



Short communication

A polytriphenylamine-modified separator with reversible overcharge protection for 3.6 V-class lithium-ion battery

S.L. Li, X.P. Ai*, H.X. Yang, Y.L. Cao

Department of Chemistry, Hubei Key Lab. of Electrochemical Power Sources, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:

Received 19 June 2008

Received in revised form 5 August 2008

Accepted 6 August 2008

Available online 14 August 2008

Keywords:

Lithium-ion battery

Overcharge protection

Potential-switchable separator

Electroactive polymer

Polytriphenylamine

ABSTRACT

A polytriphenylamine (PTPAN)-modified separator was prepared simply by impregnating triphenylamine monomers into a commercial Celgard separator and in situ polymerizing the monomers into electroactive phase by oxidant ozone. This type of electroactive separator can transform from an insulating state to a conductive state at overcharged voltage of ~ 3.7 V (vs. Li^+/Li) and act as a self-actuating potential-switchable separator for overcharge protection of LiFePO_4/C Li-ion batteries. The experimental results demonstrated that this electroactive separator can reversibly control the cell's voltage at the safe value less than 4.15 V at high rate overcharge of 2C current without obvious negative impact on the normal charge–discharge performances of the commercial LiFePO_4/C batteries even at prolonged overcharge cycling, showing a potential application in 3.6 V-class lithium-ion batteries.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Safety concern has been a main obstacle for the applications of large-size or high-rate lithium-ion batteries (LIBs) in many high technology fields, such as electric vehicles and electric storage devices. Among the inducing factors for safety hazards, such as overcharge, short-circuit or high-temperature operation, overcharge of battery seems to be the most dangerous abuse for LIBs. Because the non-aqueous electrolytes commonly used in LIBs are incapable of being reversibly oxidized or reduced, they cannot provide a spontaneous intrinsic limitation for cell voltage runaway during overcharging. When overcharged, the voltage of the battery would uncontrollably climb up and then a number of exothermic reactions, such as decomposition of the cathode material, oxidation of organic electrolyte, etc., would take place inside the cell [1–5]. These reactions produce excessive heat and flammable gas, which may lead to a thermal runaway, causing cell cracking, firing or even explosion.

To solve this problem, great efforts have been focused in recent years on developments of internal and self-actuating overcharge protection mechanisms for LIBs. Various types of electrolyte additives, such as redox shuttles [6–10] and polymerizable monomers [11–14], have been proposed for using as safety additives in electrolyte to prevent the LIBs from overcharging. Unfortunately, due to

the poor solubility in non-aqueous electrolytes, the shuttle molecular reported so far can only provide a limited shuttling current and therefore fail to function effectively even at normal operating current, while the polymerizable monomers, such as biphenyl [12,13] and xylene [14], can just function as shutdown additives to increase the cell's overcharge tolerance to some extent. In comparison, use of electroactive polymer separator to clamp the charge voltage seems to be a more attractive means for overcharge protection of LIBs, because this type of separator can provide not only reversible overcharge protections, but also sufficiently high shunting currents for the overcharged batteries.

The idea of using electroactive polymer separator for overcharge protection is based on the intrinsic property of the conducting polymer, which can switch reversibly between insulating and conductive states with the changes in the charging potential. During normal cell operation, the potential of the positive electrode lies below the oxidation potential of the electroactive polymer, and the polymer separator stays in an electronic insulating phase, functioning as a normal separator to allow the electrolyte to pass through. Once the cell is overcharged to raise the cathode potential above the oxidation potential of the polymer, the polymer will convert to a conducting state, causing an internal short-circuit in between both electrodes of the cell, producing a current bypass so as to prevent the battery from voltage runaway.

The concept of using conductive polymers to prevent batteries from overcharge is first proposed by Denton et al. [15]. Subsequently, Chen et al. reported an electroactive polymer membrane [16], which is prepared by incorporating a polymer,

* Corresponding author. Tel.: +86 27 68754526; fax: +86 27 87884476.
E-mail address: xpai@whu.edu.cn (X.P. Ai).

poly(3-butylthiophene) or P3BT, into the pores of separator membrane. However, the oxidation potential of P3BT is only 3.2 V (vs. Li^+/Li), considerably lower than the working voltages of the Li-ion batteries currently commercialized. To search for an electroactive polymer separator suitable for use in conventional 3.6 or 4.2 V-class LIBs, Xiao et al. [17] and Chen et al. [18] 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 battery applications.

In a previous publication [19], we reported a single layer polytriphenylamine (PTPAN)-based polymer membrane with a relatively high clamping potential of ~ 3.75 V (vs. Li^+/Li), and demonstrated its feasibility and suitability for use in charging voltage control of the LiFePO_4 -based cell. However, the separator membrane reported, therein, is made by roll-pressing process with a thickness of ~ 100 μm , which is difficult for industrial production and commercial applications. In this paper, we reported a simple processing method for the preparation of the PTPAN-modified membrane by impregnating triphenylamine monomers into a commercial separator and then oxidatively polymerizing the triphenylamine monomers by ozone into an electroactive phase in the separator membrane. Also, the overcharge protection behaviors of this type of PTPAN-modified separator in the commercial LiFePO_4 -based LIBs were described.

2. Experimental

Triphenylamine (purity $\geq 99.0\%$, Zhenjiang Haitong Chemical Industry Co., Ltd., Jiangsu, China) was used as received without further purification. The electrolyte used in this study was 1 M LiPF_6 in a 1:1:1 (v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl-methyl carbonate (EMC) purchased from Zhangjiagang 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 350 mA h, manufactured in Fenghua Lithium battery Co., Ltd. (Zhaoqing, China).

The PTPAN-modified separator was prepared by immersing a commercial porous membrane (Celgard 2500) with a thickness of 25 μm into a diethylene glycol dimethyl ether solution containing 0.8 M triphenylamine monomer for 1 h to ensure sufficient amount of triphenylamine monomer to be absorbed by the separator, then transferring the impregnated membrane into an ozone-filled container for 30 min, in which the triphenylamine monomers within the separator were chemically polymerized by the oxidation of ozone, and finally, evaporating the solvents to leave a PTPAN-modified separator membrane. The resulting membrane was ~ 27 μm thick, in which the weight percent of PTPAN to separator is $\sim 15\%$. To be different from the conventional chemically oxidative polymerization method using FeCl_3 as oxidant to synthesize PTPAN polymer [20], oxidant ozone is used in this study so as to simplify the experimental process for preparation of PTPAN-modified separator. This choice is based on the consideration that, as one of the most powerful oxidizing agents (oxidation potential +2.076 V), ozone can attack the C–H bonds of the organic compounds readily with the generation of free radicals [21] and therefore, should be capable of using as an oxidant to polymerize the triphenylamine monomers into polymer. The morphological changes of the separators before and after incorporation of PTPAN were examined using a Quanta 200 Scanning Electron Microscope (FEI Company, Netherlands).

The electrochemical behaviors of the PTPAN powder synthesized from ozone oxidation of triphenylamine were studied with cyclic voltammetry (CV) at a powder microelectrode (diameter = 100 μm).

The preparation method for powder microelectrode has been described in detail in Ref. [22]. The voltammograms were recorded on a two-electrode cell using a large lithium sheet as both counter electrode and reference electrode on a CHI 600C electrochemical workstation (Shanghai, China).

The effects of PTPAN-modified separator on the overcharge behaviors of the cells were investigated by charge–discharge of the prismatic LiFePO_4/C batteries at a voltage range of 2.0–4.5 V. The charge and discharge measurements were carried out using a programmable computer-controlled battery charger (BTS-55 Neware Battery Testing System, Shenzhen, China).

3. Results and discussion

As aforementioned in our previous paper [17,19], the first criterion for choosing an electroactive polymer to work for overcharge protection is its 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 LIBs, the potential of fully charged cathode is ca. 3.6 V.

Fig. 1 compares the CV curves of LiFePO_4 and PTPAN in a 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ electrolyte. As shown in Fig. 1, the PTPAN polymer gives a pair of well-defined redox peaks between 2.0 and 4.5 V, the anodic and cathodic branches of which are very symmetric in the peak shape and peak areas, indicating the very reversible and rapid electrochemical oxidation and reduction of the polymer. According to the electrochemical knowledge of polymer electrode reactions [16,23], the electrooxidation of PTPAN can be regarded as a reversible electrochemical p-doping process. When p-doped, the PF_6^- anion from the electrolyte as a dopant is inserted to balance the charge. Comparing the CV curves, it can be found that the oxidation peak for LiFePO_4 arises from the onset potential of 3.4 V and reaches its maximum current at 3.55 V, whereas the anodic current of PTPAN, representing its p-doping process, appears at the onset potential of 3.6 V, at least 50 mV positively shifted from the oxidation peak of LiFePO_4 . In the reversed scans, the cathodic current of PTPAN, corresponding to the de-doping process of the oxidized PTPAN, starts at the reversed potential of 4.5 V and completes at 3.5 V, at which the electrochemical reduction of the oxidized LiFePO_4 just starts to occur. This comparison implies that the electrooxidation of PTPAN polymer can occur only after the complete oxidation of LiFePO_4 and the electrochemical reduction of PTPAN polymer takes place before the cathodic discharge of LiFePO_4 electrode. These results indicate that the PTPAN polymer

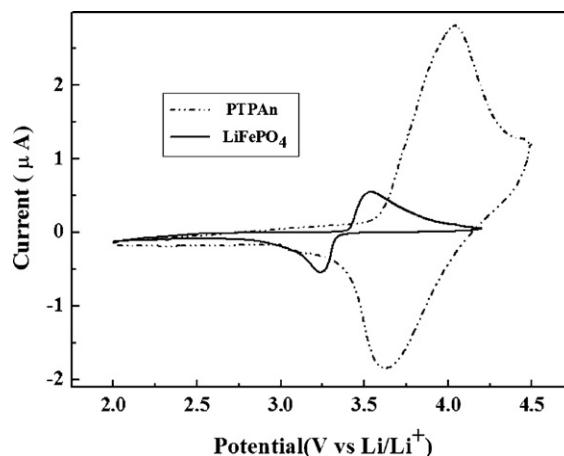


Fig. 1. The CV curves obtained from LiFePO_4 (—) and PTPAN (---) powder microelectrodes in 1 M $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{EMC}$ electrolyte. Scan rate: 10 mV s^{-1} .

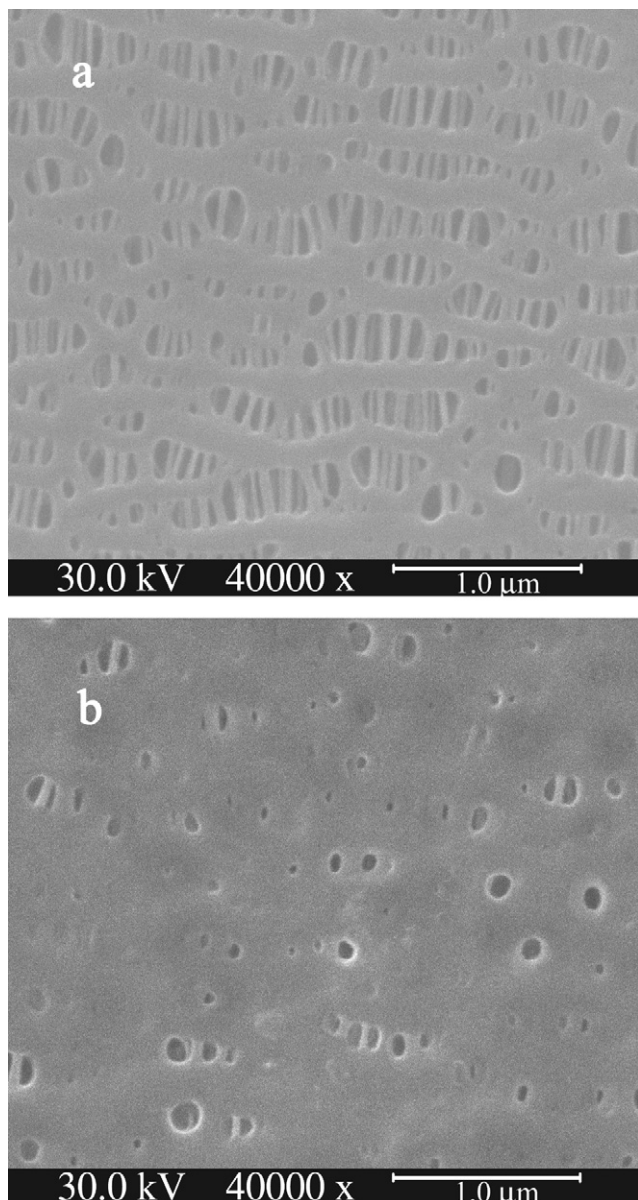


Fig. 2. A comparison of SEM photographs for Celgard 2500 separator before (a) and after (b) PTPAn modification.

synthesized from ozone oxidation can be suitably used for charge voltage control of the LiFePO_4 -based LIBs, and that the use of PTPAn-modified membrane as separator may not interfere in the normal charge–discharge reactions of LiFePO_4 -based LIBs.

The problem for practical use of the PTPAn-modified membrane is how to incorporate the PTPAn polymer into the commercial porous separator effectively and conveniently. The simplest way is to impregnate the PTPAn polymer into the pores of commercial separator. However, there existed a number of difficulties for a simple impregnation method to achieve a PTPAn-modified membrane, because PTPAn polymer has only an indiscernible solubility almost in all the organic solvents. To solve this problem, we tried to impregnate soluble triphenylamine monomers into a commercial separator firstly and then polymerize the triphenylamine monomer by ozone oxidation. The morphologies of microporous separator before and after PTPAn modification are compared in Fig. 2. As can be seen in Fig. 2a, the commercial porous separator has a clear surface and uniform pore distribution. In contrast, the PTPAn-modified

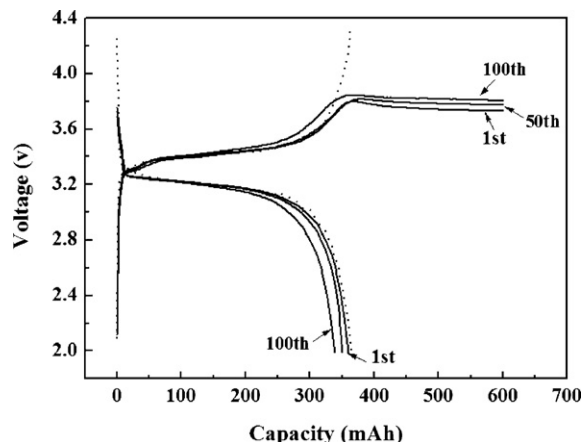


Fig. 3. The charge–discharge curves of the prismatic LiFePO_4/C batteries using both a PTPAn-modified separator (—) and a conventional Celgard 2500 separator (···) at 0.5C rate.

separator (Fig. 2b) shows a vague image and a blocked pore structure, indicating that PTPAn polymer was successfully filled into the pores of the separator. Certainly, it also should be noticed that the pores of the substratal separator were only partially filled with PTPAn polymer. Therefore, it can be expected that the PTPAn-modified separator thus prepared can not only act as a normal separator to pass through electrolyte by the remaining void pores, but also function as an internal self-actuating potential-sensitive membrane.

Fig. 3 compares the charge–discharge performances of prismatic LiFePO_4/C cells using both PTPAn-modified separator and conventional Celgard 2500 separator at 0.5C rate. As it is shown in the figure, the potential profiles of the LiFePO_4 cells both displayed a normal voltage plateau at ~ 3.45 V, which characterized the lithium deintercalation from LiFePO_4 phase and suggested no discernible impact of PTPAn-modified separator on the charging performance of the test cell at normal charge. Once overcharged, the voltage of the cell using commercial Celgard 2500 separator climbs up uncontrollably to the terminating charge voltage of 4.3 V. In contrast, when a PTPAn-modified separator is used, the charging voltage of the cell climbed up steeply at first and then gradually dropped to produce a voltage plateau at ~ 3.7 V, showing an effective control of the charging voltage. This phenomenon could be well explained that, at the beginning of overcharge, the electrochemical p-doping of PTPAn cannot proceed so quickly that the

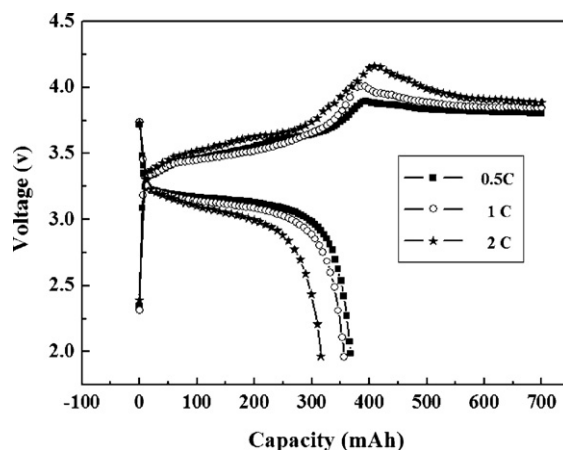


Fig. 4. The charge–discharge curves of the prismatic LiFePO_4/C battery using a PTPAn-modified separator at various rates.

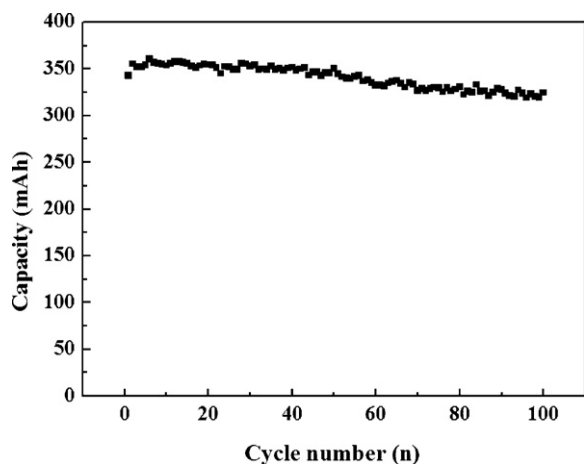


Fig. 5. The cycling performance of the prismatic LiFePO₄/C battery using a PTPAn-modified separator at normal voltage interval of 2.0–3.7 V at 0.5C rate.

PTPAn-modified separator is not entirely conductive, which results in an ohmic polarization and thereby causes the charging voltage slightly higher than expected. As the overcharge proceeded, PTPAn polymer became conductive gradually, which leads to a decrease in the ohmic polarization and the charge voltage. Once the PTPAn-modified separator turned into a completely conductive phase, the charging voltage is stabilized at the p-doping potential of PTPAn, showing a stable voltage plateau at ~ 3.7 V as observed. Also, it can be seen from Fig. 3 that the test cell can deliver a capacity of about 360 mAh at the following discharge even subjected to a 100% overcharge of its nominal capacity, suggesting that the PTPAn-modified separator has no negative impact on the discharge performance of the battery. After 100 testing cycles, the overcharging voltage plateau is only slightly elevated to ~ 3.8 V, indicating a very reversible and effective overcharge protection for the test cells by the PTPAn-modified separator.

An important factor determining the feasibility of the electroactive polymer separator is its sustainable current at charge and discharge. Fig. 4 gives the charge–discharge curves of the prismatic LiFePO₄/C batteries using a PTPAn-modified separator at various current rates. It can be seen that although the charge rates were increased from 0.5 to 2C, the overcharge voltage plateaus of the test cell were only slightly elevated and could still be well controlled at the values below 4.15 V. The phenomenon that overcharge voltage plateaus of the test cell elevated with the increase of C rate could be explained as: the higher overcharge rate, the higher conductivity in the polymer short needed to sustain the electronic current. Since the conductivity of the polymer depends upon its degree of oxidation, the higher conductivity, the higher oxidation degree needed and thus, higher potential also needed. In addition, it also can be seen that even though both the charge and discharge rate were increased to 2C, the discharge capacity of the cells were still kept at 320 mAh, showing an excellent high rate charge and discharge capability.

As an applicable separator, it is not only required to provide an effective voltage control at overcharge, but also required to have no adverse impacts on the normal charge–discharge performances of

the batteries. To evaluate the influence of the PTPAn-modified separator on the cycling performance of the batteries, we cycled the prismatic LiFePO₄/C batteries using the PTPAn-modified separator at normal charge–discharge voltage of 2.0–3.7 V at 0.5C rate. The typical cycling performance of these batteries is shown in Fig. 5. It can be found that after 100 cycles, the discharge capacities of the batteries still stabilized at ~ 325 mAh, showing a good cycling performance.

4. Conclusions

In summary, we prepared a PTPAn-modified separator membrane and introduced it into the practical LiFePO₄/C lithium-ion batteries as a self-actuating overcharge protection separator. The experimental results demonstrated that the separator could transform from an electronically insulating state to a conductive state at overcharged voltage, leading to an internal short-circuit to prevent the cells from voltage runaway. In addition, this membrane works reversibly and has no significant impact on the charge–discharge performance of the batteries at normal charge–discharge condition, showing a great prospect for practical application in 3.6 V-class lithium-ion batteries.

Acknowledgments

This research was financially supported by the National 973 Program of China (No. 2009CB220100), the National Science Foundation of China (No. 20773095) and the National 863 Program of China (No. 2007AA03Z224).

The ozonizer used in this work is provided by Prof. Y.Q. Zhou, many thanks for his kind assistance.

References

- [1] J.R. Dahn, E.W. Fuller, M. Obrovac, U. von Sacken, *Solid State Ionics* 69 (1994) 265–270.
- [2] Z. Zhang, D. Fouchard, J.R. Rea, *J. Power Sources* 70 (1998) 16–20.
- [3] Ph. Biensan, B. Simon, J.P. Pérès, A. de Guibert, M. Broussely, J.M. Bodet, F. Pertont, *J. Power Sources* 81–82 (1999) 906–912.
- [4] S. Tobishima, J. Yamaki, *J. Power Sources* 81–82 (1999) 882–886.
- [5] D.D. MacNeil, J.R. Dahn, *J. Electrochem. Soc.* 149 (2002) A912–A919.
- [6] C. Buhrmester, J. Chen, L.M. Moshuchak, J. Jiang, R.L. Wang, J.R. Dahn, *J. Electrochem. Soc.* 152 (2005) A2390–A2399.
- [7] Z. Chen, K. Amine, *Electrochem. Commun.* 9 (2007) 703–707.
- [8] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, *Electrochem. Commun.* 9 (2007) 25–30.
- [9] M. Taggougui, B. Carrie, P. Willmann, D. Lemordant, *J. Power Sources* 174 (2007) 1069–1073.
- [10] L.M. Moshuchak, C. Buhrmester, J.R. Dahn, *J. Electrochem. Soc.* 155 (2008) A129–A131.
- [11] S. Tobishima, Y. Ogino, Y. Watanabe, *J. Appl. Electrochem.* 33 (2003) 143–150.
- [12] H. Mao, U. von Sacken, US Patent 6,033,797 (2000).
- [13] L.F. Xiao, X.P. Ai, Y.L. Cao, H.X. Yang, *Electrochim. Acta* 49 (2004) 4189–4196.
- [14] X.M. Feng, X.P. Ai, H.X. Yang, *J. Appl. Electrochem.* 34 (2004) 1199–1203.
- [15] F.R. Denton, J.N. Howard, A.A. Anani, J.M. Fernandez, US Patent 6,228,516 (2001).
- [16] G. Chen, T.J. Richardson, *Electrochem. Solid-State Lett.* 7 (2004) A23–A26.
- [17] L.F. Xiao, X.P. Ai, Y.L. Cao, Y.D. Wang, H.X. Yang, *Electrochem. Commun.* 7 (2005) 589–592.
- [18] G. Chen, T.J. Richardson, *Electrochem. Solid-State Lett.* 9 (2006) A24–A26.
- [19] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, *J. Power Sources* 161 (2006) 545–549.
- [20] C.M. Zhan, Z.G. Cheng, J.Y. Zheng, W. Zhang, Y. Xi, J.G. Qin, *J. Appl. Polym. Sci.* 85 (2002) 2718–2724.
- [21] T.G. Denisova, E.T. Denisov, *Polym. Degrad. Stab.* 60 (1998) 345–350.
- [22] C.S. Cha, C.M. Li, H.X. Yang, P.F. Liu, *J. Electroanal. Chem.* 368 (1994) 47–54.
- [23] D. Kumar, R.C. Sharma, *Eur. Polym. J.* 34 (1998) 1053–1060.