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The importance of heat evolution during the overcharge process and the protection mechanism of electrolyte additives for prismatic lithium ion batteries

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ABSTRACT

In this work, the rate of heat generation in the overcharge period for 103450 prismatic lithium ion batteries (LIBs) of the $LiCoO_2$–graphite jellyroll type with a basic electrolyte consisting of 1 M $LiPF_6$–PC/EC/EMC (1/3/5 in weight ratio) has been found to be more important than the gas evolution which was traditionally considered as the main reason in the overcharge protection mechanism. The cell voltage, charge current, and skin temperature were monitored during the charge process. For a single battery or batteries in parallel, LIBs without any additives is an acceptable design if the cell voltage is not charged above 4.55 V under the common charge program. The rate of heat generation from the polymerization of 3 wt% cyclohexyl benzene (CHB) is high enough to cause the explosion or thermal runaway of a battery, which is not found for an LIB containing 2 wt% CHB + 1 wt% *tert*-amyl benzene (TAB). In the 12 V overcharge test at 1C, the thermal fuse was broken by the high skin temperature (ca. 80 °C) due to the polymerization of 3 wt% CHB, which was also the case for LIBs containing 2 wt% CHB + 1 wt% TAB. The disconnection of the thermal fuse, however, did not interrupt the thermal runaway of LIBs without any additives because the battery voltage was too high (ca. 4.9 V). The influence of specific surface area of active materials in the anode on the polymerization kinetics of additives has to be carefully considered in order to add correct amount of overcharge protection agents.

1. Introduction

With the popularization of cell-phones, laptops, and 3C products, the lithium ion batteries (LIBs) have been widely recognized as the most promising batteries with the best performance in these applications. Due to the wide introduction of LIBs into the human's lives, the safety issue becomes more important behind the battery design. Moreover, the urgent demanding on the high-capacity and high-power performances for LIBs makes more and more challenges on developing new/exist electrode materials as well as on improving the battery design. However, this may result in the recall battery cases for some famous battery manufacturers. In fact, overcharge is one of the most important safety issues in the battery design. No matter how good the performance of a battery shows, this battery is considered to be completely worthless if there is no overcharge protection mechanism in it. Hence, clear understanding on the overcharge mechanism of LIBs is very important, especially in designing new types of energy-/power-oriented batteries.

For common prismatic batteries, there is a safety valve on the external can but without positive thermal coefficient (PTC resistor) or a low-pressure protective device (such as the internal electrical disconnect device in cylindrical batteries) inside the batteries [1,2]. Once the prismatic batteries without such protective agents were overcharged, the cell voltage would be increased to extremely high values (such as 5 V) until the safety valve is activated, i.e., venting. It is very dangerous for LIBs under such high voltages, which may explodes or even thermally runaway before 5 V. Due to the generation of heat and gases resulting in the high pressure, the flammable electrolyte, and the unstable active materials in the overcharged battery, it is still dangerous and harmful to the users if the battery vents. Accordingly, some downstream manufacturers even request the ability that LIBs do not vent under certain overcharge conditions. Therefore, a new protection mechanism through using the overcharge protection agents has been studied in the past 10 years [3–7]. Unfortunately, how to use and choose the correct quantity and kind of overcharge protection additives is still an art.

Biphenyl (BP) is a famous and patented overcharge protection additive in LIBs [1,8–13], which has been widely studied in the literature, and its function and overcharge protection mechanism have been widely discussed [3–7]. The critical potential for initiating the polymerization of BP is around 4.5 V (for LIBs), resulting in

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the formation of a poly(*p*-phenylene)-type polymer [14]. This BP-derived polymer film (combined with the other mechanisms active to interrupt the surplus current) effectively stops the charging process. Besides BP, cyclohexyl benzene (CHB) is also a promising overcharge protective additive [14,15]. Although BP has a lower polymerized potential and better gassing ability in comparison with CHB [15], the presence of BP generally results in a shorter cycle life and relatively poorer reversibility in capacity, especially for the graphite-anode system [5]. Since CHB only shows a very slightly negative effect on the cycle life, more LIB manufacturers introduce CHB into their electrolyte formulations. Recently, co-use of CHB and BP was reported to show better results on overcharge and cycle life than using BP or CHB alone [14]. In addition, *tert*-amyl benzene (TAB), a similar organic compound with the same function of BP and CHB, was found to have a higher polymerization potential than BP and CHB [16,17]. Moreover, the polymerization of TAB generates more heat when LIB was overcharged, implying the possible importance of heating during the overcharge process.

In the past, researchers generally focused on the gassing mechanism as the main function of these overcharge protection additives when LIBs were overcharged [3–7,14,15]. Gassing is very useful and important for the traditional cylindrical batteries (such as 18,650 size) with a rupture disk design and safety valve inside [1]. For prismatic batteries (using in cell-phone, digit camera and some laptops, etc.), however, the protection function is not from gassing but through heating because the only protection design related gassing is the safety valve. Once too much gas is generated during overcharging, the battery will be leakage. In this study, we emphasize the importance of heating during the overcharge process for $LiCoO_2$–graphite prismatic LIBs by using the CHB–TAB mixtures since CHB and TAB have their intrinsic characteristics in overcharge protection. In addition, we emphasize the temperature control, from the heat generated by adding such overcharge protection additives, acting as an important function besides gassing.

2. Experimental

The battery system studied in this work is so-called 103450 (10 mm × 34 mm × 50 mm) prismatic batteries with an aluminum can, which consisted of $LiCoO_2$ cathodes and graphite anodes with a 20-μm separator of trilayer PP/PE/PP (PP: polypropylene, PE: polyethylene). The electrodes are prepared by a reverse coater and wound as jellyrolls. A safety valve is designed on the aluminum can and the basic electrolyte is 1 M LiPF6 in the solution with the weight ratio of PC:EC:EMC = 1:3:5. CHB and TAB in various ratios were added into the basic electrolyte. The whole procedures for the electrolyte preparation and the filling of electrolyte into the batteries were performed in an Ar-atmosphere glove box where the moisture and oxygen contents were controlled less than 5 ppm. The temperature inside the glove box was kept at 25 ± 2 °C.

The nominal capacity of every battery is 2.0 Ah and the charge/discharge currents called as 1C and 3C are equal to 2.0 and 6.0 A, respectively, and so on. Before the overcharge test, a stand charge/discharge procedure has been applied to all batteries to confirm their good quality. The battery was covered by a fiberglass with a fixed size and shape to simulate the insulated situation of a packed battery. A thermal couple was tied with the body of batteries to record the skin temperature. The battery which does not explode or vent during the whole overcharging process is called a safe one. Three charge and discharge measurements were performed using a programmable computer-controlled battery charger at room temperature.

Table 1
Formulations of overcharge protection additives in the basic electrolyte and their overcharge test results

Electrolyte	Composition of electrolytes			Test results of overcharge	
	Base[a] (%)	CHB (%)	TAB (%)	2C, 4.55 V	1C, 12 V
I	100	0	0	Passed	Failed
II	97	3	0	Failed	Passed
III	97	2	1	Passed	Passed

[a] Basic electrolyte is 1 M LiPF6 solution with weight ratio of PC:EC:EMC = 1:3:5.

3. Results and discussion

The common overcharge criteria for the single battery case of LIBs are 4.55 V by 2C charging and 4.65 V by 3C charging. On the other hand, in the series applications, such as laptop's battery pack, 3S2P or 4S2P, the common standard is 12 or 18 V by 1C charging. In this work, the charge current is constant (e.g., 2C) when the cell voltages are equal to or lower than the upper limit (e.g., 4.55 V for 2C) in the single battery case. As the cell voltage reaches the upper limit, a constant-voltage charge mode is applied. Note that the responses of cell voltage, charge current, and skin temperature against the charge time are recorded during the charge process, which are systematically compared for the batteries with various formulations of overcharge protection additives. The formulations of overcharge protection additives, as shown in Table 1, include no additives, only CHB, and the co-use of CHB and TAB, and the typical results for the single battery case are shown in Fig. 1a–c.

Fig. 1a shows the typical overcharge behavior of a $LiCoO_2$–graphite battery without overcharge protection additives in the electrolyte. The skin temperature was only slightly increased from 23 to 45 °C during the constant current (denoted as CC) charging step. When the charge mode was changed to be the constant-voltage (denoted as CV) model, the charging current was decreased gradually. This effect resulted in the decrease of heat generation from the charge process and the battery skin temperature decreased gradually to the room temperature. The above results reveal that the heat generated in the CV charging step is lower than that during the CC step, reasonably attributed to the absence of the overcharging protection additives in the electrolyte. Accordingly, for the applications of single battery or batteries in parallel, this design is acceptable because the cell voltage of batteries would not be charged above 4.55 V by most chargers or adapters. However, such batteries may be charged over 4.9 V due to the absence of the overcharge protection mechanism, probably resulting in explosion. In addition, it is not a good idea to employing such batteries without the overcharge protection additives in the series applications.

Fig. 1b shows the effect of 3 wt% CHB in the electrolyte on the cell voltage, charge current, and skin temperature during the charge process. From a comparison of Fig. 1a and b, all curves in Fig. 1b almost follow the same trace for those shown in Fig. 1a when the cell voltage is lower than 4.55 V. This result indicates the good reliability of all batteries prepared in this work and the absence of CHB polymerization. Note the sharp rise in the battery skin temperature when the cell voltage reaches 4.55 V for about 9 min in Fig. 1b. This phenomenon is reasonably attributed to the heat evolution through the polymerization of CHB when the cell voltage reaches 4.55 V (the polymerization potential of CHB) although the charge current is gradually decreased. Actually, the gas generated from the electrolyte decomposition and the CHB polymerization is not high enough to activate the safety valve (i.e., makes the battery vent). However, the heat generated from the polymerization of CHB may cause the battery explosion or thermal runaway. After charging for 1 h, the battery skin temperature is over 80 °C, indicating that the temperature inside the battery should be much

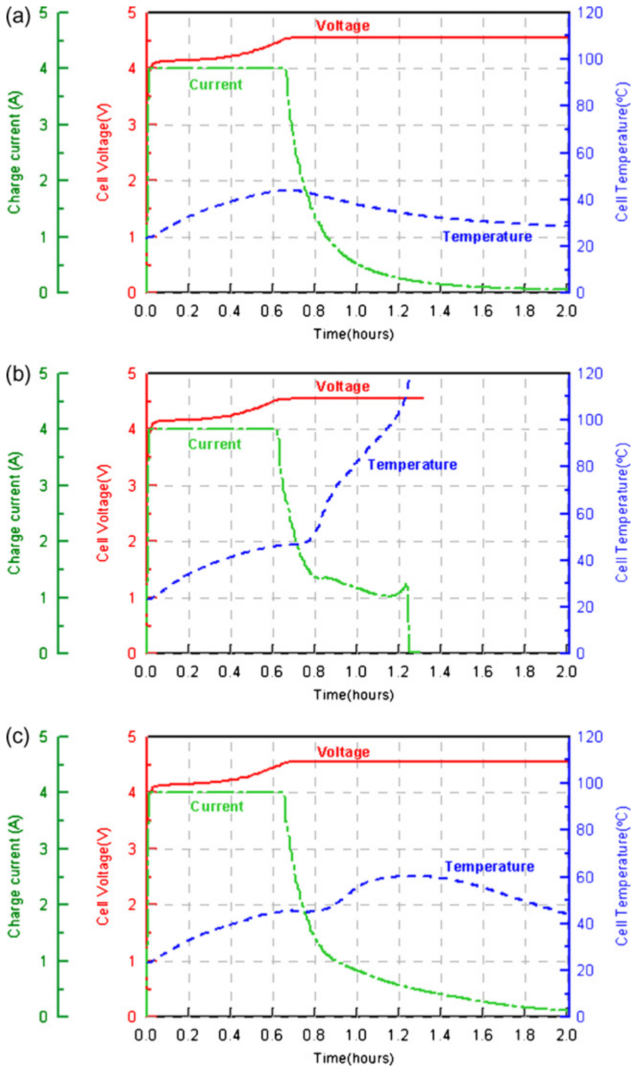

Fig. 1. Profiles of battery voltage, charge current and skin temperature during overcharge tests for LiCoO2–graphite prismatic LIBs with 1 M LiPF6–PC/EC/EMC mixed electrolyte containing: (a) no additives; (b) 3 wt% CHB; (c) 2 wt% CHB + 1 wt% TAB. Overcharge condition is 2C constant current charging with 4.55 V constant-voltage limit.

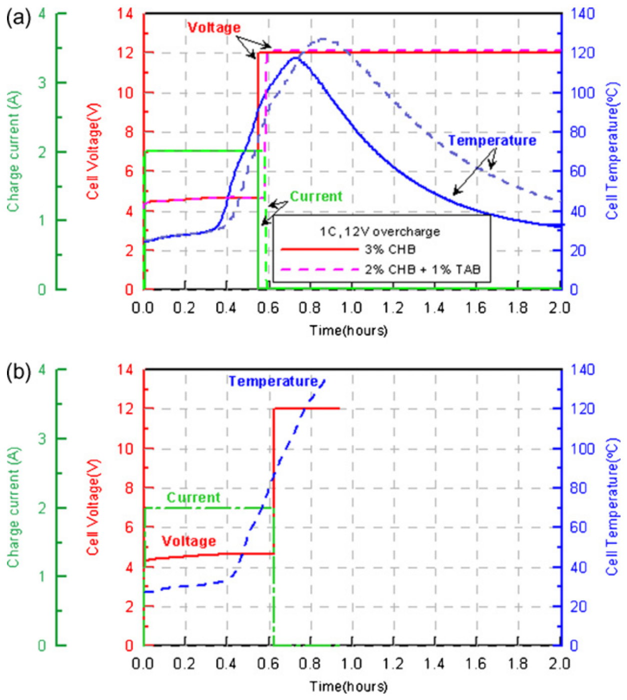

Fig. 2. Profiles of voltage, current and temperature during overcharge tests for the prismatic LIBs with (a) 3 wt% CHB (solid line) and 2 wt% CHB + 1 wt% TAB (dash line); (b) no additives in the electrolyte under the 12 V overcharge test at 1C charge rate.

higher (above 90 °C). Under such a high-temperature and high-voltage environment, the internal solid-electrolyte interface (SEI) layer, anode and cathode materials, and electrolyte are very unstable, probably resulting in the propagation of decomposition (i.e., the chain reaction among the SEI layer and the unstable active materials as well as the electrolyte decomposition) and the generation of more heat. Such huge heat will make the meltable separator shrinkage and could not separate the cathode and anode from the edge although the meltable separator, widely used in current LIBs, should be expanded and melted at high temperatures to stop the movements of ions between cathode and anode. The shrinkage of the separator due to the evolution of too much heat will make the large area contact between anode and cathode (i.e., short), inducing the explosion. Accordingly, Fig. 1b demonstrates a typical case with too much heat generated from the polymerization of CHB, making the battery fail.

Fig. 1c shows the effect of 2 wt% CHB in the electrolyte on the cell voltage, charge current, and skin temperature during the charge process although there is 1 wt% TAB in the electrolyte. Note that the polymerization potential of TAB (ca. 4.6 V) is significantly higher than 4.55 V, the 1 wt% TAB should not be polymerized to generate heat during this test. Again, during the CC charging step, very similar responses in the cell voltage, charge current, and skin temperature are found in Fig. 1c. When the charging time is longer than 0.8 h, a gradual increase in the skin temperature is found. However, the skin temperature reaches a maximum (ca. 61.5 °C) and then, decreases gradually. Accordingly, the charging current was decreased gradually when the charge mode was changed from the CC to the CV mode. The above results indicate that the heat generated from the polymerization of 2 wt% CHB is much lower than that for the electrolyte containing 3 wt% CHB. Hence, the highest skin temperature is much lower than that obtained in Fig. 1b.

From the above results and discussion, TAB seems to be inactive for the overcharge protection. However, in the series applications, when the same batteries with different electrolytes (as shown in Table 1) were tested by overcharging to 12 V at 1C, the effect of adding TAB can be clearly observed (see below). In usual, there is a thermal fuse welded onto the pack because more batteries in a pack are employed in the series applications. Note that the thermal fuses can be activated by two mechanisms. First, a current passing by the thermal fuse at or above a critical temperature would make the fuse break; this current becomes lower with a higher temperature. Second, when the skin temperature reaches the melting point of fuses, this will also make the fuse break even there is no current passed by. A battery in the pack without any overcharge protection additives in the electrolyte may be charged to around 5 V or higher, which will vent or explode behind such high overcharge conditions.

Solid lines in Fig. 2a show the overcharge behavior of a battery in 1C/12 V overcharge test with 3 wt% CHB added into the electrolyte. The battery skin temperature is increased slowly during the initial 0.3 h. After that, the battery voltage reaches the polymerization potential of CHB, about 4.55 V (for LIBs), resulting in the sharp increase in the skin temperature due to the CHB polymerization. At about 0.5 h, the battery temperature reaches 80 °C, renders the breaking of the thermal fuse, and stops the overcharging process. Hence, the charge current has been interrupted, which was decreased to zero dramatically. Due to the time lag in heat transfer, the skin temperature of batteries was kept rising up for a while and then, went down because of the generation of insufficient heat under such an effective protection mechanism. This result also indicates that the temperature during the initial half-hour charging step is not high enough to cause the propagation of decomposition. Since the thermal fuse would break and stop the charge current entirely at about 80 °C, this device is considered to be the best mechanism in overcharge protection from the safety viewpoint.

Dash lines in Fig. 2a describe the overcharge behavior of a LIB pack containing 2 wt% CHB and 1 wt% TAB. When the charge time is longer than 0.35 h, the skin temperature, very similar to solid lines, is increased because this pack also contains CHB in the electrolyte. However, due to the different contents of CHB, the slopes of the skin temperature against time curves in Fig. 2a are somewhat different. From 0.35 to 0.7 h, the skin temperature of the pack containing 3 wt% CHB is higher than that of the pack containing 2 wt% CHB and 1 wt% TAB, which is reasonably attributed to more heat generated from the CHB polymerization in the former LIBs (a higher concentration of CHB). When the charge time was above 0.55 h, the battery voltage (see dash line) was charged to reach the polymerization potential of TAB. Accordingly, another temperature against time profile was found from this moment and the highest battery temperature of this pack is higher than that of the pack containing 3 wt% CHB although the thermal fuses were activated at the same temperature, about 80 °C. These voltage–current–temperature against time profiles reveal that if only TAB is added in the electrolyte to act as an overcharge protection additive, the battery will be charged to a higher voltage (e.g., 4.65 V) to make the polymerization of TAB. Besides the higher risk from a higher overcharge voltage, the battery temperature will also be increased very quickly. Accordingly, it is not good to choose the protection agent with a relatively high polymerization potential for the prismatic LIBs even the thermal fuse has already been broken.

Fig. 2b shows the typical failure behavior of a battery without any overcharge protection additives in 1C/12 V overcharge test. Note that the charged current could not be interrupted by the disconnection of the thermal fuse and the active materials were continued to be charged to a very unstable state. The battery skin temperature was suddenly increased at 0.7 h and the battery voltage was close to 4.9 V. Unlike the cases with CHB or TAB, the battery temperature did not reach a maximum through means of the breaking of the thermal fuse. Instead, the sharp increase in the skin temperature is attributed to the chain reaction among the SEI layer, electrolyte decomposition, and unstable active materials, causing the thermal runaway of this pack. Although the thermal fuse was also broken when the skin temperature reached about 80 °C, this action was too late to avoid the explosion because the propagation of decomposition had been started when the battery voltage higher than 4.65 V.

The above results and discussion in Fig. 2 demonstrate the danger for a pack of the prismatic batteries in series with inefficient or without any overcharge protection additives in the 12 V overcharge test at 1C. Moreover, from the results and discussion in Fig. 1, there is also a risk for the 4.55 V overcharge test at 2C when too much CHB, TAB or BP are added in the electrolytes for a single battery without considering their negative effect on the cycle life of batteries. Hence, how to correctly add the overcharge protection additives in order to pass various overcharge tests and to keep the good performance of batteries is very important for the battery manufacturers [18].

For most prismatic batteries, there are many types of active materials for the anode, such as mesophase carbon (MCMB), natural graphite and artificial/synthesis graphite with various treatment technologies from different suppliers while they generally consisted of the $LiCoO_2$ cathode. Hence, in this study, we compare the effect of active materials for the anode on the overcharge behavior of batteries and do not consider the effects of active materials in the cathode. In this work, the anodes consist of the same type artificial graphite with different specific surface areas (SSAs) (i.e., 1.0 and 1.4 $m^2\,g^{-1}$ denoted as GA10 and GA14, respectively). From Fig. 3, the skin temperature of the battery with the anode consisting of GA14 is higher than that consisting of GA10 although an identical electrolyte with the same quantity of overcharge protection additives is used in both batteries. Due to the fact that the higher SSA an anode is, the more an electrolyte will be reacted to form a thicker SEI layer. Since the SEI layer will start to decompose when the additives are oxidized/polymerized to cause the inside temperature of the cell above 80 °C, the inside temperature of a cell with more SEI decomposition (an exothermal reaction) will become higher. This higher temperature will accelerate the polymerization rate of the overcharge protection additives. Therefore, the heat originally generated from the cathode by additive polymerization induces the decomposition of the SEI layer on the anode (above 80 °C), and then the heat generated from the SEI decomposition further increases the polymerization rate of additives (i.e., a phenomenon of auto-accelerating heat generation). Accordingly, the skin temperature of a battery with the anode consisting of GA14 is reasonably higher than that consisting of GA10 because of a thicker SEI layer formed on the anode of the former battery. The above phenomena point out the fact that the influence of physicochemical properties (e.g., SSA in this case) of active materials in the electrodes on the poly-

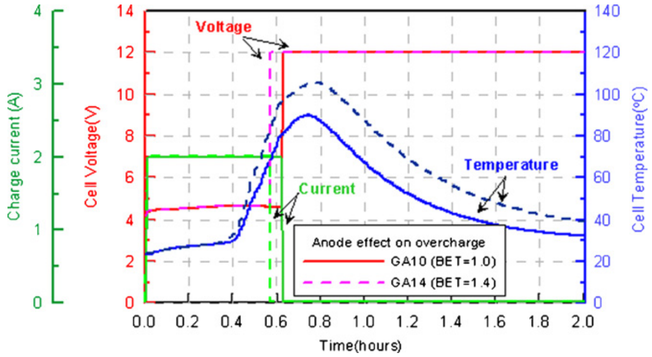

Fig. 3. The effect of artificial graphite with the specific surface area of (1) 1.0 (GA10, solid lines) and (2) 1.4 $m^2\,g^{-1}$ (GA14, dash lines) as the anode on the overcharge behavior of a single battery in the electrolyte with 2 wt% CHB and 1 wt% TAB. Overcharge condition is 1C constant current charging with 12 V constant-voltage limit.

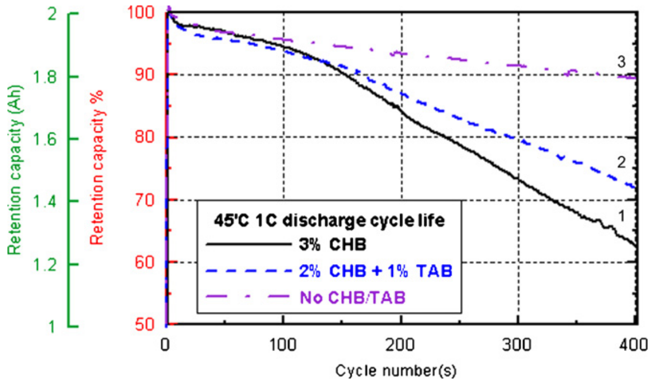

Fig. 4. Effect of CHB and TAB on 1C discharge cycling measured at 45 °C of $LiCoO_2$–graphite prismatic LIBs. The additive content in electrolyte was (1) 3 wt% CHB; (2) 2 wt% CHB + 1 wt% TAB; (3) 0 wt%, respectively.

merization kinetics of additives has to be carefully considered in order to add correct amount of overcharge protection agents.

The negative effect of the above overcharge protection additives on the cycle life of LIBs at a relatively high temperature is very important [5,15,18]. Accordingly, typical data of the 1C discharge cycle life measured at 45 °C are shown in Fig. 4. Note that the fade rate of batteries without any additives is relatively slow, keeping about 90% of the initial capacity after 400 cycles. Unfortunately, the fade rates of LIBs containing 3 wt% CHB or 2 wt% CHB and 1 wt% TAB are much faster than that without any additives. Only about 63.5 and 72% of the initial capacity are maintained after discharge at 1C for 400 cycles when batteries contain 3 wt% CHB and 2 wt% CHB + 1 wt% TAB, respectively. The above result indicates the cycle life of LIBs containing 2 wt% CHB + 1 wt% TAB is better than that containing 3 wt% CHB only.

4. Conclusions

The function of CHB, TAB and the similar organic compounds as additives for the overcharge protection of prismatic LIBs mainly depends on how much heat generated in the polymerization of these additives when the battery voltage reaches their corresponding polymerization potentials. This is very different from the gas evolution mechanism in the traditional thinking for the cylindrical batteries. From the overcharge characteristics of TAB and CHB, TAB will be polymerized at a higher voltage than CHB, which also produce more heat in a short time to make the thermal fuse break in order to interrupt the charge process. For the single battery or the batteries in parallel, LIBs without any additives is an acceptable design if the cell voltage is not charged above 4.55 V under the common charge program. However, the batteries have chances of explosion or thermal runaway if too much additives are added into the electrolytes (i.e., 3 wt% CHB) in the single battery applications. The influence of SSA of active materials in the anode on the polymerization kinetics of additives has to be carefully considered in order to add correct amount of overcharge protection agents.

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