

Safety properties of liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite electrodes

Yan-Bing He · Guo-Wei Ling · Zhi-Yuan Tang ·
Quan-Sheng Song · Quan-Hong Yang · Wu Chen ·
Wei Lv · Yan-Jun Su · Qiang Xu

Received: 3 March 2009 / Revised: 3 April 2009 / Accepted: 11 April 2009 / Published online: 29 April 2009
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Abstract The carbon-coated LiFePO₄ materials were synthesized, and their structure and morphology were characterized by X-ray diffraction and transmission electron microscopy. The safety and heating mechanism of the 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite electrodes under abusive conditions, such as overcharge, overdischarge, and short current were extensively investigated. It was found that the increase in the temperature of the LiFePO₄/graphite high power batteries during overcharge was attributed to the reaction of the electrolyte decomposition and the Joule heat. The batteries were heated rapidly by the irreversible heat generated from the current passing through the electrodes during short current. The temperature rise of the batteries which were overdischarged to 0 V was mainly due to the Joule heat. The overdischarge at 1 C/0 V almost did not influence the cycling performance of the batteries. The batteries did not fire, smoke, and explode under the above-mentioned abusive conditions. Therefore, the 066094-type liquid state soft film pack high power batteries with carbon-coated LiFePO₄/graphite electrodes showed excellent safety performance.

Keywords Carbon-coated LiFePO₄ · High power batteries · Safety performance · Overcharge · Short current · Overdischarge

Introduction

Lithium-ion batteries are widely used in portable electronic devices and their electrochemical performance has been improved greatly. However, the safety of batteries is still the main concern of both consumers and manufacturers in the hybrid electric vehicle applications. The concern becomes more severe when the batteries work under abusive conditions such as overcharge, overdischarge, and short current. The main reason for the firing and explosion of LiCoO₂/graphite batteries can be attributed to rapid exothermic reactions of the electrode materials with the electrolyte components under abusive conditions [1–7].

LiFePO₄ material possesses the advantages of excellent thermal stability, low cost, high reversibility of Li insertion/extraction, and no toxicity, making it a very promising cathode material for rechargeable Li-ion batteries used in large-size appliances, such as hybrid electric vehicles, electric vehicles, and power tools [8–13]. Nevertheless, the synthesis process of LiFePO₄ is usually difficult and time-consuming. LiFePO₄ is characterized by low conductivity, mainly resulted from a low lithium-ion diffusion rate and low electronic conductivity [10, 14]. These disadvantages have hindered the practical application of LiFePO₄ as a cathode material. Therefore, numerous research efforts have been focused on improving the electronic and ionic conductivity of LiFePO₄, such as using the approaches of carbon coating [10, 15–17], particle size reduction [14, 16, 18, 19], and transition metal ions doping [20–22]. The carbon coating is an effective method to improve the

Y.-B. He (✉) · G.-W. Ling · Z.-Y. Tang · Q.-S. Song ·
Q.-H. Yang · W. Lv · Q. Xu
Department of Applied Chemistry, School of Chemical
Engineering and Technology, Tianjin University,
Tianjin 300072, China
e-mail: hezuzhang_2000@163.com

W. Chen · Y.-J. Su
McNair Technology Co., Ltd,
Dongguan, Guangdong 523700, China

electronic and ionic conductivity of LiFePO_4 and the coated LiFePO_4 powders have achieved good electrochemical performance [10, 13, 17, 23].

However, so far there are few studies on safety and heating mechanism of the commercial liquid state Al–plastic film-pack high power batteries with carbon-coated LiFePO_4 /graphite electrodes under abusive conditions, such as overcharge, overdischarge, and short current. In this paper, the carbon-coated LiFePO_4 materials were synthesized. The commercial 066094-type liquid state soft pack high power batteries were assembled with carbon-coated LiFePO_4 and graphite as the respective cathode and anode materials, and the safety and heating mechanism of batteries under abusive conditions were extensively studied. The results showed that the high power batteries prepared in this work had excellent safety performance.

Experimental

The precursors of $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, and $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) were mixed stoichiometrically and the molar ratio of $\text{Li}:\text{Fe}:\text{P}:\text{C}_6\text{H}_{12}\text{O}_6$ is 1:1:1:0.15. The precursors were ground for 8 h by wet ball-milling in an acetone solution. The resulting stable gel was dried at 60°C under vacuum to form a mixed dry precursor, and then it was thoroughly reground. The as-prepared precursor powders were calcined at 350°C for 5 h, then thoroughly reground, and then heated to a temperature of 600°C and kept for 12 h in argon atmosphere. Finally, the samples were cooled to room temperature and reground for 8 h by ball-milling to obtain the carbon-coated LiFePO_4 products [15, 24].

X-ray diffraction (XRD) patterns of the samples were obtained by a PANalytical X'Pert powder diffractometer using $\text{Co K}\alpha$ radiation in an angular range of $10\text{--}90^\circ$ (2θ) with a 0.02° (2θ) step. The structural parameters were calculated by using the MDI Jade 5.0 profile matching refinement method for the XRD diagrams. The morphology observation of the LiFePO_4 samples was conducted by using a transmission electron microscope (TEM, Tecnai G² F20, FEI) operating at 200 kV.

Commercial 066094-type liquid state soft pack lithium-ion batteries, which are nominally 6 mm thick, 60 mm wide, and 94 mm long, were assembled to investigate the safety performance of LiFePO_4 /graphite high power batteries. The nominal capacity of the batteries was designed to be 2,000 mAh. The batteries used the prepared carbon-coated LiFePO_4 as the cathode, graphite as the anode, and polyethylene as a separator. The cathode consisted of 83.5 wt.% carbon-coated LiFePO_4 , 10 wt.% conductive carbon (6 wt.% Super-P + 4 wt.% conductive carbon black), and 6.5 wt.% poly(vinylidene fluoride). The

graphite anode consisted of 90 wt.% composite graphite, 5 wt.% Super-P, 3 wt.% styrene-butadiene rubber, and 2 wt.% carboxymethyl cellulose. LiPF_6 , 1 M, in a 1:1:1 mixture of ethylene carbonate, dimethyl carbonate, and ethylene methyl carbonate (1 M $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{EMC}$) was used as the electrolyte. The anode, cathode, and separator were rolled together to form the battery core and then the core was set into a 066094-type Al–plastic film box used as soft pack. The electrolyte was thereafter injected and the batteries were sealed with a sealing machine.

The formation and rate-discharge tests of batteries were performed by using the BS-9300 and BS-9366 lithium-ion battery testers. After the formation, all batteries were charged and discharged three times between 2.0 and 4.0 V at 1,000 mA (0.5 C) to stabilize the performance of batteries. The rate-discharge performance of batteries was examined between 2.0 and 4.0 V at room temperature. The safety tests of batteries included overcharge, overdischarge, and short current. The overcharge tests were conducted by further charging the batteries with a constant current of 2 A (1 C) using a 10 V power supply (1 C/10 V) after they were fully charged to 4.0 V. The short current tests were conducted by connecting the cathode tab with the anode tab using a low resistance lead ($<5\text{ m}\Omega$) after the batteries were fully charged to 4.0 V. A multimeter was also connected to the cathode and anode tab to measure the voltage of batteries in the short circuit experiment. The overdischarge test of batteries was conducted by discharging the fully charged batteries to 0 V with a current of 1 C (1 C/0 V). A type-K thermal couple was attached to the center of the largest face of batteries to record the temperature change during the safety tests. The electrochemical impedance spectra (EIS) of batteries before and after the overcharge and overdischarge testing were measured by using LiFePO_4 cathodes as the working electrode and graphite anodes as both the reference and counter electrodes.

Results and discussion

Figure 1 shows the XRD patterns of the synthesized LiFePO_4 powder. All the peaks are indexed as an orthorhombic olivine-type structure with a space group of $Pnma$. Through the MDI Jade 5.0 profile software calculation, the lattice constants for the orthorhombic cell are $a=10.320$, $b=6.004$, and $c=4.691\text{ \AA}$. These values are consistent with those reported in the literature [19, 24, 25].

Figure 2 shows TEM images of the LiFePO_4 samples. From the low-resolution TEM image (Fig. 2a), thin-layer coatings can be identified on the LiFePO_4 particles. The high resolution TEM image (Fig. 2b) shows that layered carbons with interlayer spacing of around 0.4 nm and a

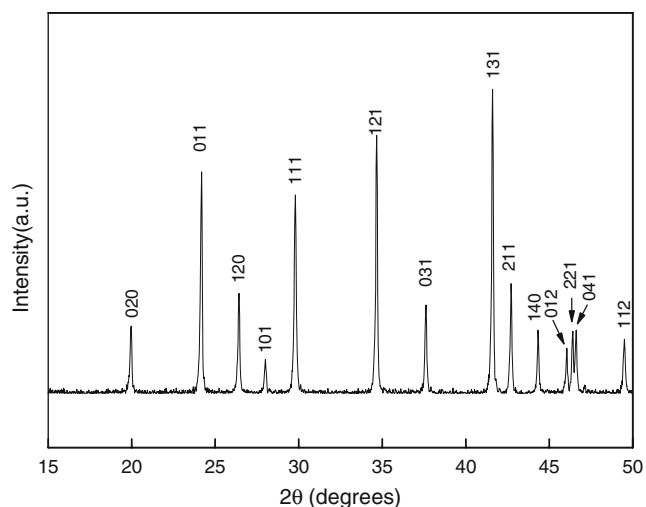


Fig. 1 XRD patterns of as-prepared carbon-coated LiFePO_4 powder

thickness of ~ 3 nm are uniformly coated on the well-crystallized LiFePO_4 particles, which are responsible for good electronic conductivity of the composite material.

Figure 3 shows the rate-discharge performance of high power batteries. The specific capacity of high power batteries at discharge rates of 1, 3, 5, 8, 10, and 15 C is 125.2, 120.7, 118.2, 115.8, 114.8, and 109.2 mAh g^{-1} , respectively. The capacity retention at rates of 5, 8, 10, and 15 C is respective 94.4%, 92.4%, 91.7%, and 87.2% of that at the rate of 1 C. These results show that the high power batteries can deliver most of their capacity at a discharge rate as high as 15 C, indicating very good kinetic characteristics. This may be attributed to the improved interface connection of LiFePO_4 active particles by carbon [10, 16], suggesting that the carbon coating can markedly improve the apparent diffusion coefficients of lithium ions and the kinetics of lithium intercalation and deintercalation [23, 26].

Figure 4 shows the voltage, temperature, and current profiles of high power batteries for 1 C/10 V overcharge test. During the testing, the batteries did not fire, smoke, and explode, indicating good overcharging safety performance. When a battery is overcharged, the main reactions may include the reaction of electrolyte decomposition, the exothermic reaction between the delithiated cathode and the electrolyte, and the violent reaction between the overcharged anode and the electrolyte at high temperature [2–4]. It is well known that the LiFePO_4 phase changes into the FePO_4 phase during the charge course. The FePO_4 phase almost does not react with the electrolyte below 200°C and the heat from the reaction above 200°C is also smaller than that for the fully charged LiCoO_2 [8, 9]. The violent exothermic reaction between the lithiated anode and the electrolyte occurs above 240°C , which is activated by the rapid exothermic reaction between the delithiated

cathode and the electrolyte [3, 27, 28]. Figure 4 shows that the battery temperature during the overcharging testing never reaches 240°C , so the violent exothermic reaction between the lithiated anode and the electrolyte almost does not occur.

Figure 5 shows the EIS of high power batteries before and after overcharged to 4.8 V. It can be seen that the total resistance (R_{cell}), which is composed of the bulk resistance (R_b), solid-state interface resistance (R_{sci}), and charge transfer resistance (R_{ct}), increases greatly after overcharge. The batteries generate much Joule heat ($Q = i^2 R_{\text{cell}} t$) during overcharge, where Q represents the heat generated, i is discharge current, R_{cell} is the total cell resistance, and t is time. A great part of electrical energy from the constant current overcharge is converted into Joule heat in the form

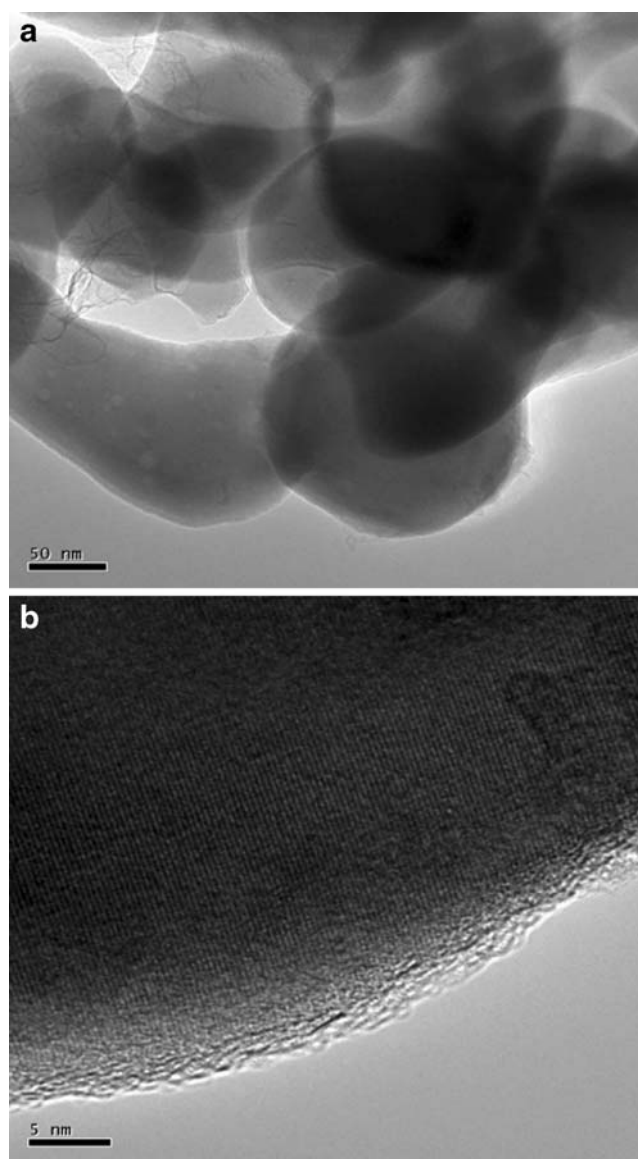


Fig. 2 TEM images of LiFePO_4 samples: **a** low-resolution and **b** high resolution

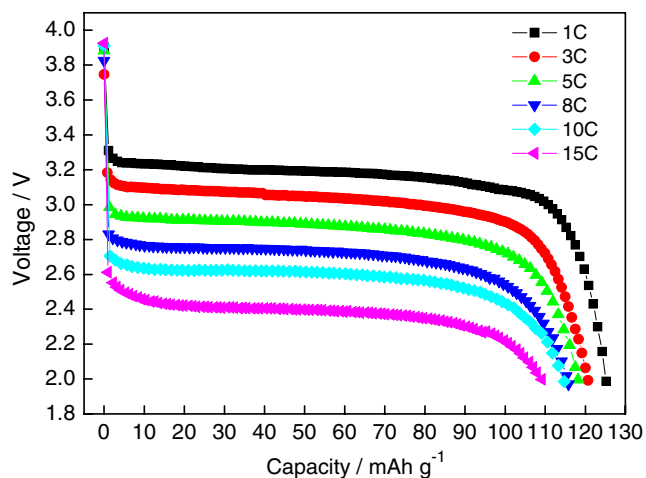


Fig. 3 Rate-discharge performance of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite

of $i^2R_{\text{cell}}t$. So the increase in the temperature of LiFePO₄/graphite high power batteries during the overcharge testing results from the reaction of electrolyte decomposition and the Joule heat generated.

It can be seen from Fig. 4 that the battery voltage increases greatly from 4.0 to 4.9 V after the batteries are overcharged for 2 min. This characteristic is obviously different from that of the LiCoO₂/graphite batteries, which need about 40 min when the battery voltage reaches 4.9 V during the 1 C rate overcharge [2–4]. The reason might be that the de-lithiation becomes very difficult and the electrochemical reaction resistance increases obviously due to a low lithium ion concentration of the fully charged LiFePO₄ (see Fig. 5). Thus, the polarization of electrochemical reactions increases greatly for the fully charged LiFePO₄, which leads to the great increase in the battery voltage. At this stage, the battery temperature also increases due to the heat generated by $i^2R_{\text{cell}}t$.

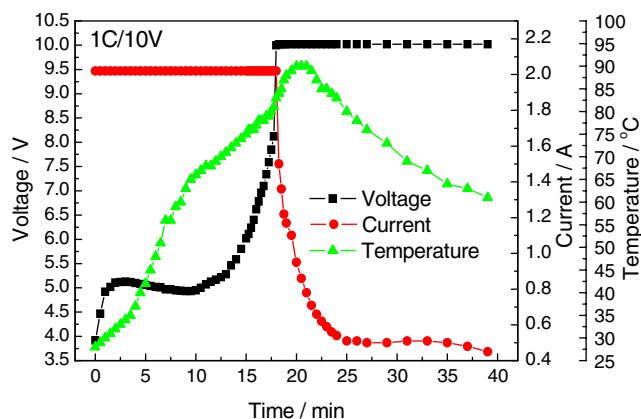


Fig. 4 Voltage, temperature, and current profiles for the 1 C/10 V overcharge test of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite

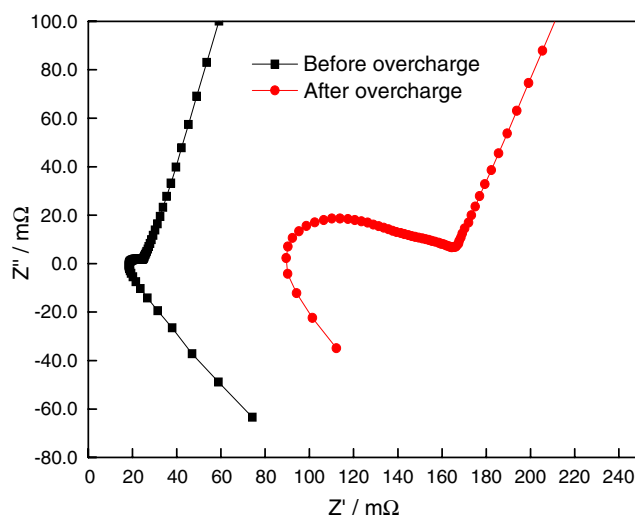


Fig. 5 EIS of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite before (square) and after (circle) overcharged to 4.8 V

The battery temperature goes up gradually when the battery voltage reaches 4.9 V. It also can be observed from Fig. 4 that the voltage shows some complicated changes from 4.9 to 5.5 V, where it increases slowly from 4.90 to 5.15 V and subsequently shows a short plateau for about 1 min, then decreases gradually to 4.93 V, and then increases slowly to 5.5 V. When the battery voltage and temperature reach some values, the electrolyte will be decomposed. The electrolyte decomposition consumes overcharge current. When the battery voltage reaches 5.15 V, the amount of the charge consumed by the electrolyte decomposition is equal to that supplied by the overcharge. So the voltage of the overcharged battery shows a short plateau at the overcharging time of 2.5–3.5 min. The electrolyte decomposition rate will increase along with the rise of the battery temperature. When the charge consumption exceeds the charge supply from overcharge, the charge shortage will be supplied by the inner discharge of the battery. Therefore, the battery voltage decreases to some degree. The electrolyte decomposition gradually decreases the quantity of the electrolyte. The amount of the charge consumed by the electrolyte decomposition is less than that supplied by the overcharge, which leads to the rise of the battery voltage again.

It also can be found from Fig. 4 that the charge current decreases greatly when the battery voltage reaches 10 V. The battery temperature reaches the maximum value of 90°C when the charge current decreases to 0.86 mA. From then on, the heat generated from the reaction and Joule heat is less than that dissipated into environment. Thus, the battery temperature decreases gradually.

Figure 6 shows the voltage and temperature profiles of high power batteries for the short current testing that is

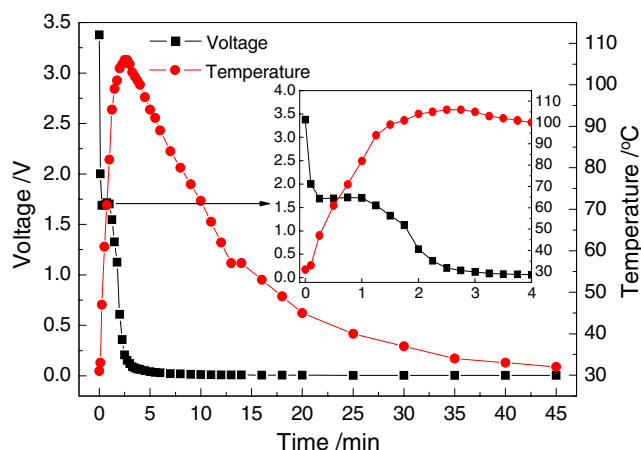


Fig. 6 Voltage and temperature profiles for the short current test of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite

similar to the huge current discharge testing. The batteries did not fire, smoke, and explode during the testing. It can be seen that the voltage decreases to about 1.6 V and subsequently shows a short plateau, and then gradually decreases to 0 V. The battery temperature rises greatly with the maximum value of about 105°C. In the short circuit testing, the battery can be heated much rapidly by the irreversible heat generated from the current passing through the electrodes. This rapid heating process produces a steep temperature profile with the highest temperature at the core. The LiFePO₄ phase is thermally stable in the electrolyte, so the positive decomposition reaction cannot be activated. However, the other exothermic reactions such as the solvent reactions proceed significantly.

Figure 7 shows the voltage and temperature profiles of high power batteries for the 1 C/0 V overdischarge testing.

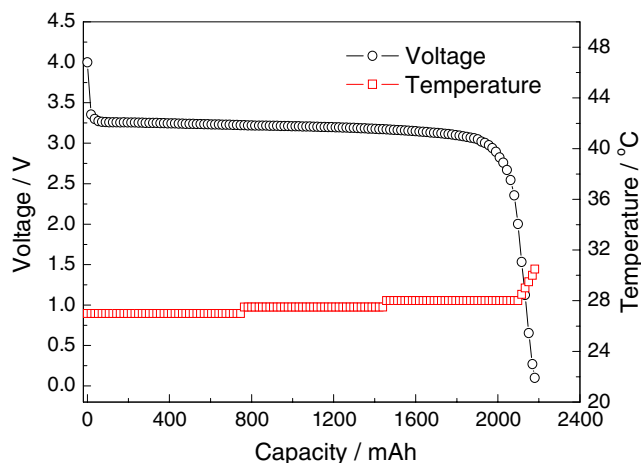


Fig. 7 Voltage and temperature profiles for the 1 C/0 V overdischarge test of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite

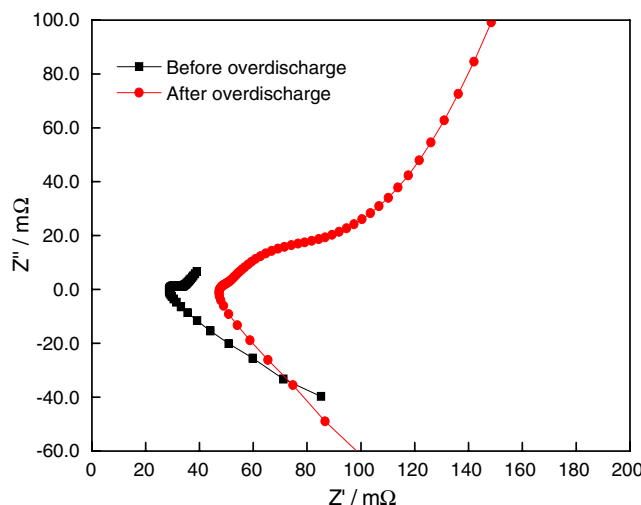


Fig. 8 EIS of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite before (square) and after (circle) overdischarge

In this stage, no distinct temperature increase is observed and nothing dangerous occurs, because almost all the lithium ions in the carbon anode have disappeared in the stage of the standard full discharge. Figure 8 shows the EIS of the high power batteries before and after overdischarged. It can be seen that the R_{cell} increases greatly after overdischarged. So the batteries also generate Joule heat ($Q = i^2 R_{cell} t$) during the overdischarge, which leads to the temperature rise.

Figure 9 presents the cycling performance of high power batteries after overdischarged at 1 C/0 V. It can be seen that the overdischarged batteries also show excellent cycling performance, suggesting that the overdischarge almost does not influence the battery performance.

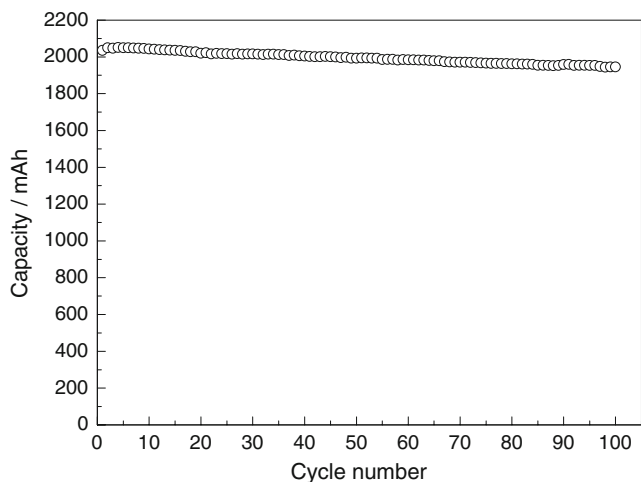


Fig. 9 Cycling performance of 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite after the 1 C/0 V overdischarge

Conclusions

The commercial 066094-type liquid state soft pack high power batteries with carbon-coated LiFePO₄/graphite electrodes were prepared and their safety and heating mechanism under abusive conditions, such as overcharge, overdischarge, and short current was extensively studied. It was found that the increase in the temperature of the LiFePO₄/graphite high power batteries during the overcharge resulted from the reaction of electrolyte decomposition and the Joule heat. During the short current, the battery voltage firstly showed a short plateau at about 1.6 V, and then gradually decreased to 0 V. The batteries were heated rapidly by the irreversible heat generated from the current passing through the electrodes. The temperature rise of the batteries, which were overdischarged to 0 V, was mainly due to the Joule heat. The power batteries could pass the abusive tests without firing, smoking, and explosion. The overdischarge at 1 C/0 V almost did not influence the cycling performance of the batteries. Thus, the high power batteries prepared in this work showed excellent safety performance.

Acknowledgement This work was supported by the public bidding program of Guangdong and Hong Kong (special program of Dongguan: 200716841).

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