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Effects of 2,4-difluorobiphenyl as an Electrolyte Additive to Enhance the Overcharge Protection of Cylindrical $LiCoO_2$/graphite Batteries

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Combined with the use of a pressure-sensitive cap, 2,4-difluorobiphenyl (DFBP) is investigated as an overcharge safety additive for the protection of 4.4 V commercial cylindrical $LiCoO_2$/graphite batteries. DFBP can be electrochemically polymerized when the $LiCoO_2$ is charged to approximately 4.60 V (vs. Li^+/Li), resulting in the release of large amounts of gases; this release can be utilized to activate the current interrupt device (CID) and solve overcharge risk issues. With the addition of DFBP to the electrolyte from 0–6% (wt.%), the CID activation status of charge (SOC)% of $LiCoO_2$/graphite batteries decreases from 175% to 140.5%, and quite noteworthy the DFBP amounts of 2% to 4% in the electrolyte can be used to prevent the overcharge explosions. In addition, it is also demonstrated that the DFBP additive has no obvious negative influences on the cycle and temperature performances of $LiCoO_2$/graphite batteries under normal conditions, indicating the promising prospect of DFBP as an overcharge safety additive for the protection of commercial cylindrical $LiCoO_2$/graphite batteries.

Keywords: 2,4-difluorobiphenyls, $LiCoO_2$/graphite battery, electrolyte additive, overcharge protection, battery performances.

1. INTRODUCTION

Lithium ion batteries (LIBs) improve the voltage and energy density using an organic electrolyte but also increase the risk of safety during use as compared to traditional water solvent batteries such as Ni–Cd, Ni/MH and lead/acid batteries [1,2]. The voltage of the LIBs would increase uncontrollably once the protection device fails because of a short of a spontaneous intrinsic restriction for the voltage increase. The oxidation of organic electrolytes at the oxidizing cathode lacking in lithium and the reduction of the electrolyte on the active anode would occur inside the cell. Flammable gases and excessive heat are produced by these reactions, and easily lead to a thermal runaway, battery cracking, explosion and even fire [3]. A key obstacle for high energy density LIBs is their safety issues, which were used in fields such as power, smartphones, and military applications [4,5]. The battery charging explosions of Samsung devices in 2016 and Apple in 2017, as well as the electric vehicle recharging accidents in China, all reflect the importance of avoiding battery overcharging risks.

In practice, commercial LIBs are equipped with the positive temperature coefficient of resistance (PCT) or the protection board integrated circuit (ICs), which can avoid the overcharge phenomenon under normal circumstances. However, these remedies increase the cost and reduce the energy density of the battery system because they occupy space. When the external conditions change, the components fail or cannot achieve the desired effects, it is easy to produce rechargeable security issues. It is urgent to develop a self-protection mechanism among the LIBs to improve battery safety based on the development of battery manufacture technology.

To solve battery overcharge risks during the charging process, a very good choice is to use a non-combustible electrolytic liquid system and separator material. However, a commercial electrolyte must meet several requirements such as solubility, stability, electrochemical window, etc., which represent a variety of technical difficulties for selecting a non-combustible solution and separator material [6]. The addition of overcharge protection additives in the electrolyte has proven to be an economical and effective method. These functional additives include the redox shuttle substances and the polymerizable chemicals. The former has reversible oxidation–reduction electrochemical characteristics between the cathode and the anode; these characteristics can protect the LIBs from overcharge by locking the potential of the cathode at the oxidation potential of these shuttle molecules [7-9]. The redox shuttle mechanism of this additive is similar to the oxygen cycle in the aqueous solution battery system. Up to now, because of the poor solubility in non-aqueous electrolytes, most of the shuttle molecules reported before can only supply a limited shuttling current, and therefore fail to function even at normal operating current. In addition, the electrochemical stability of shuttle molecules on a long-term operation, large capacity loss and low oxidation potentials are also issues for their practical applications. For example, 2,5-di-tert-butyl-1,4-dimethoybenzene (DDB) [10] has a potential ~ 3.9 V (vs. Li^+/Li), which cannot meet the above 4.2 V chemical system and large current charging requirements. The polymerizable additives are also known as interrupt-type additives and have been used in some commercial electrolytes. It can be polymerized on the cathode surface to increase cell impedance and prevent the further overcharging of the cathode. In the previous studies, several aromatic compounds such as biphenyl [11], cyclohexene [12], xylene [13] can be used as polymerizable functional molecules for the overcharge protection of LIBs. Unfortunately, these substances also have problems with the protection of low voltage, which cannot be adapted to the application in the high charging cut-off voltage battery system [14-17]. Recently, Huang [18] reported a polymerizable additive of 2,4-difluorobiphenyl (DFBP) matching the $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode. It was indicated that a high impedance fluoropolymer film was formed to reduce the charging current and improve the overcharge safety when an overcharge to 4. 6-4. 8 V was performed. The oxidation potential of DFBP was 0. 2 V higher than that of biphenyl, which is favor to the battery operated under

4.35 V at room temperature. Considering the properties of DFBP, it is still important to investigate the potential application of DFBP in the LIBs with other cathode materials, and find some now additives to meet the overcharge protection requirements of the commercial LIBs

In fact, combined with the structure design of LIBs such as the current interruption devices used in the cylindrical batteries, adding similar interrupt additives in the electrolyte can further improve the overcharge prevention of LIBs. On this occasion, the choice of the overcharge protection additives and battery design should be based on the following consideration, namely, the charge cut-off voltage of commercial LIBs is about 4.4 V, and the decomposition potential of electrolyte solvents are general at approximately 5.5 V. Therefore, to avoid the oxidative decomposition of the electrolyte solvent and the overcharge of the cathode materials, the polymerization potential of overcharge protection additive should be between 4.4 V and 5.5 V. At the same time, the reaction rate of the additive should be fast enough to ensure that the electrode material will not be charged and the electrolyte will not be decomposed. In addition, from a battery use point of view, these additives must not have obvious negative impacts on other performances of the LIBs. In this paper, according to the above requirements and the general application of $LiCoO_2$/graphite batteries, the fluorine functionalized molecule DFBP is evaluated as an overcharge protection additive in the commercial cylindrical $LiCoO_2$/graphite batteries, and the protection mechanism and the effects of DFBP on the battery performances are discussed.

2. EXPERIMENTAL

2.1 Preparation of the test batteries

DFBP was purchased from GST Chemical Co. Ltd. (China, 99.5%) and dissolved in the commercial electrolyte of 1.0 mol/L $LiPF_6$/EC+EMC+DEC (EC/EMC/DEC = 30/40/30, by weight, Smoothway, China, 99.99%) with mass weights of 1%, 2%, 3%, 4%, 5%, and 6%. Using the general method in McNair New Power Co. Ltd., the 32650 type cylindrical $LiCoO_2$/graphite batteries with a capacity of 6 Ah was prepared to evaluate the effects of DFBP as a functional additive to the overcharge protection of LIBs. The cathode consists of LCO (Shanshan energy, 99.8%) as an active material (97 wt.%), carbon nanotubes (Cnano Technology, 99.8%, China) as a conductive additive (1.6 wt.%), and polyvinylidene fluoride (PVDF, Solvay, France) as a binder (1.4 wt.%). Graphite (CMS, Shanshan, China) was the active material with 1.2 wt.% sodium salt of carboxy methyl cellulose (CMC, DAICEL, Japan), 1.5 wt.% styrene-butadiene rubber (SBR, ZEON, Japan), and 1.0 wt.% conductive carbon was employed as an anode. The ceramic coating was a porous polyethylene film with a bare separator thickness of 9 μm, and a ceramic layer of 3 μm was purchased from Xuran Co. Ltd. and was used as the separator. The capacity of full cell was determined by the cathode side; the anode capacity vs. cathode capacity ratio (cell balance) was 1.12. In addition, because it is difficult to observe and measure the gas volume generated in the cylindrical battery during the overcharge, the pouch polymer $LiCoO_2$/graphite batteries with the same capacity of the cylindrical batteries were also prepared to define the gas volume during the charge process.

2.2 Electrochemical measurements

The electrochemical behaviors of 2,4-difluorobiphenyls (DFBP) dissolved in the electrolyte were examined by line cyclic voltammetry (CV) using a Pt micro-electrode (0.1 mm in diameter) as the working electrode. The prepared electrolyte was investigated using a two-electrode cell with a metal lithium foil as both reference electrode and counter electrode. The data detection and analysis were carried out by using a CHI 660A electrochemical workstation (Chenhua, China). The conductivity of the electrolyte with different amounts of DFBP was measured using a conductivity meter (DDS-307A, Shanghai, China).

The electrochemical compatibility of the DFBP-containing electrolytes was measured by the cylindrical batteries. In the potential range between 4.4 V and 3.0 V, the batteries were cycled three times before the overcharge testing. The overcharge measurements were conducted in an explosion-proof box and used a computer-controlled programmable battery charger (CTS-PWM20V10A type, Shenzhen, China) to record the charge information. The battery temperature was measured by a thermocouple (LR8403, HIOKI, Japan). The EIS measurements were performed at the 50% SOC discharge state, the AC perturbation was 5 mV, and the frequency range was from 1 Hz - 500 kHz by using Zehner impedance analyzer (IMex6, Germany). To study the influence of DFBP on the cycling performance of $LiCoO_2$/graphite batteries, the full batteries were charged to 4.4 V at 0.7 C, followed by a constant voltage charging at 4.4 V until the current decreased to C/20, and discharged at constant current of 0.5 C until the voltage reached 3.0 V using Neware battery cycle (BTS-PWM5V10A, Shenzhen, China). Capacity retention was determined by the ratio of the discharge capacity to the initial capacity after cycle. The high temperature storage performance of the battery with 100% SOC was carried out at 85 °C for 4 h. The impendence and residual capacity were checked before and after the storage.

2.3 Gas analysis and electrode characterization

The gas composition originating from the charge process was measured by Gas Chromatography (TRACE 1300, Thermo Fisher, Germany). The volume change of the pouch battery was examined using a water drainage method as described below. The cell was connected with a rigid wire. The wire was fixed to a specially designed jig, then dipped into a beaker filled with de-ionized water (not touching the beaker bottom) and kept the system in static equilibrium. Afterward, by high precision balance (accuracy of 0.001 g), the weight changes of the beaker at 160% SOC were monitored, and the cell volume changes were calculated using Archimedes principle ($V = m/\rho_{water}$).

To characterize the morphology and element distribution of the cycled electrodes, the cells were carefully dismantled in a dry environment with a controlled dew point (-40 °C) to avoid a short circuit after the cycling tests. After the dissection of the jelly roll, the morphological changes for cathode, anode, and separator after the overcharge were observed by scanning electron microscope (JEOL, JSM-6510, JEOL, Japan). The element distribution on the electrodes was determined by energy dispersive spectroscopy (EDS, Oxford, England).

3. RESULTS AND DISCUSSION

3.1 Electrolyte performances with the DFBP additive

Fig. 1a shows the linear sweep curves of the Pt electrodes in 1 mol·L^{-1} $LiPF_6$/ EC+EMC+DEC (3:4:3 by weight) at a scan rate of 10 mV s^{-1} without an additive and with 5 wt.% DFBP. The oxidation current appears when the voltage reaches about 4.60 V, then increases quickly as the scanning potential increases and reaches the maximum value at 5 V. Compared to the cell without the DFBP additive in the electrolyte, the oxidation current can be viewed as the electrochemical oxidation reaction of DFBP on the Pt electrode. It can be observed that the potential interval of the oxidation current peak coincides with the need to prevent the battery overcharging process, and especially, the voltage range of the oxidation is slightly higher than the work voltage of the commercialization of LIBs. With continued voltage increases, the oxidation current of the electrolyte reappears at 5.7 V, which is similar to the curve of the electrolyte without DFBP additive, and corresponds to the oxidation decomposition reaction of the electrolyte on the Pt electrode. The oxidation potential of DFBP and the rapid oxidation kinetics indicate that the DFBP additive is with the first condition as an overcharge protection additive [11-14].

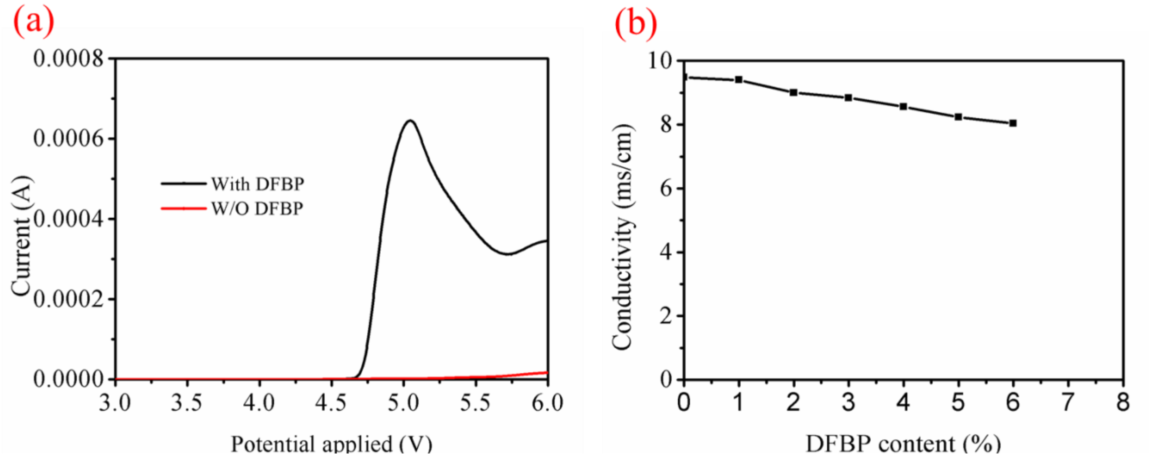

Figure 1. a) LSV curves of the Pt electrode in 1 M $LiPF_6$/ EC+EMC+DEC electrolyte containing 5 wt. % DFBP. b) The conductivity of electrolyte with different DFBP amounts.

In addition, as an important parameter, the conductivity of the electrolytes with different amounts of DFBP additive was also measured and is shown in Fig. 1b. The ionic conductivity of 1.0 M $LiPF_6$ EC/EMC/DEC electrolyte was 9.48 mS cm^{-1}. With increasing the addition of DFBP from 2% to 3%, 4%, 5%, and 6%, the ionic conductivity of the electrolyte decreased from 9.48 to 9.4, 9.0, 8.84, 8.56, 8.23 and 8.04 mS cm^{-1}, respectively. The lower ionic conductivity of the electrolyte with DFBP additive can be mainly ascribed to the viscosity increase of the electrolyte with the addition of DFBP, which do not favor the rate performance of LIBs to some extents [18].

Table 1. The results of the overcharge tests with different amounts of DFBP

DFBP contents	2%	3%	4%	5%	6%	0%
Pass/Total	5/5	5/5	5/5	5/5	5/5	3/5
CID activation SOC%	160.5	155.5	150.5	144.2	140.5	175

Remark - CID and SOC are the abbreviation of current interrupt device and state of charge, respectively.

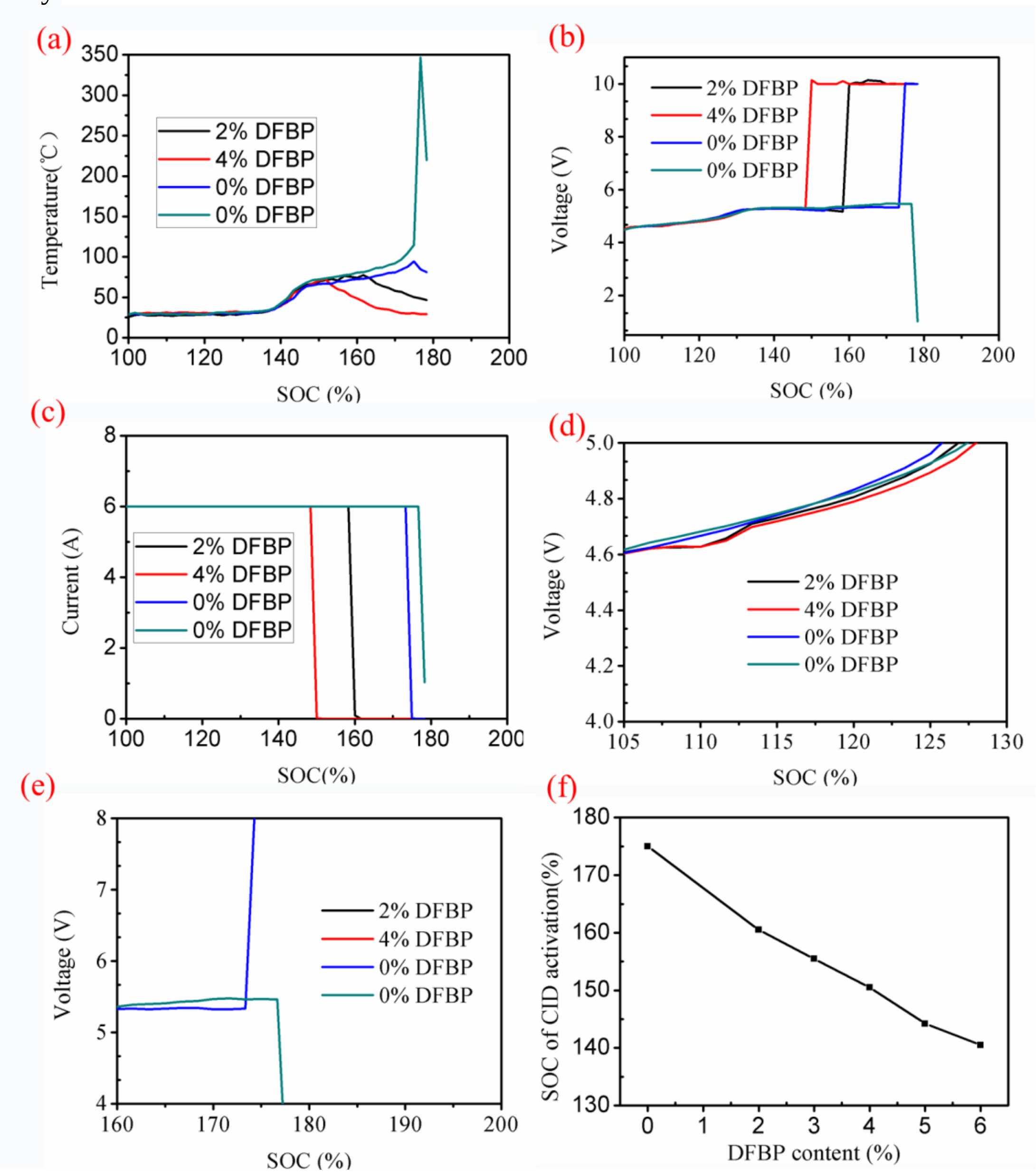

Figure 2. a) Temperature curves of the batteries with different amounts of DFBP during the overcharge. b) Voltage curves of the batteries with different amounts of DFBP during the overcharge. c) Current curves of the batteries with different amounts of DFBP during the overcharge. d) Enlarged voltage curves of the overcharge from 105% SOC to 130% SOC. e) Enlarged voltage curves of the overcharge from 160% SOC to 200% SOC. f) The relationship between the SOC of CID activation and the DFBP amount.

The evaluation data of DFBP as an electrolyte functional additive to protect the overcharge accidents of $LiCoO_2$/graphite cylindrical batteries are listed in Table 1. The overcharge test was carried out from 3.0 V to 10 V at a charge current of 1.0 C. Table 1 shows that there is greater risk of overcharge failure for a battery without the DFBP additive because two batteries failed due to the occurrence of an explosion during the overcharge test. In contrast, all five batteries with DFBP were safe and did not catch fire or explode. With the content increase of DFBP as protection additive in the electrolyte, the current interrupt device (CID) activation state of charge (SOC) % decreases from about 175% to 140.5%. The higher values of CID activation SOC% mean the greater risk of electrolyte decomposition [11,12,18], while the lower values may lead to an easy failure of LIBs. These results suggest that DFBP can help the battery to pass the overcharge test, and the suitable DFBP contents in the electrolyte may be set in the range of 2%-4% considering the practical application of LIBs. In the later sections, the DFBP contents of 2% and 4% will be expressly evaluated.

Fig. 2a shows the typical temperature curve of the batteries with 0%, 2% and 4% DFBP during the overcharge. As seen from Fig. 2a, the temperature of the batteries with different content of DFBP was relatively stable when the batteries were overcharged from 100% SOC to 140% SOC. When the SOC was over 140%, the temperature rose rapidly, in which case the charge capacity of $LiCoO_2$ was the equation of the theoretical capacity (~ 273 mAh g^{-1}) [2]. The rapid temperature rise is due to almost all lithium ions being virtually emerged from the cathode materials. As the overcharge proceeded, the temperature of the battery with 4% DFBP reached the highest temperature of 72.7 °C; when the battery was charged to 151% SOC, the temperature decreased. To confirm the root cause of the temperature decrease, Fig. 2 b and c describe the voltage and current curves of the batteries with 2% and 4% DFBP, as well as without DFBP during the overcharge. As shown in Fig. 2b, the voltage of the battery with 4% DFBP increased suddenly from 5.3 V to 10 V at 150.5% SOC. It was confirmed that the CID of the battery had been thrusted, and the charge current was cut off. This phenomenon could explain the previous temperature drop and voltage increase during the overcharge process for the battery with 4% DFBP. A similar phenomenon was also observed in the 2% DFBP battery and the battery without DFBP. The SOC of the CID that was broken was slightly slower, specifically at 160.5% and 175%. In contrast, as shown in Fig. 2d, the temperature of other batteries without DFBP rose quickly as the overcharge process proceeded. Finally, the battery exploded when the SOC was 177%; the temperature rose sharply to 346.9 °C.

As seen in Fig. 2 c, the explosive batteries have higher voltage than the unexploded batteries without DFBP, and the voltage of the explosive batteries dropped to 1 V; this indicated that there was a serious internal short circuit, which caused an instantaneous release of a large amount of heat and a thermal runaway [1,3,4]. Therefore, when the SOC of a battery exceeds 175% and continues to overcharge, the failure risk of the battery is very high. As such, the charging current of the battery must remain under 175% SOC to avoid the occurrence of thermal runaway. From Fig. 2d, we see that batteries with DFBP have a small platform from 4.6~4.7 V, according to the LSV curve; this current consumption should be attributed to the reaction of DFBP. Fig. 2f illustrates the relationship between the SOC of CID activation and the content of DFBP. The SOC of CID activation appeared in advance for all batteries with DFBP during the overcharge process, and the SOC decreased as the amount of

DFBP increased, which suggests that the overcharging state of their CID activation is associated with the addition of DFBP [11-15].

3.2 Analysis of the overcharge protection mechanism of the DFBP additive

For the cylinder cell, it is difficult to observe the gassing increase phenomenon during the overcharge test. Therefore, a polymer battery, which is prepared by electrodes with the same capacity, coating weight, and calendar density as the cylinder cell, is used instead (dimensions 4.4 mm*63 mm*112 mm); the amount of gas generated can be detected by using a water drainage method. Thus, it allows a better understanding of the mechanism between the content of DFBP in the electrolyte and the CID activation in the cylinder cell during the overcharge. Fig. 3 a-1/2/3 shows a cell photo with the different DFBP amounts at the overcharging state of 160% SOC. The swelling volume of the battery is significantly larger than that with 2% DFBP and without DFBP. From Fig. 3b, it can be seen that compared to the battery without DFBP additive, the cell with 2% DFBP generated 7.7 ml more gas during the overcharge, and more 9.6 ml gas was found for the battery with 4% DFBP. It is fully demonstrated that the addition of DFBP in the electrolyte will produce more gas when the batteries are overcharged [18].

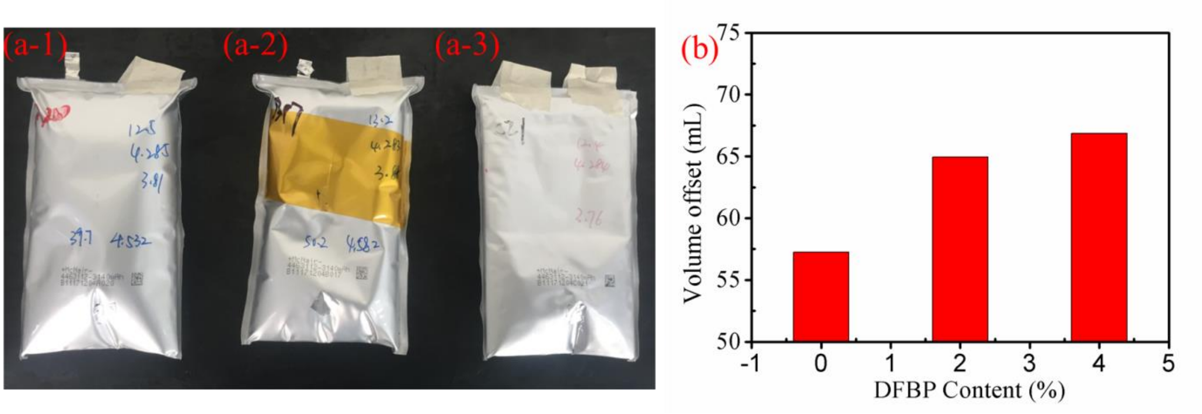

Figure 3. Influence of DFBP contents on the battery swelling overcharged to 160% SOC, and the DFBP content is (a-1) 4 wt.%, (a-2) wt.% and (a-3) 0 wt.%. b) Influence of DFBP contents on the volume offset of the batteries overcharged to 160% SOC.

If the battery is equipped with electronic circuit components, such as a pressure-sensitive CID, the battery can realize charging protection by generating the gas in advance. Fig. 4a shows the schematic of the cylindrical battery. The CID is normally installed in the positive side of the battery, connecting the cathode electrode and the cap. For the current interruption function to work under abnormal conditions, CID requires the following functional components to work together: a positive temperature coefficient (PTC), vent, cap, and gasket, Normally, the convex surface of vent faces the CID and is welded on the CID, as shown in Fig. 4g. Generally, the reverse pressure of the vent is 0.8 ~ 1.0 MPa, and the burst pressure of the vent is 1.8 ~ 2.2 MPa. If the internal battery pressure is greater than the reverse pressure, the vent will be activated and then destroy the connection with the CID, as shown in Fig. 4h. The current will be cut off immediately; this is the first protection. Further increasing the pressure to its burst point results in a rupture of the battery vent and pressure release; this is the secondary protection [1,18].

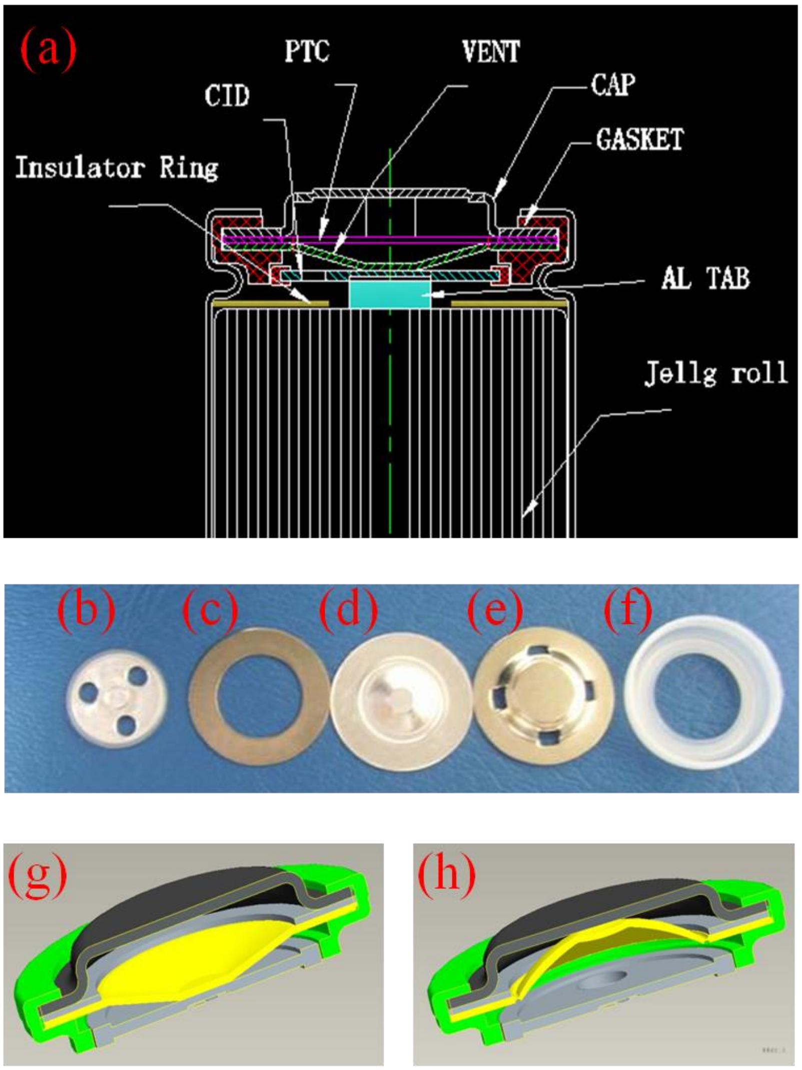

Figure 4. a) Schematic of the cylindrical $LiCoO_2$/graphite battery. b) The current interrupt device (CID). c) The positive temperature coefficient (PTC). d) The vent, e) the cap, f) the gasket, g) the normal vent, and g) the active vent.

The gases generated in the $LiCoO_2$/graphite batteries due to the electrochemical oxidation of DFBP during the overcharge process will lead to a rapid increase of the inner pressure. Correspondingly, these gases trigger the CID in the cap to cut off the charge current and improve the battery safety characteristics. Without DFBP in the electrolyte, the batteries have no obvious overcharging characteristics in the overcharging process, and the batteries are in a dangerous charging state. Therefore, the introduction of DFBP can significantly improve the overcharge safety performance of lithium ion batteries [14-18].

Table 2. Gas composition in the $LiCoO_2$/graphite batteries with different amounts of DFBP after the overcharge

Composition	2% DFBP	0% DFBP
H_2	31.7	/
CO	18.9	29.4
CH_4	2.7	2.4
CO_2	34.1	56.9
C_2H_6	12.1	11.7

Table 2 lists the gas compositions in the $LiCoO_2$/graphite batteries with the addition of DFBP in the electrolyte after an overcharge of 160% SOC. It is interesting to find that a large amounts of the mixed gas with H_2, CO, CH_4, CO_2, and C_2H_6 could be obtained when the batteries contained DFBP additive was overcharged, they were attributed to the resultant of the polymerization reaction of the DFBP monomers. It is consistent with the polymerization mechanism of biphenyl [9,17]. CO_2 and CO were generated by the electrochemical oxidation of the electrolyte on the cathode side. Meanwhile, CH_4 and C_2H_6 formation can be attributed to the solvent reduction on the anode side [18]. Generally, the increase of CO_2 followed the increase of the SOC but increased markedly at the end of the overcharge. It is reasonable to deduce that the violent reaction that took place between the cathode material and electrolyte was prevented by the addition of DFBP in the electrolyte.

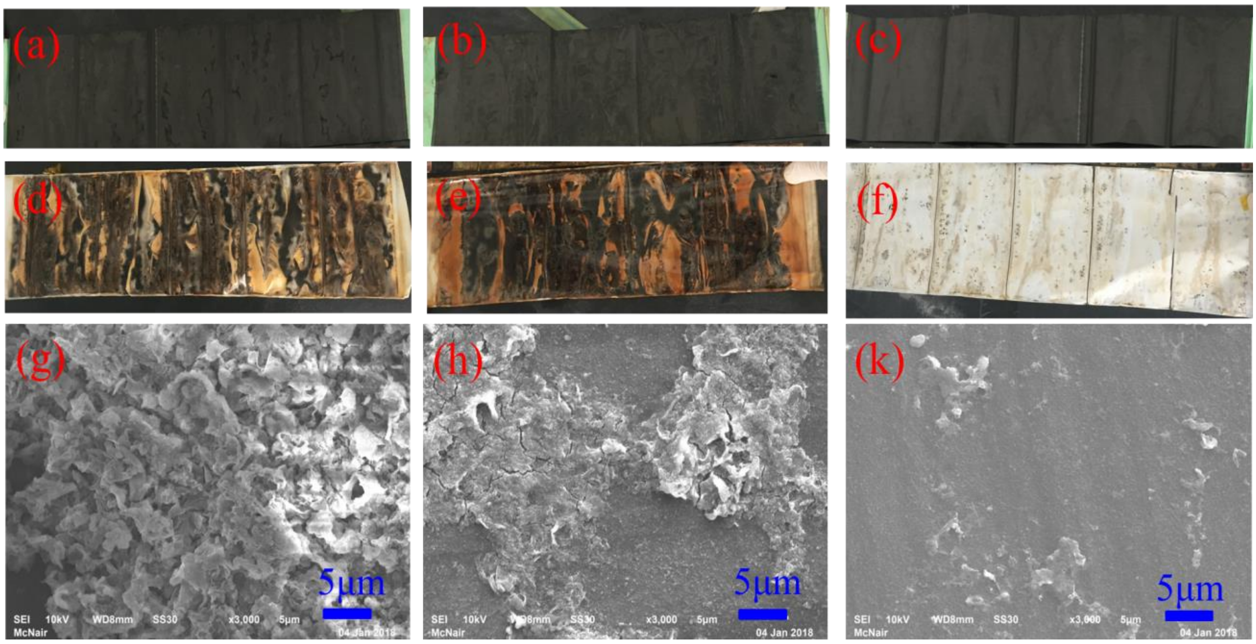

Figure 5. Digital photos of the cathode electrode after the overcharge dissembled from the $LiCoO_2$/graphite batteries containing different amounts of DFBP; the DFBP content was (a) 4 wt.%, (b) 2 wt.%, and (c) 0 wt.%. Digital photos of the separator facing the cathode after the overcharge dissembled from batteries containing different amounts of DFBP; the DFBP content was (d) 4 wt.%, (e) 2 wt.% and (f) 0 wt.%. SEM photos of the separator enlarged 3000 times for Fig. 4d~f; the DFBP amounts were (g) 4 wt.%, (h) 2 wt.% and (k) 0 wt.%.

Fig. 5a-c represents the digital photo of the cathode electrode after the overcharge to 160% SOC dissembled from the $LiCoO_2$/graphite batteries containing different amounts of DFBP. The surface of the cathode is very similar for batteries containing DFBP, which is rough, uneven, and clearly accompanied by a thin film. Fig. 5d-f shows digital photos of the separator facing the cathode dissembled from batteries containing different amounts of DFBP. It is clearly indicated that the surface of the separator without DFBP in the electrolyte is white at the stage of 160% SOC. Small amounts of by-products were also found on the separator surface. However, the separator containing the DFBP in the electrolyte was yellow and covered with a layer of black materials. These black materials appeared as a membrane was characterized by the SEM technique with an enlarged 3000 times, as shown in Fig. 5 g-k; with the help of the EDS results, it is confirmed that the black material is rich in F element, as shown in Table 3. Clearly, these depositions are ascribed to the polymerization of DFBP during the overcharge process [18].

Table 3. Elements deposited on the separator surface after the overcharge from the $LiCoO_2$/graphite batteries containing different amounts of DFBP

Element	4% DFBP	2% DFBP	0% DFBP
C	65.72	75.28	68.44
O	8.46	5.41	21.74
F	23.01	18.87	8.47
P	0.46	0.16	0.69

Remark - data is quantity percent.

These results clearly show that DFBP can polymerize and generate the mixed gases during the overcharge. The polymerization mechanism may proceed as follows: the DFBP molecules are oxidized and simultaneously release the electrons to the cathode electrode when the overcharge voltage is approached; the electro-polymerization product forms both on the cathode and the separator. The hydrogen ions move to the anode under the force of electric power, capture the electrons and then are reduced to the gases. Following the gas pressure increase inside the battery, the vent inversion cuts off the current and prevents the charging current from flowing into the batteries. Thus, the battery overcharge protection is achieved [11,12,18].

3.3 Effects of DFBP on the performances of full $LiCoO_2$/graphite batteries

As an applicable and safe additive, it is also necessary that no significant negative impact can occur on the other performances of the battery. Fig. 6a shows the electrochemical impedance spectra of the $LiCoO_2$/graphite batteries with different amounts of DFBP additive at 50% SOC. All spectra consisted of a semicircle (high-to-medium frequency range) and a straight line (low frequency range) with a slope of about 45° from the real axis. The first intersection R_s reflects the ohm impedance, as shown in Table 4, which includes the physical resistance and the transfer resistance of lithium ions in the electrolyte. The semicircle R_f can be ascribed to the transportation of Li^+ through the surface layer of the electrode, and the straight line shows the solid-state Li^+ diffusion into the active mass [15]. The semicircle impedance of the cell with DFBP is significantly increased. This powerfully supports the conclusion and puts forward above that a thick polymerized layer formed on the cathode surface, which results in an increase of the surface layer impedance and postpones the potential increase of the batteries during the overcharging stage [18].

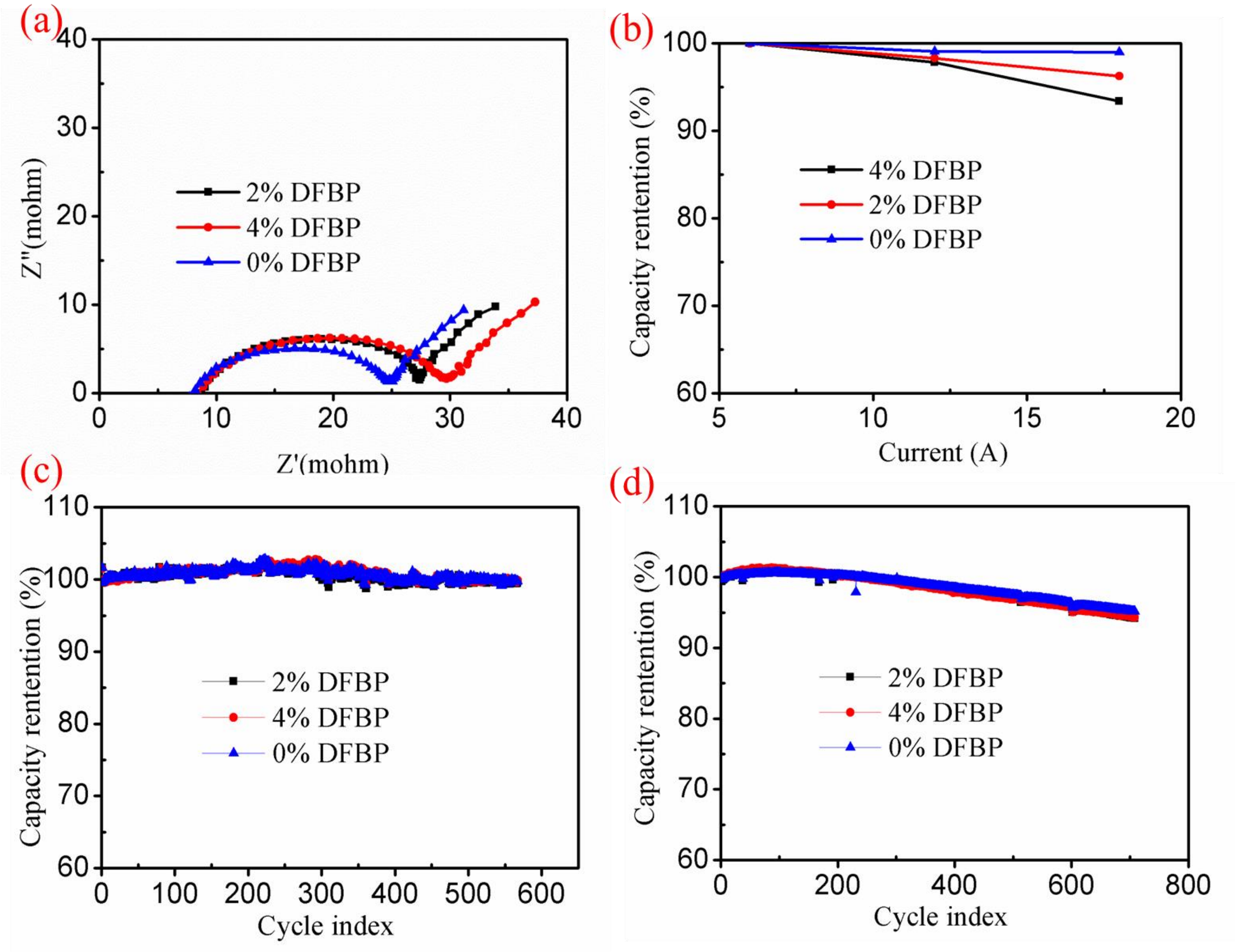

Figure 6. a) Electrochemical impedance spectra of $LiCoO_2$/graphite batteries with different amounts of DFBP at 50% SOC. b) Discharge capacity of the batteries with different amounts of DFBP at various discharge rates. c) The cycling performance of the batteries with different amounts of DFBP at a normal charge-discharge voltage interval of 3.0–4.4 V at 25 °C. d) The cycling performance of the batteries with different amounts of DFBP at a normal charge-discharge voltage interval of 3.0–4.4 V at 45 °C.

Fig. 6b shows the rate performances the full $LiCoO_2$/graphite battery with 2% DFBP, 4% DFBP, and without DFBP at various discharge rates. When the discharge rates were increased from 1 to 3 C, the discharge capacity of the full cells decreased slightly. The lowest rate performance was found for 4% DFBP. This result indicates that the ionic conductivity of the electrolyte doesn't be distinctly affected by the addition of DFBP additive, and this is also consistent with the impedance results presented in Table 4.

Table 4. Impedance data of $LiCoO_2$/graphite batteries with different amounts of DFBP at 50% SOC

Group	R_s (mohm)	R_f (mohm)
2%DFBP	8.3	19.1
4%DFBP	8.5	21.2
0%DFBP	8.0	17.1

Remark- R_s, the first intersection with the real axis on EIS spectra, R_f is width of the semicircle on EIS spectra

To investigate the effect of DFBP on the cycling performances of the $LiCoO_2$/graphite batteries, the cycling performances of the batteries with different amounts of DFBP were measured at 25 °C and 45 °C. The typical cycling performances of these batteries are shown in Fig. 6c and 6d. It can be seen that after 560 cycles at 25 °C, the discharge capacity retention of the batteries with 2%-4% DFBP remains at 99%, while the capacity retention is 95% after 700 cycles at 45 °C, showing that $LiCoO_2$/graphite batteries with DFBP additive exhibit good cycling performances and are similar to the $LiCoO_2$/graphite batteries without DFBP. This result indicates that the addition of 2% to 4% DFBP as the electrolyte additive does not affect the cycle performances of the $LiCoO_2$/graphite batteries.

Table 5. Influences of the DFBP on the storage performances of $LiCoO_2$/graphite batteries at 85 °C

Item	2%	4%	0%
Impedance offset	2.3%	3.1%	2.0%
Residual capacity offset	-4.0%	-5.8%	-3.2%

Remark- Impedance offset = Impedance value after the storage - Impedance value before the storage.

To evaluate the DFBP effect on the self-discharge of a battery, the storage performance of the fully charged $LiCoO_2$/graphite batteries with different amounts of DFBP were also tested at 85 °C for 4 h. The impedance and capacity were recorded before and after the storage, as shown in Table 5. The internal impedance offset of the battery increases slightly with increasing DFBP after the storage. The impedance offset of the battery without DFBP is 2.0%, and it increases to 3.1% for the battery with 4.0% DFBP. This outcome may be partly ascribed to the coverage of material surface by the polymerization products; this surface interferes with lithium ion migration to the electrode surface and correspondingly causes the increase of internal resistances [18]. The residual capacity offset of the battery with 2.0% DFBP was not as significant. Whereas the DFBP amounts increase, the residual capacity offset is distinctly enlarged relative to the battery without DFBP. This outcome suggests that DFBP causes the impedance increase and a small capacity loss and but that it can be mitigated by the addition optimization.

4. CONCLUSIONS

In summary, DFBP was tested as an overcharge safety additive for the protection of 4.4 V cylindrical $LiCoO_2$/graphite batteries. The experimental results indicated that DFBP electro-polymerized at approximately 4.60 V on the cathode when the batteries were overcharged and simultaneously released large amounts of gases. It was confirmed that DFBP is an effective additive for overcharge protection, which can activate the vent reversal device to cut off the charge current in an emergency. In addition, no obvious negative influence was found on the cycle performances of LIBs with DFBP electrolyte additive under normal charge–discharge conditions. Although its application in the batteries slightly increases the internal impedance and reduces the discharge capacity at the high-rate current, these negative effects can be mitigated by the addition optimization. Over all, DFBP shows great promise as an additive for the practical application in 4.4 V-class commercial LIBs.

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