under magnetic stirring, and then add 0.025 mol FeCl_3 oxidant into the reaction solution at the interval of 1 h. The total amount of FeCl_3 used was four times of TPAn. The oxidative polymerization of TPAn usually takes two more hours in the solution under aerating of nitrogen. After completion of the solution polymerization reaction, the reaction mixture was poured into methanol to deposit the polymer product, which was filtered and washed with methanol several times. For purifying the synthetic PTPAn, the collected polymer powders were dissolved again in CHCl_3 solvent to remove the insoluble residues by filtration. The filtrate was concentrated and re-precipitated with acetone containing small amount of aqueous ammonia. Finally, the polymer product was filtered and dried in vacuum at 50°C for 12 h.

All the chemicals were obtained commercially and used without further purification except otherwise noted. Chloroform was distilled over CaH_2 before use.

2.2. Electrochemical measurements

The electrochemical behavior of the PTPAn powders was examined by microelectrode cyclic voltammetry (CV). The preparation method for powder microelectrode has been described in detail in [22]. The microelectrode voltammograms were recorded on a two-electrode cell using a larger lithium sheet as both counter electrode and reference electrode, using a CHI660 electrochemical workstation (Shanghai, China).

The PTPAn composite membrane was prepared firstly by roll-pressing the mixed paste of 30% PTPAn powder, 30% Al_2O_3 powder and 40% (net wt.%) polytetrafluoroethylene in emulsion into ca. $100\ \mu\text{m}$ thick film.

To evaluate the overcharge properties of the membrane separators, the charge–discharge behaviors of the electroactive polymer membrane and conventional porous polypropylene membrane were measured using the simulated Li– LiFePO_4 cells. The positive LiFePO_4 electrode was consisted of 80% LiFePO_4 powder (Valence Corp.), 12% acetylene black and 8% PTFE (wt.%) and prepared by roll-pressing the mixture into an electrode film, then pressing the electrode film onto an aluminum net. The reference and counter electrodes were lithium sheets. The electrolyte used in this study was 1 M LiPF_6/EC (ethylene carbonate) + DMC (dimethyl carbonate) (1:1 v/v), purchased from Merck. The cells were constructed in an argon-filled glove box. The charge–discharge measurements were carried out using a programmable computer-controlled battery charger (BTS-0518001 type, Shenzhen, China).

The electronic conductivities of the membrane separators were obtained by direct measurements of the ohmic resistances of the separator membranes before and after charging, according to the method reported previously in Ref. [18]. The p-doped

separators were taken from the fully charged cells, washed with acetone and then dried in vacuum oven.

3. Result and discussions

3.1. Electrochemical properties of PTPAn

The working mechanism of an electroactive polymer used for overcharge protection is based on the intrinsic nature of the conducting polymer to transform from an insulating state to a conductive state upon electrochemical oxidation or reduction. At normal cell operating voltages, the polymer separator is electronic isolating and functions as a normal separator to allow the electrolyte to pass through. However, when the cell is overcharged to the oxidation potential of the electroactive polymer, the polymer framework will convert to a conducting state and cause a resistive and internal short-circuiting to maintains the cell potential within a safe range so as to prevent the cell from voltage runaway.

The prime criterion for a polymer to work for overcharge protection is that the redox potential of the polymer should be higher than the terminating potential of the cathode for complete charge and should also be considerably lower than the decomposition potential of electrolyte. In addition, the electroactive polymer should be chemically and electrochemically stable at the voltage range of normal charge–discharge of the cells.

The choice of PTPAn as an electroactive polymer in this work is mainly based on the consideration that polyaniline (PAn) is a well-studied conductive polymer with very reversible and kinetically favorable oxidation–reduction behaviors at $\sim 3.3\ \text{V}$ (versus Li^+/Li) in organic solvents [23]. Though this redox potential is somewhat lower than the charging voltages of most commercial rechargeable lithium batteries, it is possible to use PAn-based derivatives to achieve a highly reversible polymer with higher oxidation potential. Fig. 1 shows the CV curves of PTPAn in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$. The main CV feature of the polymer is a pair of overlapped redox current peaks at the potential

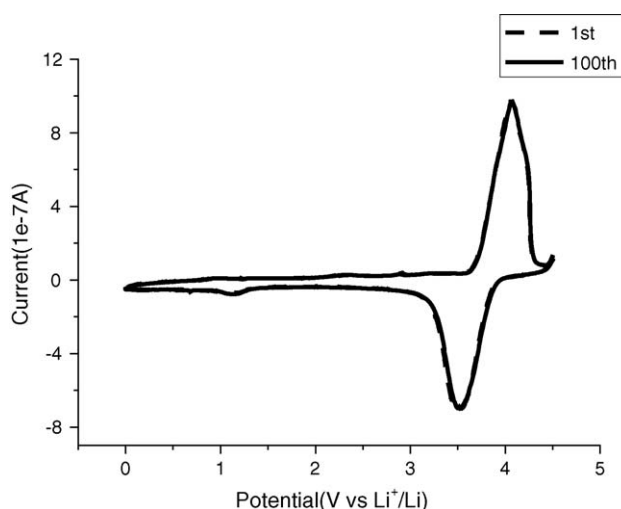


Fig. 1. The CV curves of PTPAn in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$, scanned at $10\ \text{mV s}^{-1}$.

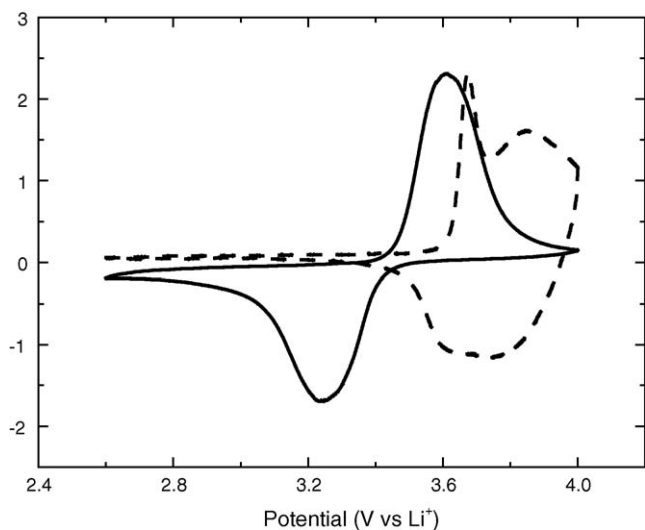


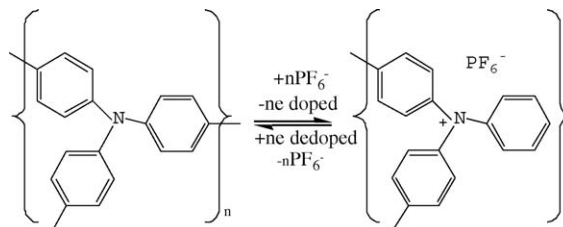
Fig. 2. A comparison of the CV curves of PTPAn (a) and LiFePO₄ (b) using microelectrode votammtry. Scan rate: 1 mV s⁻¹. The charge and discharge rate is 0.5 C.

region of 3.65–4.0 V, which are very close to each other in the peak positions and peak areas for the anodic and cathodic branches, indicating the very reversible and rapid electrochemical oxidation–reduction properties of the polymer compound. Except for these redox pairs, there are no other current peaks detectable in the potential range from 3.65 to 0 V, suggesting the electrochemical stability of the material in the more negative potentials. In addition, the CV peaks of the PTPAn powder remain almost unchanged during a 100 of successive scans, demonstrating an excellent electrochemical reproducibility of this compound. Though this oxidation potential of the polymer is not high enough for overcharge protection of commercial small Li–LiCoO₂ batter system, it may be suitably used for charging voltage control of the rechargeable lithium batteries of next generation such as Li–LiFePO₄ cells.

Fig. 2 gives a comparison of the redox potentials of PTPAn and LiFePO₄ in commonly used 1 M LiPF₆/EC + DMC electrolyte. It can be seen that the CV peaks of PTPAn are well separated from those of LiFePO₄. In the CV curves, LiFePO₄ shows a single anodic peak with the onset potential of +3.4 V and the peak current at +3.5 V, whereas the anodic current of PTPAn arises at the onset potential of +3.65 V, which is 250 mV more positive than the oxidation potential of LiFePO₄. On the cathodic scans, the electrochemical reduction of PTPAn starts at the reversed potential of +4.0 V and completes at 3.5 V, at which the cathodic reaction of the oxidized LiFePO₄ just starts to occur. This comparison demonstrates that PTPAn can take place in electrooxidation reaction only after the complete oxidation of LiFePO₄ and accomplishes its reduction earlier before the cathodic discharge of LiFePO₄. Thus, it is possible that the use of PTPAn as an electroactive separator material for Li–LiFePO₄ cells may not affect the normal charge and discharge of the cells.

In previous studies of the conductive polymer electrodes of PAN type, it is well recognized that the electroactive polymers can change their electronic conductivities from an isolating state to a metallic-like conductor after electrochemical oxidation (p-

doping) [23]. In the case of PTPAn, we measured the electronic conductivities of the PTPAn membranes before and after electrochemical oxidation and found that the conductivity of the membrane changes from 10⁻⁹ to 10⁻¹ S cm⁻¹ when charged to 4 V, in consistent with the conductive transformation observed for electroactive polymer electrodes. According to the electrochemical knowledge of polymer electrode reactions [24–27], the electrooxidation of PTPAn can be regarded as a reversible electrochemical p-doping process:



3.2. Overcharge performances of the electroactive PTPAn separator

The charge–discharge performances of the Li–LiFePO₄ cells using both the PTPAn separator and conventional Celgard 2500 separator are compared in Fig. 3. It can be clearly seen that when subjected to overcharge, the voltage of the cell using normal polypropylene separator climbs up sharply to above 4.0 V, and attains directly to the decomposing potential (~4.8 V) of the electrolyte if the charge is not terminated. Obviously, this runaway voltage may cause a number of hazardous oxidation reactions and lead to an unsafe state for a practical cell. In contrast, when the PTPAn separator is used, the charging voltages of the test cells show a very flat plateau at 3.75 V even at prolonged overcharge of 200% their capacity, demonstrating an effective control of the charging voltage in acceptable region. Since the charging voltage plateau of the cell is in a close accordance with the oxidation potential of the PTPAn polymer, it is reasonable to attribute the overcharge reaction of the cell to the electrochemical p-doping of the PTPAn polymer, which leads the separator to be electronically conductive and result in a resistive bypass charging current.

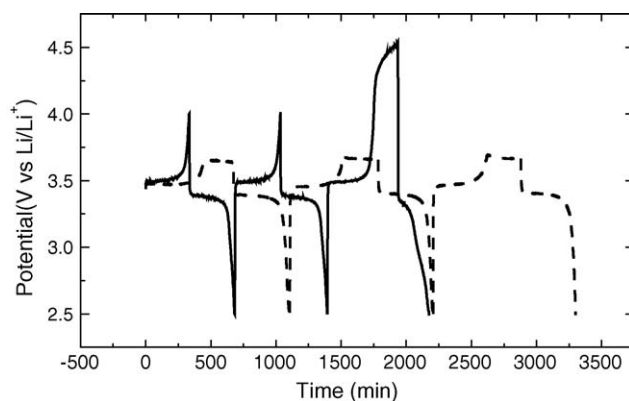


Fig. 3. A comparison of the charge–discharge performances of the Li–LiFePO₄ cells using both the PTPAn separator and conventional Celgard 2500 separator.

It can also be seen in Fig. 3 that with the PTPAn separator, the cell shows a very stable discharge capacity of $\sim 140 \text{ mAh g}^{-1}$ even subjected to overcharge of 200% its capacity, whereas the cell using conventional separator exhibits a rapid decrease in the discharge capacity once it is overcharged. These phenomena also suggest that the electroactive PTPAn separator can very well protect the cell from further oxidation of the cathodic material and electrolyte.

3.3. Effects of the PTPAn separator on the performances of Li–LiFePO₄ cells

Fig. 4 shows the cycling performances of the Li–LiFePO₄ cells with the PTPAn polymer separator at a charge–discharge rate of 0.5 C. It is clearly shown in the figure that the capacity of the cells remains quite stable from initial 130 to 116 mAh g⁻¹ after 40 cycles at prolonged charge, showing a quite good reversibility and cycling stability of the PTPAn polymer as a separator material. It should be mentioned that in comparison with commercial batteries, the Li–LiFePO₄ cells with PTPAn separator show a faster capacity decay and voltage polarization during increased cycles. This performance deterioration may not be simply attributed to the polymer separator and is possibly due to the disadvantages of experimental cell assembling.

Another important factor determining the feasibility of the electroactive polymer is its sustainable current density at normal charge and overcharge. Fig. 5 gives the potential profiles of the test cells using the electroactive polymer at various current densities. Though the charging voltage plateau of the Li–LiFePO₄ cells is elevated with increasing current density, it can all be controlled at the values less than 4.0 V. Even the charge rate is increased to a 4 C rate, the discharge capacity still attains to 95 mAh g⁻¹, showing excellent high rate capability at charge and discharge. An interesting phenomenon in Fig. 6 is that with increase in the charging current, the charging voltage of the cells rose up steeply at first at the onset of overcharge and then dropped to produce a steady voltage plateau. This phenomenon is possibly due to the fact that at the beginning of overcharge,

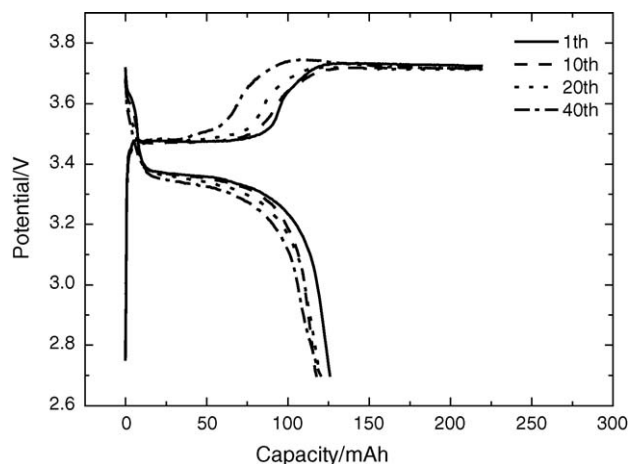


Fig. 4. The CV curves of the Li–LiFePO₄ cells using the PTPAn separator at overcharged condition. The charge and discharge rate is 0.5 C.

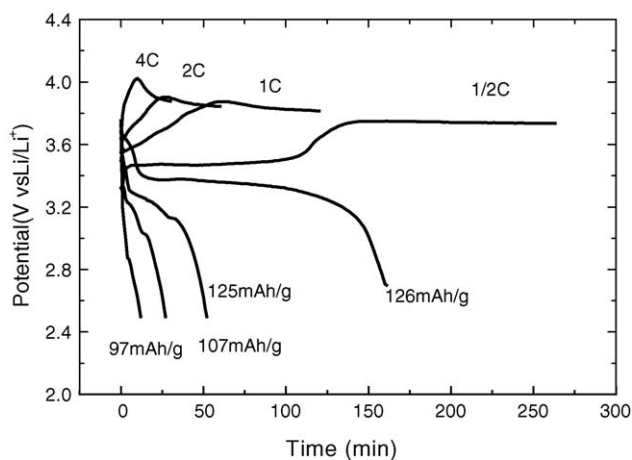


Fig. 5. The charge–discharge curves of using the PTPAn separator at various charge–discharge rates as labeled at each curve.

the electrochemical p-doping of the PTPAn polymer cannot proceed so quickly to make the polymer separator wholly conductive and thus a larger resistive polarization arises to produce a higher charging voltage as observed. Once the separator turns to be completely conductive at increased charge, the resistive polarization is decreased and therefore the charging voltage is decreased to a lower value, which is stabilized by the electrochemically oxidative p-doping reaction of the PTPAn separator.

It is very required that the electroactive separator can not only exert a voltage control at overcharge but also have no negative effects on the normal charge and discharge of the battery. To evaluate the effects of the PTPAn separator on the cycling performances of the cells, we measured comparatively the capacity retention of the test Li–LiFePO₄ cells cycled at normal charge (2.5–3.65 V) and at overcharge. The data in Fig. 6 shows that the capacity retention are almost identical for the cells cycled at different regimes of charging, indicating that the PTPAn separator have no negative impact on the normal discharge of the cells.

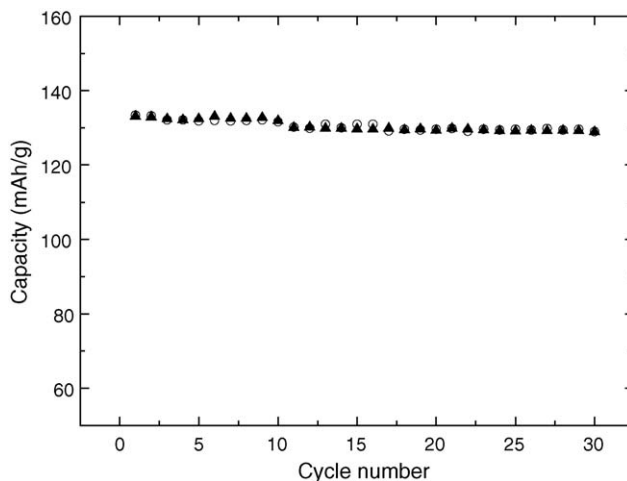


Fig. 6. The discharge retention of the Li–LiFePO₄ cells using the PTPAn separator overcharged (▲) and normally charged (◇) at 0.5 C.

4. Summary

In summary, we prepared a PTPAn composite polymer membrane and used as a self-activating overcharge protection separator for lithium ion batteries. The experimental results demonstrated that the separator could transform from an electronically isolating state to a conductive state at overcharged voltage, producing an internal short circuit to prevent the cell's voltage from exceeding the safety value. In addition, the electroactive membrane works reversibly and has no negative influences on the normal charge–discharge behaviors of Li-ion batteries.

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