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Short Communication

4-Bromoanisole (4BA) as Additive for Overcharge Protection of Lithium-Ion Batteries

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4-Bromoanisole (4BA) is recommended for $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM 622) cathode materials as a safety electrolyte additive. The effect of anti-overcharge on NCM 622 cathodes are analyzed by cyclic voltammetry, constant current charge and discharge, AC impedance and scanning electron microscopy (SEM) measurement. The overcharge test results show that 4BA can be effectively electropolymerized at 4.45 V (vs. Li/Li^+), which can consume the overcharge current and protect the working electrode from voltage runaway. The time for the voltage rising to the overcharge state is availably delayed from about 16 hours to about 37 hours. The strategy can block off further oxidation of the active material and electrolyte, and finally promote the overcharge tolerance of the Li-ion batteries. Moreover, it is also found that the use of 4BA as a safety electrolyte additive does not obviously effect the electrochemical performance of NCM 622 and can effectively improve its cycle stability at high cut-off voltage (4.7 V).

Keywords: $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$; 4-Bromoanisole; additive, overcharge, lithium-ion batteries

1. INTRODUCTION

The lithium-ion batteries (LIBs) have been widely used in portable electronic products and hybrid field with its high capacity, long service life, green environmental protection and other advantages [1-3]. The layered transition-metal oxides $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM 622) has good thermal stability, high voltage platform, high energy density, low toxicity and low cost, which is considered to be a ideal cathode material of LIBs [4,5]. However, safety issues have severely restricted the further development and application of NCM 622 [6,7]. Since the state-of-the-art electrolytes of NCM 622 use highly voltage sensitive carbonate based electrolytes, which might cause serious hazards of firing and explosion at overcharge or high-pressure conditions [8].

Two typical strategies are applied by many researchers to solve this problem. Firstly, the commercial batteries are generally protected against overcharge by providing safety valves and an overcharge protection circuit [9]. The second effective strategy is to focus on the development of overcharge protection additives or nonflammable electrolytes [10]. Thus, a number of fire-retardant additives have been investigated. Xiao [11] used biphenyl as an electrolyte additive, and found that the oxidation and electropolymerization of biphenyl in 4.50~4.75 V were happened and a conductive film was formed on the cathode surface to prevent overcharge behaviors. Wang [12] considered N-phenylmaleimide (NPM) as a new polymerizable electrolyte additive because of the fact that NPM can electrochemically polymerize at the overcharge potential and form a thin polymer film on the surface of the cathode, thus preventing voltage runaway. These studies have illustrated that electrolyte additives can provide reliable protection for Li-ion batteries in some burdensome conditions based on the previous researches, adding additives to the electrolyte can use its redox potential or electropolymerization potential to control the voltage of the battery [13]. The common overcharge protection additives include 1,3,5-trihydroxybenzene [14], 2,5-Difluoro-1,4-dimethoxybenzene [15], cyclohexyl benzene [16], and so on. In this work, 4BA was firstly used as an electrolyte additive for NCM 622 lithium ion batteries. The effect of 4BA on the electrochemical performance of NCM 622 and the anti-overcharge protection effect of 4BA were also investigated.

2. EXPERIMENTAL

2.1 Electrolyte configuration, electrode sheet preparation, batteries assembly

The electrolyte used in this work was 1 mol L^{-1} $LiPF_6$ (Aladdin reagent) dissolved in a 1:1:1 mixture (by weight) of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyle methyl carbonate (EMC) solvents. The electrolyte was prepared in a vacuum drying oven. The water and free acid (HF) contents in the electrolyte were kept below 20 and 50 ppm, respectively. The desired amount (0 wt.%, 1 wt.%, 2 wt.%, and 3 wt.%) of 4BA (Aladdin reagent) were added to 1 mol/L $LiPF_6$ standard electrolyte and labeled as B0, B1, B2, and B3, respectively. The prepared electrolyte was sealed and stored in a Ar-filled glove box for 24 hours without further purification.

The positive material that consisted of 80 wt.% of NCM 622 active material (L&F materials), 10 wt.% of conductive acetylene black and 10 wt.% of polyvinylidene fluoride (PVDF) binder were dissolved in N-methyl-2-pyrrolidone (NMP) solvent. And then, coated onto Al foil and dried at 120°C for 4 h under vacuum to obtain electrode sheet.

The CR2032 coin type cells were assembled in a Ar-filled glove box. The NCM 622 electrode sheet was used as the positive electrode, the metal lithium sheet was used as the negative electrode, and the Celgard-2400 was used as the separator. The electrolyte was a 1 mol/L $LiPF_6$ standard electrolyte (B0, B1, B2 and B3) added with different content of 4BA.

2.2 Electrochemical measurement

The cyclic voltammetry (CV) test of NCM 622 powder microelectrode were carried out using an electrochemical workstation (CHI 720B, China). CT-3008 battery test system (Shenzhen Newware Electronics, Ltd.) was used to perform constant current overcharge test and a long period overcharge test on the NCM 622/Li coin cells to examine the overcharge protection performance of the cells. The electrochemical impedance spectroscopy (EIS) of the NCM 622 cathode material before and after overcharge was measured through the electrochemical workstation (CHI 720B, China).

2.3 Morphological representation

The overcharged cells were disassembled in the argon-filled glove box. The NCM 622 electrode was washed with high purity dimethyl carbonate (DMC) three times to remove the residual electrolyte, and then was dried in a vacuum chamber at 80°C for 10 h prior to analysis. The surface morphology of the NCM 622 cathode material before and after overcharge were observed by scanning electron microscope (JSM-5600LV) with an accelerating voltage of 15 kV.

3. RESULTS AND DISCUSSION

To explore the anti-overcharge performance of 4BA, a long period overcharging experiment is conducted. The cells with and without 4BA are normally charged at a constant current of 0.2 C rate to 4.2 V, followed by overcharged at a constant current of 0.1 C rate. Fig. 1 shows a long period overcharging experiment curves for NCM 622 working electrode with or without addition of 4BA additive. As can be seen from Fig. 1, the voltage of the battery rises sharply to 5 V after 15 h in the basic electrolyte (B0). As expected, the charge curves appeared a longer voltage plateau in the range of 4.5 to 5 V after adding 4BA additive. As for B1, B2 and B3 samples, the time of charging 5 V cut-off voltage is effectively prolonged, corresponding to 39.1 h, 42.6 h and 37.2 h, respectively. This results show that 4BA additive can effectively improve the overcharge protection performance of NCM622 cathode, and the working electrode with 2 wt.% 4BA has the best *overcharge tolerance*. because the 4BA additive may trigger an oxidation reaction near the oxidation potential, which consumes the excess current caused by overcharge, so that the voltage of working electrode can be prevented from rising too fast [17].

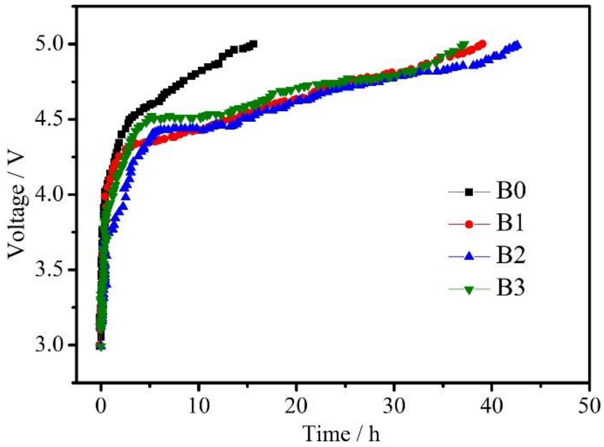

Figure 1. V-t profiles of Li/NCM 622 cells for long period overcharging state with the electrolyte 1.0 M $LiPF_6$/EC/DMC/EMC (1/1/1) with and without 4BA.

In order to evaluate the influence of 4BA on the overcharge behavior of a NCM 622 electrode, the galvanostatic charge-discharge tests are carried out on Li/NCM 622 coin cells. The coin cells were cycled at 0.2 C rate in the potential range of 3.0-4.2 V and followed charge to 5 V at the same current. Fig. 2. displays the constant current charge and discharge curves of the NCM 622 cells with various content of 4BA.

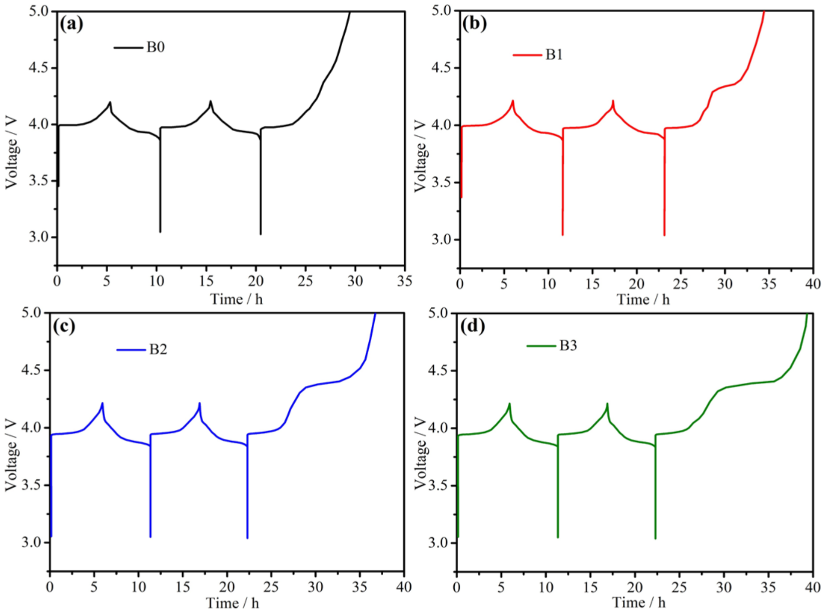

Figure 2. V-t curves of NCM 622 batteries containing electrolytes: (a) without 4BA, (b) with 1 wt.%, (c) with 2wt.%, and (d) with 3 wt.% 4BA at normal charge/discharge and overcharge operations.

As can be seen from Fig. 2, for all the samples, the V-t curves exhibit no obvious difference when they are charged and discharged between 3.0 and 4.2 V at 0.2 C, indicating that the 4BA additive does not influence the intercalation and deintercalation of Li-ions within normal working voltage (4.2 V). However, when the applied voltage is higher than the maximum voltage (4.2 V) as can be clearly seen from Fig. 2, the voltage of B0 NCM 622 cells increases rapidly at the overcharge condition. compared to the B0 sample, with the increase of the additive content, the voltage of B0, B1 and B2 half-cells slowly rises to 5 V, and the time of the overcharge resistance is effectively prolonged. Once the batteries are overcharged to rise up the charging voltage to 4.3 V, the 4BA molecules begin to polymerize at the NCM 622 cathode electrode, which forms an internal electronic wiring in the batteries and protect the charging voltage from runaway [18]. Therefore, the internal resistance of the battery is increased, and the safety of the battery is improved. [19].

The electrochemical behaviors of 4BA are studied with cyclic voltammetry (CV) on the NCM 622 powder microelectrode. The Pt microelectrode is etched out of a microcavity in an acidic solution and NCM 622 powder is filled into the microcavity to make a NCM 622 microelectrode, and the lithium electrode was used as counter electrode and reference electrode. Fig. 3 compares the CV curves of NCM 622 powder microelectrode in 1 mol·L^{-1} $LiPF_6$/EC/DMC/EMC (1:1:1) with or without addition of 4BA additive at a scan rate of 0.1 mV·s^{-1}. From the CV curve, it can be clearly seen that the B0 sample exhibts a pair of redox peaks appear in the range of 3.75-4.0 V, corresponding to the reversible Li-ions intercalation in NCM 622 sample [20]. For the B2 sample, the oxidation peak at 3.8 V is related to the extraction of Li-ions from NCM 622. When the potential is extended to more positive region, the oxidation current of 4BA is also observed at 4.45 V. At the reverse scan, no current peak can be found on the cathodic branch and also the cathodic peak current of lithium deintercalation from the NCM 622 electrode is greatly reduced. These phenomena illustrate that the 4BA additive may not affect the normal lithium insertion reactions at potentials below 4.2 V, but can polymerize at 4.45 V at the NCM 622 electrode, leading to a deactivated NCM 622 surface for lithium insertion reactions. The absence of a reduction peak for 4BA containing electrolyte is attributed to the electro-polymerized film, which blocks the insertion of Li-ions into the NCM 622 electrode [21]. In other words, the 4BA additive exhibits a higher electro-oxidation polymerization potential, and it is suitable for overcharge protection of high-potential lithium-ion batteries.

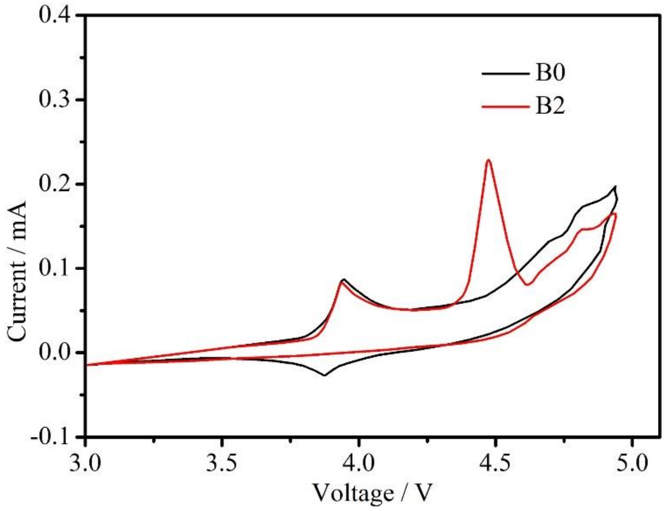

Figure 3. CV curves of NCM 622 microelectrode in 1 mol·L^{-1} $LiPF_6$/EC/DMC/EMC (1/1/1) with B0 and B2, scan rate 0.1 mV·s^{-1}.

Fig. 4 presents the electrochemical impedance spectra of the NCM 622/Li cells with and without 2wt.% 4BA additive before and after overcharged. It can be seen form in Fig.4 that all impedance curves consisted of a semicircle in the high-to-medium frequency range and a straight line in the low frequency range. Among them, Rs is the electrolyte resistance, the semicircle in the high-to-medium frequency represents the charge transfer resistance (Rct), and the oblique line in the low frequency region symbolizes the Warbrug impedance [22,23]. It can be seen from Table 1 that compared to B0 sample, there is a small increase in the electrolyte resistance Rs of B2 before overcharged, and the Rct of the two samples have no much difference. While after overcharge, the Rct of sample B2 increases sharply from 223.5 Ω to 416.7 Ω, much higher than that of sample B0 (155.8 Ω and 174.2 Ω). The sharp increase in the charge transfer resistance may be the fact that the oxidation polymerization product of the 4BA additive deposited on the surface of the pole piece to form a polymer layer, thereby hindering the charge transfer process [24]. This is consistent with the previous conclusion of the overcharge test.

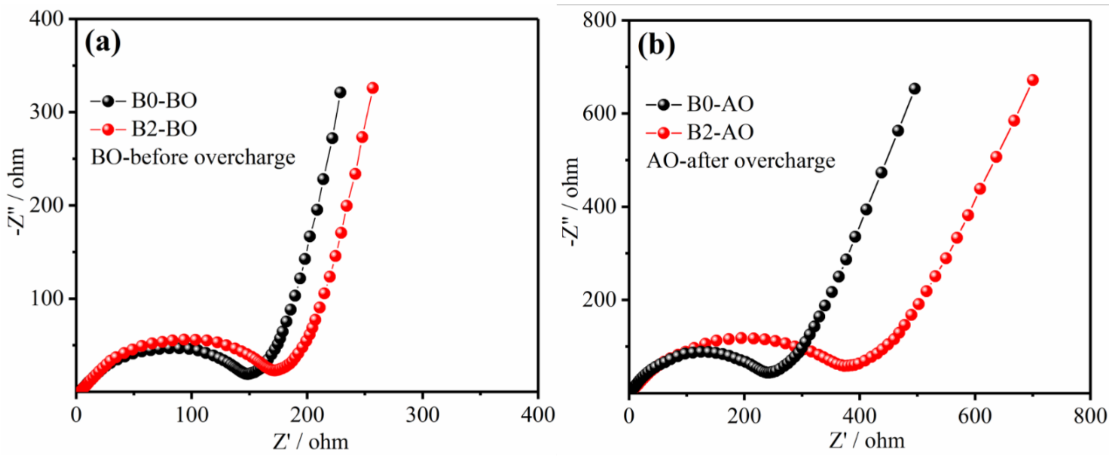

Figure 4. Electrochemical impedance spectra of Li/NCM 622 cells without and with 2 wt.% additive before and after overcharge test.

Table 1. Impedence data of Li/NCM 622 cells without and with 2 wt.% additive before and after overcharge test at equilibrium state

	B0		B2	
	Rs/ohm	Rct/ohm	Rs/ohm	Rct/ohm
Before overcharge	2.451	155.8	2.637	174.2
After overcharge	3.298	223.5	3.469	416.7

We compared the overcharge potential and cycling performance of similar materials. The relevant comparison data is shown in the Table 2. It is noted that the 4-Bromoanisole (4BA) as additive for overcharge protection of lithium-ion batteries exhibit good overcharge potential and cycling performance compared to other similar materials. It is proved that the 4-Bromoanisole is an effective additive for overcharge protection of lithium-ion batteries.

Table 2. Table 4. The comparison with the overcharge potential and cycling performance of similar materials

Sample	overcharge potential	Cycling performance
Biphenyl [11]	4.5-4.75 V	1 C, 100 cycle, 4.2 V, 90%
Dimethoxydiphenylsilane [25]	4.9 V	0.2 C, 35 cycle, 4.2 V, 83.8%
Methylbenzenes [26]	4.3-5.0V	1 C, 50 cycle, 4.2 V, 94%
N-Phenylmaleimide [12]	4.3-4.4 V	1 C, 12 cycle, 4.2 V, 97%
4-Bromoanisole (our work)	4.4-4.5 V	1 C, 100 cycle, 4.2 V, 88.2%

To further investigate the effect of 4BA additives on the cycle stability of lithium-ion batteries, the cycling performance of Li/NCM 622 cells are tested at different cut-off voltages (4.2 V and 4.7 V), and the results are shown in Figure 5. It is noted from Fig.5 (a) that the cycling performance of the Li/NCM 622 cells with 4BA additive is slightly decreased, while capacity fadingis not significant. The decrease of batteries capacity may be due to the fact that the polymerization of 4BA on the positive electrode generates a continuous increase of polymer and covers the surface of the positive electrode and the separator. As a result, the charge transfer impedance of Li/NCM 622 cells is increased, which in turn reduces the transmission efficiency of Li^+ [27]. This is consistent with the overcharge and impedance test results. Notably as can be seen from Fig. 5(b) that the cycling performance of the Li/NCM 622 cells with 4BA additive is obviously increased, and the capacity retention ratios of B0, B1, B2, and B3 after 100 cycles are 58%, 63.98%, 66.49%, and 68.50%, respectively. The result indicates that the 4BA electrolyte additive can effectively enhance the cycling performance of the NCM 622/Li cells at high cut-off voltage.

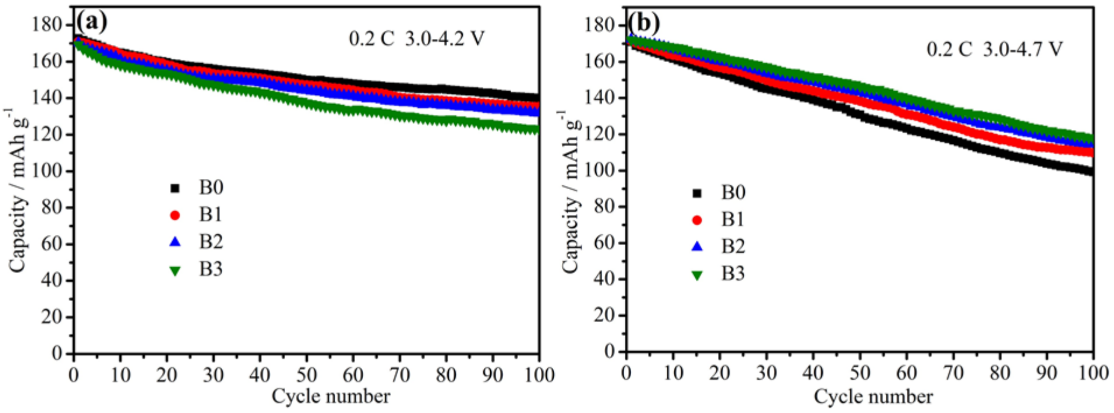

Figure 5. Effect of 4BA on cycling performance of lithium-ion batteries.

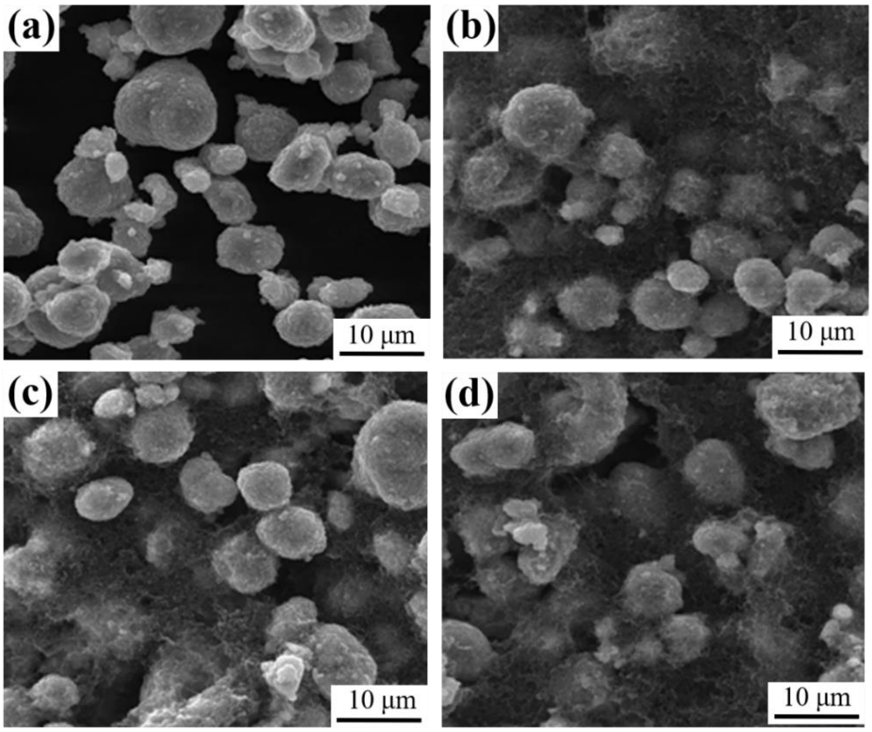

Figure 6. SEM images of the NCM 622 electrode taken from the overcharged cells containing: (a) without 4BA, (b) with 1 wt.%, (c) with 2wt.%, and (d) with 3 wt.% 4BA.

The surface morphology of the four different pristine and overcharged NCM 622 cathode was investigated by SEM. It can be clearly seen from Fig. 6(a) that the pristine NCM 622 presents a regular ball-like particles. After 100 cycles at high voltage and overcharged, the morphology of the sample B0 exhibits a marked change (Fig. 6(b)), the integrated balls are cracked into some loose particles and it is getting hard to observe the interstitial structure. However, there was little difference between cycled electrode with B1, B2, B3 and the fresh NCM622 particles (Fig. 6(c-e)). Moreover, a thin film is observed on the NCM622 cathode surface with the addition of 4BA (Fig. 4(f)), which indicates that the continuous decomposition of the electrolyte and the structural damage under high voltage is effectively restrained by 4BA additive.

4. CONCLISIONS

This work has proved that 4BA as an electrolyte additive is an effective safety additive to prevent overcharge of NCM622 electrode. This molecule can also be polymerized at 4.45 V (vs. Li/Li$^{+)}$ to form a conducting polymer, which consumes excess charging current, and resulting in a blocking effect for the oxidation of the NCM622cathode material and electrolyte. Since this electrolyte additive exhibit a negligible influence on the electrodes performance, it provided a potential application prospect as an anti-overcharge additives for other positive electrode materials.

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