Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Application of biphenyl additive in electrolyte for liquid state Al-plastic film lithium-ion batteries

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ARTICLE INFO

Article history: Received 28 May 2008 Received in revised form 27 June 2008 Accepted 2 July 2008 Available online 11 July 2008

Keywords: Al-plastic film lithium-ion batteries Biphenyl Electro-polymerization Overcharge

ABSTRACT

In order to investigate the influence of the biphenyl (BH) as a polymerizable electrolyte additive on the properties of Al-plastic film lithium-ion batteries, we examined the electrochemical properties of batteries which containing different amounts of BH. The main analysis tools were overcharge tests, linear sweep voltammetry, cycling tests, rate capability, thermal stability, AC impedance, etc. The results showed that the BH can electrochemically polymerize at the overcharge potential of 4.5–5.5 V to form a layer on the cathode surface, the internal resistance was increased rapidly after the electrode covered with the black electro-polymerization production, and the internal short-circuit was occurred with enough polymerization product, all of these caused to low overcharge current and good overcharge performance, meanwhile, the overcharge performance was increased with the increasing of BH content. However, the cycling performance was deteriorated with an increase in BH content, but not seriously, so the content of additive is ought to be adjusted to practical need in production.

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1. Introduction

It is very important to develop rechargeable lithium batteries with high power density, rapid rechargeable and better cyclicity to satisfy the increasing demands of power source for various electric vehicles [1]. Lithium-ion batteries are the most suitable power supply for portable application due to their long cycle life, high-specific energy, high-specific power and no memory effect [2]. However, the volatility and inflammability of electrolyte containing organic solvents are serious safety drawbacks [3], besides the safety problem, the operating temperature limit and ionic conductivity are also drawbacks of electrolyte, and therefore development of new and safe electrolyte system is high demanding [4,5]. In order to solve these problems, over the past several years, many new kinds of electrolytes are studied by researchers to meet the requirements of lithium batteries, polymer electrolyte and ionic electrolyte as a replacement of the liquid electrolyte are used to avoid those problems.

In addition to these efforts, electrolytes containing various additives are also recognized as a very effective way to improve electrochemical performance [6–8]. At present, a significant

amount of work has been carried out to improve the overcharge performance. Safety is an important issue to lithium-ion batteries under circumstance of overcharging. The voltage would be increased rapidly when overcharging, which lead to irreversible change of cathode active material and decomposition of electrolyte, lots of heat and gas are produced, meanwhile, temperature and internal pressure are also increased rapidly too, there are risk of inflammation and explosion in battery. PTC and special separators are used to improve safety performance, but they could not avoid the problems completely which caused by overcharge.

It is well known that electrolyte exhibits good overcharge performance with kinds of additives. The additive has advantages of small dosage and fast effect without increasing cost of battery obviously, compared with the other technologies. To improve the overcharge performance, several kinds of additives are proposed for overcharge protection of lithium-ion batteries. Among these additives, the use of redox shuttle additives seem to be an effective way to improve overcharge performance [9,10], redox additives are added to electrolyte to avoid overcharge problems, reaction cannot be taken place under the normal condition, however, it would be occurred when reaches to the certain potential in the process of overcharging, oxidation productions are transferred to anode and reduced, then the reduction products are transferred to cathode from anode to oxidize This process would be cycled continuously until the charge–discharge is terminated. The voltage is limited





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^{0378-7753/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2008.07.001

by reversible redox reaction to guarantee safety in overcharging. The other effective method is electrochemical polymerization protection [11–13], polymerizable additives are added to electrolyte, polymerization reaction would be occurred when reaches to the certain potential. The electrode surface is covered with polymerization products, which lead to high value resistance; consequently, the battery is protected by restricted current. Many kinds of additives are used as polymeric monomer additives, such as BH, to block off the runaway reactions of an overcharged cathode. It is reported that the use of BH as polymerizable additive in electrolyte has been researched [14–16], however, the working mechanism of this type of electrolyte additive and the influence on the performance characteristics of Al-plastic film lithium-ion batteries have not been reported up to date clearly.

In this study, we present the electrochemical performance and safety behavior of BH as an electrolyte additive in overcharged liquid state Al-plastic film lithium-ion batteries and describe the impact on the battery's performance clearly.

2. Experimental

2.1. Preparation of electrolyte

We used BH (Aldrich, spectrum-grade) additive and lithium-ion batteries electrolyte which provided by Jiangmen JJJ Battery Company Limited as received, the baseline electrolyte was $1 \mod L^{-1}$ LiPF₆ in EC (ethylene carbonate): DMC (dimethyl carbonate): EMC (ethyl methyl carbonate) (1:1:1,by volume). We prepared electrolytes with various amounts of BH additive in an argon gas atmosphere. The amounts of BH in electrolytes were 0.5, 1.0, 2.0, 3.0 and 4.0 wt.%, respectively.

2.2. Cell assembly

The cathode was prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry containing 92 wt.% LiCoO₂, 3 wt.% PVDF and 5 wt.% carbon (super-P) on an aluminum foil, dried at 120 °C overnight, then pressed at 100 kg cm⁻², and finally dried under vacuum at 120 °C for 6 h again. The anode slurry was prepared by mixing graphite, SP and PVDF in the weight of 92:3:5 in NMP solvent, the copper foil was used as current collector, the preparation of anode was carried out as described for the cathode. Al-plastic film lithium-ion batteries were prepared for experiment, the whole battery assembling process was carried out in Jiangmen JJJ Battery Company Limited. Assembling procedures of battery are shown in Fig. 1.

Three different types of batteries were manufactured for experiment due to production changes, LIPB382530, LPB303236 and LPB343944, nominal capacity were 210, 300 and 520 mAh, respectively. The classifying numbers of batteries are shown in Table 1.

Table 1

Classifying number of various batteries

Number of batteries	Kind of additives	Concentration of additives (wt.%)
BT (blank test)	-	_
BH05	Biphenyl	0.5
BH1	Biphenyl	1.0
BH2	Biphenyl	2.0
BH3	Biphenyl	3.0
BH4	Biphenyl	4.0

2.3. Measurements

2.3.1. Overcharge tests

Overcharge tests were performed at temperature of $20 \pm 5 \circ C$ with Arbin Battery Testing equipment, the cells were discharged by constant current (0.2 C) to termination voltage, four different types of overcharge regimes were shown as follows: (1) the batteries were overcharged at a rate of 1 C to 12 V followed by constant voltage at 12 V until the current declined to 10 mA. (2) The batteries were overcharged at a rate of 2 C to 10 V followed by constant voltage at 10 V until the current declined to 10 mA. (3) The batteries were overcharged at a rate of 3 C to 10 V followed by constant voltage at 10 V until the current declined to 10 mA. (4) The batteries were overcharged at a rate of 3 C to 12 V followed by constant voltage at 12 V until the current declined to 10 mA. (4) The batteries were overcharged at a rate of 3 C to 12 V followed by constant voltage at 12 V until the current declined to 10 mA.

2.3.2. Linear sweep voltammetry

The linear sweep voltammetry was carried out for studying the mechanism of additive to overcharge performance. It was conducted in three-electrode system inside an argon-filled glove box with a scan rate of 2 mV s^{-1} from 3.0 to 7.5 V. The indicator electrode and auxiliary electrode were prepared by LiCoO₂ and graphite which provided by the Jiangmen JJJ Battery Company Limited, Li foil was used as reference electrode.

2.3.3. AC impedance

AC impedance measurement of the batteries was implemented with the use of IM6e electrochemical workstation. The frequency was varied from 1 MHz to 10 mHz and the amplitude was set at 5 mV.

2.3.4. Initial charge-discharge capacity and efficiency

Battery formation was performed with BS9088A polymer Li-ion batteries automatic testing system after sealed. Initial charge–discharge tests were examined under the follow model: the charge process was dived into two steps: first, the battery was charged to 4.2 V at a constant current of 0.5 C, and then was charged potentiostatically at 4.2 V until the current declined to 0.02 C, the discharge procedure was composed of a constant current of 0.5 C until the voltage dropped to 2.75 V.



Fig. 1. The sketch map of the making batteries process.

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Table 2

The results of	overcharge	tests	with	the	third	and	fourth	modes
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Number of batteries	Current (C)	Voltage (V)	Enwrapped	Material for enwrapping	Results
BH4-1	3	12	Enwrapped	Degreasing cotton	Bulge and crack
BH4-2	3	12	Enwrapped	Degreasing cotton	Bulge and crack
BH3-1	3	12	Unwrapped	_	Bulge and crack
BH3-2	3	12	Enwrapped	Degreasing cotton	Bulge and crack
BH3-3	3	12	Enwrapped	Degreasing cotton	Bulge and crack
BH3-4	3	12	Enwrapped	Degreasing cotton	Bulge and crack
BH2-1	3	10	Unwrapped	_	Bulge and crack
BH2-2	3	10	Unwrapped	-	Bulge and crack
BH2-3	3	10	Enwrapped	Degreasing cotton	Bulge and crack
BH2-4	3	10	Enwrapped	Degreasing cotton	Explosion and inflammation
BH2-5	3	10	Enwrapped	Degreasing cotton	Explosion and inflammation
BH1-1	3	10	Unwrapped	-	Explosion and inflammation
BH1-2	3	10	Unwrapped	_	Explosion and inflammation
BT (blank test)	3	10	Unwrapped	-	Explosion and inflammation

2.3.5. Battery internal resistance tests

Internal resistance tests were examined by DK3000A battery internal resistance testing system after formation.

2.3.6. Cycle life tests

The cycling tests were carried out on Land battery test system (CT2001). The normal charge procedure was composed of a constant current of 1 C followed by constant voltage at 4.2 V until the current decreased to 0.05 C. The discharge procedure was composed of a constant current of 1 C until the voltage dropped to 2.75 V.

2.3.7. Rate capability

The rate capability of the cells was evaluated via a constant current discharge at five current drains: 0.2, 0.5, 1, 2, and 4 C. The charge process was carried out at 0.2 C rates. Cells were charged to 4.2 V with constant current/constant voltage (CC/CV) method and then discharged to 2.75 V at different current drains. The termination voltage of 4 C was set to 2.7 V due to the effect of internal resistance.

2.3.8. Thermal stability tests

First, thermal stability tests were examined in the high-low temperature chamber after batteries charged at room temperature, the test cells were stored for 6 h at the temperature of 90 $^{\circ}$ C, thicknesses of batteries were measured with a vernier caliper every

Table 3

The results of overcharge tests with the second mode

hour, the batteries were taken out from the chamber after stored for 6 h and thicknesses were measured again when cooled to room temperature, and then discharged at current of 0.5 C to examine capacity retention performance under high temperature condition. One cycle charge–discharge testing was performed at a constant current of 0.5 C to examine recovery capability after high temperature.

3. Result and discussions

3.1. Overcharge performance

Many studies make it clear that thermal runaway is the main problem of battery safety. The battery with high temperature would lead to explosion when using inflammable organic-electrolytes. In order to simulate overcharging circumstance of high-capacity batteries, test cells were enwrapped by thermal insulation materials to decrease heat output, then thermal runaway was liable to be happened, and the requirements of overcharge tolerance performances were promoted in some extent.

Table 2 is the results of overcharge tests with the third and fourth overcharge modes. It is obvious that enwrapped batteries are observed without explosion for 3.0 and 4.0 wt.% BH when using the fourth overcharge mode, so overcharge performance is well improved by adding BH to electrolyte. Unwrapped batteries using

Number of batteries	Current (C)	Voltage (V)	Enwrapped	Material for enwrapping	Results
BH2-6	2	10	Unwrapped	_	Bulge and crack
BH2-7	2	10	Enwrapped	Degreasing cotton	Bulge and crack
BH2-8	2	10	Enwrapped	Degreasing cotton	Bulge and crack
BH1-3	2	10	Unwrapped	-	Explosion and inflammation
BH1-4	2	10	Unwrapped	-	Explosion and inflammation
BH1-5	2	10	Unwrapped	-	Bulge and crack
BT2	2	10	Unwrapped	-	Bulge and crack
BT3	2	10	Unwrapped	-	Explosion and inflammation

Table 4

The results of the overcharge tests with the first overcharge mode

Number of batteries	Current (C)	Voltage (V)	Enwrapped	Material for Enwrapping	Results
BH1-6	1	12	Unwrapped	-	Bulge and crack
BH1-7	1	12	Unwrapped	-	Bulge and crack
BH1-8	1	12	Unwrapped	-	Bulge and crack
BH1-9	1	12	Enwrapped	Degreasing cotton	Explosion and inflammation
BT4	1	12	Unwrapped	-	Explosion and inflammation
BT5	1	12	Unwrapped	-	Bulge and crack

the third overcharge mode are safety with 2.0 wt.% BH, however, one of the enwrapped batteries is exploded. The results show that explosion has close relationship to temperature and heat output, it also exhibits that overcharge properties of high-capacity batteries can not meet the requirements of safety.

Table 3 is the results of overcharge tests with the second overcharge mode. Whatever with or without thermal insulation materials, all batteries are not exploded with 2.0 wt.% BH. The battery containing 1.0 wt.% BH and without additive are not safe with the second overcharge mode.

Table 4 is the results of overcharge tests with the first overcharge mode. The results show that overcharge performance is improved with 1.0 wt.% BH compared with batteries which without additive. At the same time, it is also demonstrated that it has the meaning of qualitative describe for the batteries which are enwrapped.

Overcharge curves with 3.0 wt.% BH are shown in Fig. 2, which exhibits that two of the batteries currents are declined to 10 mA rapidly when all the voltage attain to 12 V, and the charge process is terminated. Charge currents of another two batteries are failed to decline to definition value, so these batteries are charged continuously, but they could not be exploded due to the low current.

As shown in Figs. 3–5, if the current is declined rapidly when voltage attains to 10 V, the battery would be safe, in the reverse situation, resulting in explosion. When the voltage of the battery reaches to 10 or 12 V, the situation of charge current is the key aspect of overcharge curve, under such conditions, constant current charge is changed to constant voltage charge, and lead to current decline. The curves of Fig. 3 are typical representative.



Fig. 2. The overcharge curves of the batteries with 3.0 wt.% BH.

Charge currents are declined rapidly for the batteries without explosion, and appear two different situations as shown in Fig. 3a and c, one situation is like as the battery of BH2-1, the charge current is decreased to 10 mA rapidly, and then the overcharge process of battery is terminated. The other is that the charge current is decreased to several tens mA, and charge process is continuous, the battery is charged for 2 h with constant voltage charge mode, such as BH2-2, BH2-6, BH2-7 and BH2-8.

As shown in Fig. 4a, when the voltage attains to 10 V and transfers to constant voltage charge, the current cannot decrease to



Fig. 3. The overcharge curves of the batteries with 2.0 wt.% BH at the currents of (a) 3 C (unwrapped), (b) 3 C (enwrapped), and (c) 2 C, respectively.



Fig. 4. The overcharge curves of the batteries with 1.0 wt.% BH at the currents of (a) 3 C (unwrapped), (b) 2 C, (c) 1 C (unwrapped), and (d) 3 C (enwrapped), respectively.

safe regions and would be exploded in several seconds. During this course, Arbin battery testing equipment cannot record testing dates, which stopped automatically. In the experiments, it is observed that all batteries' currents are decreased, according to real-time monitoring dates, and exploded after currents declined to half.

The results revealed that the batteries are liable to be exploded without additive and with small amounts of additives. In the case of batteries without additive, the electrolyte would be decomposed when the charge voltage reaches to 10 V, a large amounts of gas is produced in the process of decomposition and lead to the rising of internal pressure of battery, which would lead to explosion. In addition, it is clear that voltage would increase from 5 to 10 V quickly when charge capacity is almost two times of the battery's nominal capacity, under these conditions, the cathode active material is reacted completely, and unstable CoO_2 is formed after all Li⁺ lost, oxidation reaction is not occurred again, which lead to voltage rising. The battery with high voltage and current is liable to be exploded under the condition of overcharging, at that moment, electric energy cannot be converted to chemical energy, and it is obvious that lots of heat is released, which result in explosion.



Fig. 5. The overcharge curves of the blank tests.



Fig. 6. The curves of the linear sweep voltammetry.



Fig. 7. Impedance spectras of the batteries in the stage of (a) discharge and (b) overcharge.

For the batteries with large amounts of BH, firstly, a layer of polymer is formed on the cathode surface by electrochemical polymerization of BH, and then the deposit layer grows gradually at continuous supply of the additive from the electrolyte, on the one hand, the resistance is increased with the polymer deposited on the cathode surface, leading to the declining of charging current, on the other hand, the separator would be penetrated by the polymer deposits when a large amounts of polymerization product of BH is aggregated, because of electron conduction of BH, resulting in internal short-circuit of the cell, and the charging current is declined, so the voltage run-away is avoided by the internal short-circuit, leading to the cell safety [17]. For the batteries with small amounts of BH. the internal short-circuit is not occurred due to without enough polymerization product, and the resistance is only increased slightly, so the test cells are easily to explode, and the overcharge results are similar to the cells without additive.

3.2. Linear sweep voltammetry

Fig. 6 shows the linear sweep voltammetry with different BH contents and without additive over the potential range of open circuit potential to 7.5 V. The scan curves show that remarkable oxidation current peaks are appeared between 4.5 and 5.5 V, indicating the electro-oxidative polymerization of BH on electrode surface [18]. Because of electrolyte decomposition, the current is increased rapidly at the potential of 7V, the cathode surface is covered with black viscous material which is the result of electro-polymerization. It is demonstrated that electro-polymerization reaction is occurred when containing BH as additive. The peaks of current are different with various amounts of BH, the results exhibit that electro-polymerization reaction degree is increased with the increase of BH. Black material is not appeared on the surface of electrode when the electrolyte is absence of additive; it is clear that only the decomposition reaction occurred.

The decomposition current of blank test is increased rapidly compared with electrolytes which containing additives from 6.5 to 7 V, this is apparently the result of the low electrical conductivity of electrolyte which caused by electro-polymerization reaction. The results show that biphenyl has the polymerization potential suitable for use as overcharge protection additive.

3.3. AC impedance spectroscopy

The AC impedance spectroscopy analysis of blank test and 3.0 wt.% additive are shown in Fig. 7. The cell resistance values obtained in the discharge state (3.3 V) is shown in Fig. 7a. AC impedance spectroscopy was tested under the condition of polarization to both electrodes at 5 V polarization potential after overcharged to 5 V, the results are shown in Fig. 7b. It is clear that AC impedance spectroscopy of the blank test is similar to the electrolyte with additive at the stage of discharge. However, as shown in Fig. 7b, not only the ohmic resistance increased, but also electrochemical resistance and interfacial resistance are increased greatly in the process of overcharging, compared with blank test.

The electrochemical impedance spectra of the two different types of batteries are similar to each other without overcharge, the blank test resistance is declined after overcharged to 5 V, which may be caused by electrolyte decomposition, and both the interfacial resistance and the electrochemical resistance are declined. Because of electro-polymerization reaction occurred, cathode surface is covered with the products of reaction, which lead to the increase resistance, under this condition, the voltage could be increased rapidly at the stage of overcharge, so current is declined too small to explode when changed into constant voltage charge.

3.4. Charge and discharge characteristic

The initial charge–discharge capacities and efficiencies are shown in Table 5. Due to different types of batteries, the initial

The discharge capacities and efficiencies of the first cycle

Number of batteries	Style of batteries	Rating capacity (mAh)	Initial charge capacity (mAh)	Initial discharge capacity (mAh)	Efficiency (%)
BT	LPB343944	520	596.1	530.5	89.00
LB05	LPB382530	210	256	223.4	87.27
LB1	LPB303236	300	359	309.25	86.14
LB2	LPB303236	300	359.38	306.06	85.16
LB3	LPB343944	520	594.45	505.5	85.04
LB4	LPB382530	210	254.75	213.15	83.67

Та	ble	6
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The internal resistan	ces of batteries
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Number of batteries	Average resistance $(m\Omega)$
BT	73.96
BH05	79.87
BH1	81.10
BH2	83.99
BH3	85.73
BH4	90.40

charge-discharge efficiency is an important aspect to reflect the initial charge-discharge characteristic. As shown in the table, the blank test has the highest initial charge-discharge efficiency, it also can be seen that the initial charge-discharge efficiency is decreased with the increase of BH, which may be caused by the declining of electrical conductivity, but it is not obvious, the efficiencies of all batteries are almost same, it is showed that efficiency does not change greatly by adding BH to electrolyte.

3.5. Internal resistance

The average values of internal resistances with various amounts of additive are shown in Table 6. It is clear that resistance is increased after BH added, in addition, it also exhibits that with the BH content increasing, larger resistance are observed. It is demonstrated that electrical conductivity decreased, which is accordance with the former results.

3.6. Cycle life performance

Fig. 8 shows the effect of the biphenyl content on the cycling performance of Al-plastic film lithium-ion batteries. It can be seen from this figure that the electrolyte without additive shows good capacity retention for 300 cycles, but there is no great difference between blank test and additives, and all the batteries show excellent cycling performance without much capacity fading for 300 cycles, more than 90% of the initial discharge capacity is obtained, when the BH content is 1.0 wt.% in the solution, the capacity retention is almost the same to blank test after 300 cycles. The results revealed that the capacity-fading rate is increased with the increasing content of BH, but not seriously. As we expected, the amount of additive is proved to control the cyclicality, compared with blank test, the electrical conductivity is decreased with an increase in BH content, according to the results of the internal resistance, the resistance is increased after adding BH to electrolyte, and the internal resistance increases with the increasing of BH content, the polarization of the cell is increased in the process of charge-discharge testing, leading to decrease of active material utilization, and the capacity fading is occurred.

On the other hand, although the linear sweep voltammetry results show that remarkable oxidation current peaks are appeared between 4.5 and 5.5 V, the electro-oxidative polymerization of BH is occurred slightly on electrode surface in the range of normal charge–discharge potentials, which are not obviously in the linear sweep voltammetry curves, in the case of large amounts of BH is added to electrolyte, BH gradually decomposes on cathode to pro-



Fig. 8. Cyclic performance curves.

duce Li⁺ insulator, leading to the big capacity fading [19], so the cycle performance is decreased with an increase in BH amount, the cycling tests results are agree well with those of internal resistance and impedance measurements.

3.7. Different discharge rates properties

The effect of different discharge rates, namely 0.2, 0.5, 1, 2 and 4C are shown in Fig. 9. Due to effect of internal resistance, the termination voltage was set to 2.7 V at a discharge rate of 4C. Discharge curves with various weights of BH are similar to each other at low currents, 0.2, 0.5, and 1C, respectively, and has 3.6 V discharge voltage plateau. However, the difference in discharge capacity become remarkable at a discharge rate of 2C, discharge properties are decreased seriously with 4.0 wt.% BH, there is no obvious discharge voltage plateau, and only 80% of the initial discharge capacity is obtained.

The results show that the properties of discharge capacity are decreased with increasing the proportion of BH, and with low discharge voltage plateau at a discharge rate of 4 C, the capacity is only 50% of the initial discharge capacity with 4 wt.% additive.

Conclusively, BH has little effect on the discharge capacity at low discharge currents, however, the influence is obvious at high current, and the effect is increased with high content of BH additive in electrolyte. This can be attributed to low electrolyte conductivity which caused by BH, and these results are coincided with the resistance.

3.8. Thermal stability

The test cells were recovered to room temperature and discharged after high temperature bulge experiment, and then one cycle charge–discharge testing was performed again, capacity retention performance under high temperature circumstance was examined, and the results are shown in Table 7. It can be seen from the table that all the batteries capacities are declined after

Table 7

The discharge capacities of the batteries after high temperature

Number of batteries	First discharge capacity after high temperature (mAh)	Charge capacity (mAh)	The second discharge capacity (mAh)
BH05	201.3	205.6	212.2
BH1	201.9	204.7	209.3
BH2	194.3	201.9	204.9
BH4	172.9	184.4	194.7



Fig. 9. Effect of the different discharge rates on the capacity of the batteries. The discharge rates were (a) 0.2 C, (b) 0.5 C, (c) 1 C, (d) 2 C, and (e) 4 C, respectively.

high temperature, which may be caused by self-discharge, subsequently, the charge–discharge capacity is increased, and the efficiency is more than 100%, which need to be studied in the future. In the condition of high temperature bulge experiment, the thicknesses of batteries were measured; the results are shown in Table 8. It is obvious that the bulge degree is increased with the increase of BH, this is attributed to the production of gas, which pro-

Table 8	
The thicknesses of the batteries after high temperatu	ire

Number of batteries	Thickness before high temperature (mm)	1 h	2 h	3 h	4 h	5 h	6 h	Thickness after high temperature (mm)
BH05-6	3.93	5.32	6.69	6.34	6.43	6.78	7.73	5.16
BH1-5	4.07	7.06	7.76	7.65	7.4	8.05	8.41	5.72
BH2-6	4.33	7.29	8.08	7.86	7.87	7.7	7.52	5.37
BH4-6	4.01	5.32	5.04	6.45	6.67	6.81	6.76	5.04

duced by reaction of BH under high temperature circumstance. The batteries have good capacity retention performance after recovered to room temperature.

In conclusion, it can be seen that the discharge capacities are decreased after high temperature with additives. The test cells are destroyed badly due to complex reactions occurred at the temperature of 90 °C, and the cells are scrapped after experiment. From the point of safety, the battery cannot be exploded after keeping for 6 h with high temperature, which has good safe capability.

4. Conclusions

Possible use of BH as a polymerizable additive for improving overcharge performance has been investigated, although the initial discharge capacity and cycle life performance were decreased after adding additive to electrolyte, but it was not serious, the results exhibited that normal electrochemical performances of Al-plastic film lithium-ion batteries does not change significantly by the use of BH as an electrolyte additive. Electro-polymerization reaction was occurred at the voltage of 4.8 V, the cathode surface was covered with a thin film which was the result of electro-polymerization reaction, and had good prospects to reduce charge-current. The overcharged battery was discharged automatically which caused by electro-polymerization reaction, and the battery was in the stage of safety. The overcharge performance was improved obviously by adding additive to electrolyte. We should add more amounts of additive to electrolyte to obtain better overcharge performance, of course, some capacity is lost. If the overcharge performance is not very important to the battery, it just needs low-dosage BH, which ensure the battery has high capacity, so the content of additive is ought to be adjusted to practical need in production.

Acknowledgements

This work is supported by the School Doctor Foundation of Zhengzhou University of Light Industry (Grant No. 000309) and Natural Science Foundation of Education Bureau of Henan Province, China (Grant No. 2008A150026).

References

- [1] X. Sun, H.S. Lee, X.Q. Yang, J. McBreen, J. Electrochem. Soc. 149 (2002) A355–A359.
- [2] E.-G. Shim, T.-H. Nam, J.-G. Kim, H.-S. Kim, S.-I. Moon, J. Power Sources 172 (2007) 919–924.
- [3] J. Xu, J. Yang, Y. NuLi, J. Wang, Z. Zhang, J. Power Sources 160 (2006) 621–626.
- [4] P.G. Balakrishnan, R. Ramesh, T.P. Kumar, J. Power Sources 155 (2006) 401-414.
- [5] J. Vetter, P. Novak, M.R. Wagner, C. Veit, K.C. Moller, J.O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, A. Hammouche, J. Power Sources 147 (2005) 269–281.
- [6] H. Nakahara, S.-Y. Yoon, S. Nutt, J. Power Sources 158 (2006) 600–607.
- [7] J. Liu, Z. Chen, S. Busking, I. Belharouak, K. Amine, J. Power Sources 174 (2007) 852–855.
 [8] H.Y. Xu, S. Xie, Q.Y. Wang, X.L. Yao, Q.S. Wang, C.H. Chen, Electrochim. Acta 52
- (2006) 636–642. [9] C. Korepp, W. Kern, E.A. Lanzer, P.R. Raimann, J.O. Besenhard, M. Yang, K.C.
- Moller, D.T. Shieh, M. Winter, J. Power Sources 174 (2007) 637-642. [10] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, Electrochem. Commun. 9 (2007) 25-30.
- [10] J.K. Feng, X.P. Al, Y.L. Cao, H.A. Yang, Electrochem. Commun. [11] H. Mao, D.S. Wainwright, US Patent 6,074,776 (2000).
- [12] H. Mao, U.S. Wallwright, US Patent 6,0 [12] H. Mao, US Patent 5,879,834 (1999).
- [12] H. Mao, OS Patent 5,879,854 (1999).
 [13] H., Mao, S.U., Von, European Patent 0,776,058 (1998).
- [14] H. Lee, J.H. Lee, S. Ahn, H.-J. Kim, J.-J. Cho, Electrochem. Solid-State Lett. 9 (2006) A307–A310.
- [15] T.-H. Nam, E.-G. Shim, J.-G. Kim, H.-S. Kim, S.-I. Moon, J. Electrochem. Soc. 154 (2007) A957–A963.
- [16] H.J. Lee, S.-Y. Cui, S.-M. Park, J. Electrochem. Soc. 148 (2001) D139–D145.
- [17] L. Xiao, X. Ai, Y. Cao, H. Yang, Electrochim. Acta 49 (2004) 4189–4196.
 [18] J.-A. Choi, S.-M. Eo, D.R. MacFarlane, M. Forsyth, E. Cha, D.-W. Kim, J. Power
- Sources 178 (2008) 832–836.
- [19] K. Abe, Y. Ushigoe, H. Yoshitake, M. Yoshio, J. Power Sources 153 (2006) 328-335.