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ORIGINAL PAPER

Screening defective lithium ion batteries of 0 V open-circuit voltage by a high current charge process in combination with in situ infrared thermal imaging technology

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Abstract How to screen defective lithium ion batteries is of great importance to the producers and consumers, which has been a challenging problem, since some lithium ion batteries will not present evident different electrochemical behaviors at the initial use stage. Here, we found that defective lithium ion batteries of zero open-voltage could be differentiated from the good ones by charging at 1,800 mA (corresponding to 3 C) in combination with in situ infrared thermal imaging technology. During the charge process, the surface temperatures of the defective lithium ion batteries of zero open-voltage showed at least 10 °C higher than that of the good one. Results of the charge voltage, charge current, temperature rise, and the analysis of the cathode strip, separator, and anode strip after full-discharge process showed that this method was effective.

Keywords Lithium ion batteries · Zero open-voltage · Charge · Defective · Infrared thermal imaging · Screening

Introduction

Because of the high output voltage, high energy density and power density, low self-discharge and long cycle life [1], lithium ion batteries have been widely studied and now have been extensively applied in a lot of industrial areas, such as mobile phones, personal computers, video cameras, electric vehicles, and electric bikes [1–3]. The structures of lithium ion batteries are similar to other rechargeable batteries, which consist of cathodes, anodes, separators, electrolytes, etc. In most commercial lithium ion batteries, the main cathode material is $LiCoO_2$ [4], while graphitic carbon remains the predominant anode material [5, 6].

It is widely acknowledged that lithium ion batteries contribute some benefit to our modern life, while it brings much potential safety problems at the same time if they are not properly used or manufactured. The main reason is that most lithium ion batteries use organic electrolytes, which are combustible [7, 8]. For example, fire and/or explosion happened even in the case of small lithium ion batteries in mobile phones. The safety of lithium ion battery is an important factor which will affect development of the battery industry since some defective lithium ion batteries will not present different electrochemical behavior during the initial use stage [5, 9]. This is also one main concern for electric vehicles which would use lithium ion batteries as their power sources. Several papers have dealt with the safety of lithium ion batteries by constructing many types of thermal models to analyze the thermal behaviors of the batteries. Most of the models simulated the temperature profile of a battery under different working conditions and tried to express the connections between the surface temperature and the electrochemical behavior of the battery [10–16]. However, there are very rare reports on how to screen poor quality or defective lithium ion batteries from good ones by directly thermal measurement.

Infrared thermal imaging technique is a non-contact surface temperature measuring method which is economic, quick, and can detect the quick temperature variation of the targets. The theory of this technique is based on that all objects at different temperature above absolute zero Kelvin

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can emit different radiation, and infrared thermography is sensitive to that radiation. Consequently, the temperature can be recorded by marking the emitted radiation. The infrared thermography was originally developed for military uses, such as night viewing meter, and in recent years, it has been widely applied to some civil applications. Recently, this technique was used to identify any defects that may be occurring while laying the active cathode material on the aluminum substrate during the manufacturing process [17].

In this paper, we proposed for the first time the use of infrared thermal imaging technique to examine the temperature differences between the good and the defective lithium ion batteries during rapid charge process, so that we can provide a rapid screening method to find the defective batteries especially of micro-short circuit.

Experimental

Prismatic lithium ion batteries of 600 mAh, consisting of graphitic anode, $LiCoO_2$ cathode, separator of Celgard 2400, and liquid electrolyte (1 M $LiPF_6$ solution in EC/DEC/DMC (volume ration 1:1:1)) were home manufactured by the normal manmade technique, and rectangular aluminum boxes were used as the cases. The batteries could be used in mobile phones. After formation and sealing, all lithium ion batteries qualified in terms of capacity (≥600 mAh) and resistance (≤45 mΩ) were taken out. After aging for 1 week, all the batteries were tested again and found that almost all the lithium ion batteries exhibited a voltage of about 3.8 V except a small portion (about 0.02%) presented zero open-voltage. We took three lithium ion batteries with zero open-voltage (marked as (B), (C), and (D)) and one good battery (marked as (A)) with 3.8 V for further testing. Their charge curves as well as the surface temperature changes of the lithium ion batteries during rapid charge process were recorded. Charge and discharge processes were performed using battery instrument PCBT-138-32D, Wuhan LISUN Power Sources Co., Ltd. and the parameters of the batteries including current, voltage, and capacity were recorded every 10 s. During the charge process, the surface temperatures of the batteries were measured by Thermal Imaging Camera DL-700 C^+, Zhejiang Dali Technology Co., Ltd. The infrared thermography system mainly consists of a camera and a controller inside the system. In the camera, there is an infrared detector that absorbs the reflected infrared radiation and in the controller, the recorded information will be converted to temperature signals. The camera has a resolution of 384× 288 pixels and the precision of the measured temperature could reach 0.1 °C. The temperature changes of the four batteries were detected and recorded, and the temperature data were fixed to record also every 10 s. The whole instrument was shown in Fig. 1.

After the rapid charge process, all the lithium ion batteries were fully discharged to 2.5 V and were disassembled. The cathode strips, anode strips, as well as the separators were extracted and unrolled, in order to discern the internal differences. The photos were captured by a normal digital camera (FMC of Cannon).

Results and discussion

Charge curves

As mentioned in the “Experimental” section, before aging, the selected lithium ion batteries were qualified in terms of capacity and internal resistance. However, after aging, (B), (C), and (D) exhibited 0 V while the normal one exhibited 3.8 V. Basically speaking, (B), (C), and (D) are defective batteries and should not come into the market.

Firstly, we modulated the charge current at 120 mA (corresponding to 0.2 C) and tested the thermal behaviors of the four batteries (A), (B), (C), and (D). No evident differences among them, including the temperature changes and the initial cycling behaviors, were found. This indicated that it was not easy to differentiate defective lithium ion batteries from the good ones according to the temperature rises only under the above experimental conditions. Consequently, considering that there may show different phenomena in rapid charge process, the charge current was changed to 3 C (that is 1,800 mA), and the charge process was continued for 10 min.

During 3 C rapid charge process, the charge curves were recorded, which were shown in Fig. 2. The curve of the good lithium ion battery (A) was very smooth. Within the beginning 60 s, the voltage increased quickly to 4.6 V, and then the increase was slowed down, and slowly reached the max voltage of 4.74 V at the end of charge process. In the case of the three defective lithium ion batteries (B), (C), and (D), there were distinct differences under this occasion. In the case of (B), the charge voltage increased at first, then fluctuated and finally dropped. The highest voltage arrived at about 5.4 V. In the case of (C), the charge voltage increased also at first and then fluctuated more evidently. The highest voltage reached to 5.7 V. As to (D), the voltage was kept at about 1.4 V for 440 s, and then increased to 6.0 V suddenly.

During the charge process, all the other three batteries except (D) showed a charge current of 1,800 mA, while the charge current of battery (D) decreased suddenly to 6 mA after the sharp increase of voltage at 440 s. This different behavior indicated that the defective lithium ion batteries were from different reasons. As to the detailed reasons for

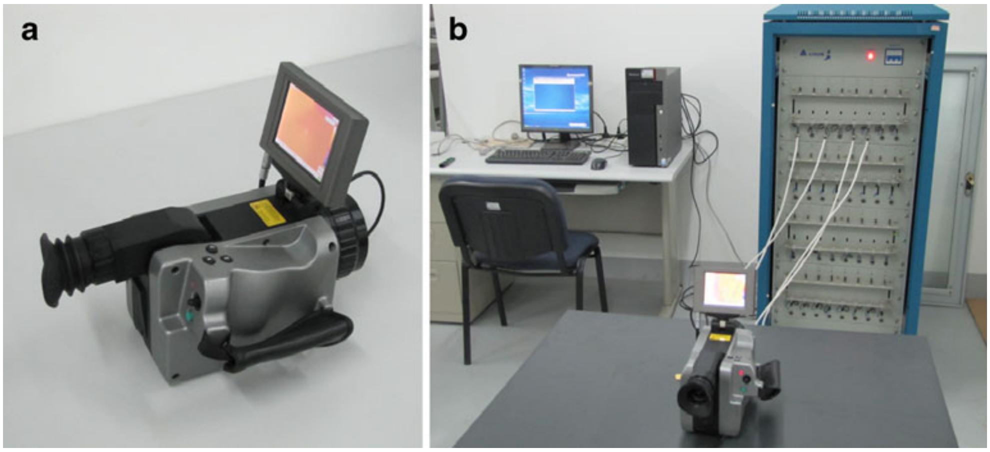


Fig. 1 **a** Thermal Imaging Camera DL-700 C$^+$, and together with **b** battery test instrument PCBT-138-32D to test the in situ surface temperature change of lithium ion batteries during charge process

the lithium ion batteries of zero open-voltage after aging, it is beyond the scope of this paper, and it will be treated separately.

Temperature rise curves

The surface temperature changes of the lithium ion batteries during the rapid charge process at 1,800 mA were shown in Fig. 3. All surface temperatures of the lithium ion batteries presented the increase tendency at first. However, the temperature rise rate was different. The three defective lithium ion batteries presented much higher surface temperatures and faster temperature rise rates.

The changing directions of temperature rise curves of the batteries (A), (B), and (C) were similar. While for battery (D), the temperature came to race up and met the top during the first 440 s and then began to decline. Compared with the charge curve of battery (D), the times when the two curves reached their peaks were almost the same, indicating when charge process ended, temperature rise process ended.

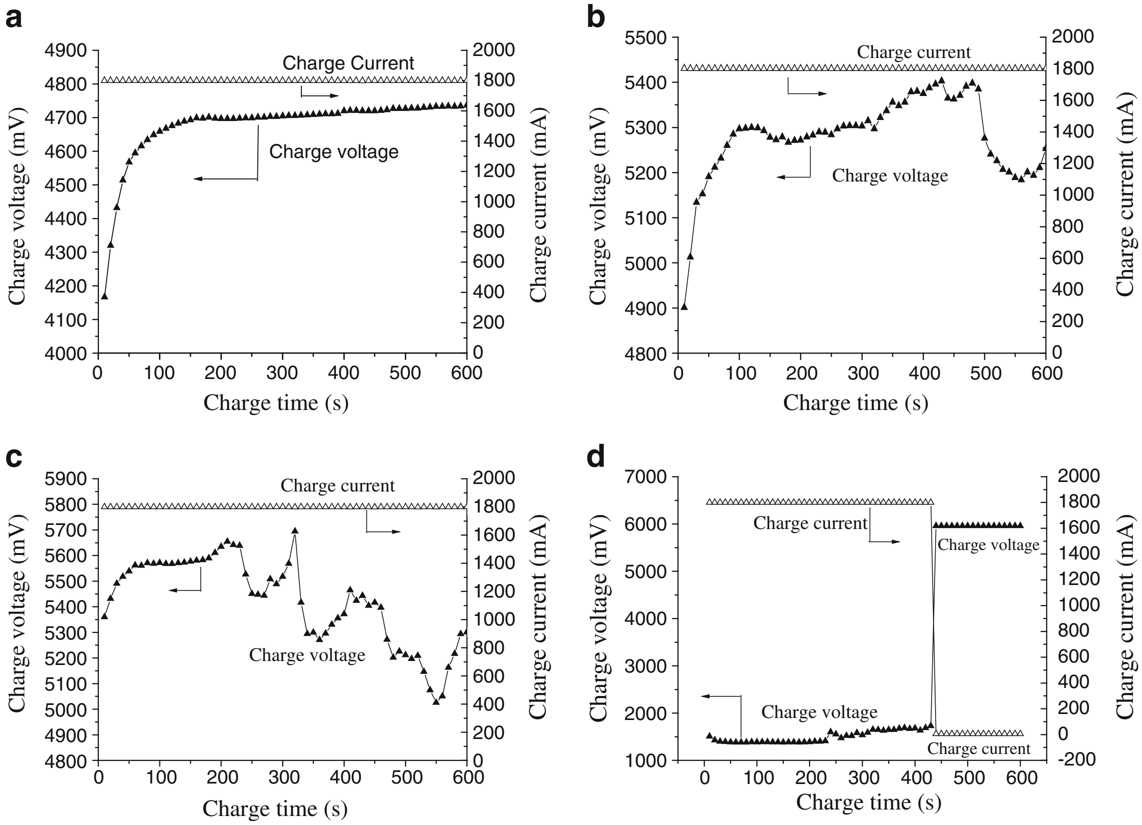


Fig. 2 Charge curves of the lithium ion batteries at the charge current of 1,800 mA (corresponding to 3 C). **a** Good lithium ion battery (A), **b**–**d** defective lithium ion batteries with zero open-voltage after aging, marked as (B), (C), and (D), respectively

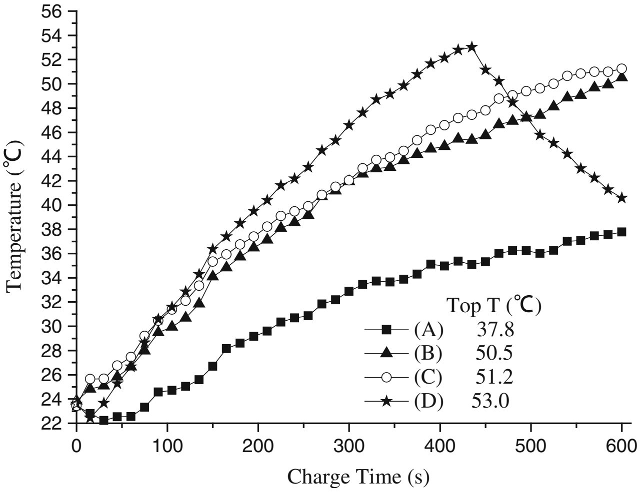


Fig. 3 Changes of the surface temperatures of the good (*A*) and the defective lithium ion batteries (*B*), (*C*), and (*D*) during over-charge process

The top temperatures of the four batteries were also different. For (A), (B), (C), and (D), the top temperatures were 37.8, 50.5, 51.2, and 53.0 °C, respectively. The top temperatures of (B), (C), and (D) were higher than that of (A), and the differences were all above 10 °C.

Internal structures

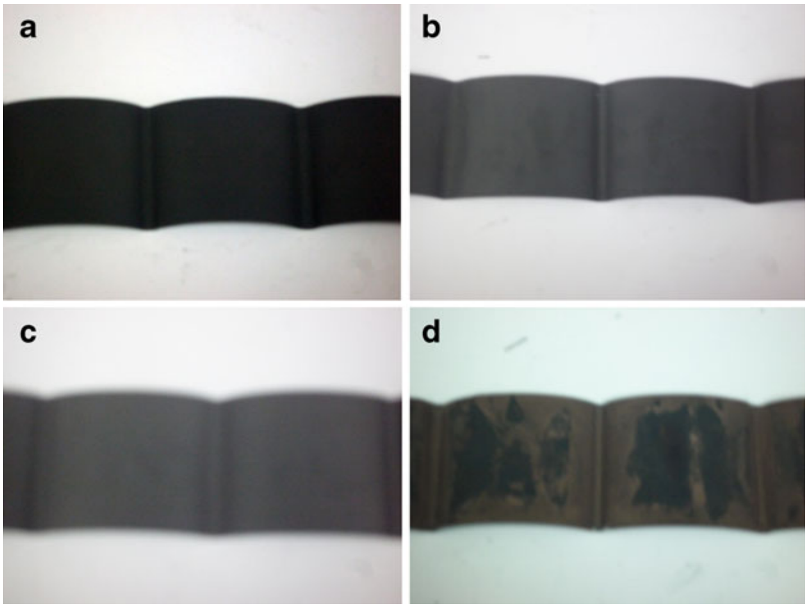
In order to look into the changes of the internal structures of the lithium ion batteries, they were dissembled after full discharge process. Figures 4, 5, and 6 showed the pictures of the cathode strips, separators, and the anode strips, respectively.

For the good lithium ion battery (A), the pictures of the cathode strip (Fig. 4a), separator (Fig. 5a), and anode strip (Fig. 6a) all showed uniform surfaces with uniform texture, and without obvious shadows or spots. For the defective lithium ion batteries of (B) and (C), the forms of the cathode strips (Fig. 4b, c) were similar to the good one. However, some spots were clearly identified in the pictures of the separators (Fig. 5b, c) and the anode strips (Fig. 6b, c), indicating that there may be some defects occurred in those uneven areas, which would induce inside micro-short circuits. For defective battery (D), there were distinct shadows not only on the anode strip (Fig. 6d) but also on the cathode strip (Fig. 4d). Moreover, there was some peeling off from the cathode and anode strips. As to the anode strip, it was more evident. The separator of (D) got on small fire when extracted from the battery system, as presented some burned holes in Fig. 5d. We carefully checked the separator and found that it was very uneven, in some places even tiny holes could be seen, indicating that the separator was pierced.

Result analysis of the experiments

There are several reasons for the defective lithium ion battery presented zero open-voltage after aging: (1) during the manufacturing process of the separator, there are some micro-voids; (2) some particles (from the ambient condition or ultrasonic welding) remained on the surface of the cathode strip; (3) some particles (from the ambient condition or ultrasonic welding) remained on the surface of the anode strip; (4) there are some blurs from the cutting process of the cathode strip; (5) there are some blurs from the cutting process of the anode strips; (6) during the rolling

Fig. 4 Cathode strips of the lithium ion batteries after the charge process at 1,800 mA and the following full discharge process. The width of each strip was 4.2 mm. **a** Good lithium ion battery (A), **b**–**d** defective lithium ion batteries with zero open-voltage after aging, marked as (B), (C), and (D), respectively



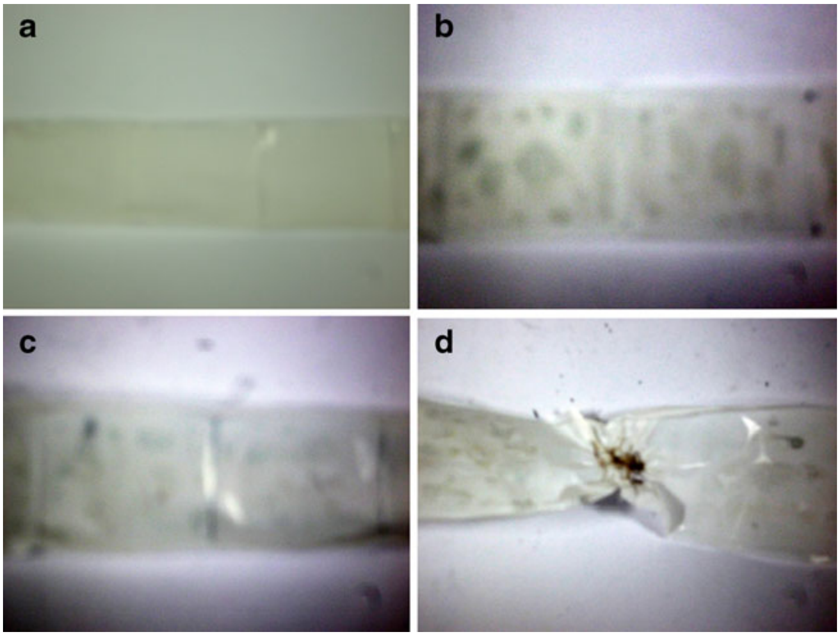


Fig. 5 Separator strips of the lithium ion batteries after the charge process at 1,800 mA and the following full discharge process. The width of each strip is 4.4 mm. **a** Good lithium ion battery (A), **b**–**d** defective lithium ion batteries with zero open-voltage after aging, marked as (B), (C), and (D), respectively

process, the hands of the workers touch the separator very heavily and very small slims are left; (7) the capacity or weight ratio for the cathode (over-capacity) and anode (less-capacity) are much uneven due to the errors from the coating process; and the like. All of them can lead to internal micro-short circuit or short circuit [1]. These kinds of short circuit will not present evident bad effects during initial use. However, after long cycling, for example 50 or 100 cycles, these bad effects will appear or accumulate slowly, and possible fire or even explosion will happen. This is the reason why there is no accident report on fresh lithium ion batteries.

In our experiments, defective lithium ion batteries (B) and (C) were mainly from micro-short circuit. As a result, their voltages fluctuated during rapid charge at 1,800 mA and the temperature increased much faster than that of the good lithium ion battery (A). Of course, the micro-short circuit of (C) would be more serious than that of (B), due to more evident fluctuation of the voltage and a little higher of the top temperature. In the case of battery (D), the micro-short circuit was much more serious, and later the micro-short circuit developed into evident short circuit. The evident short circuit caused the breaking-off of the battery, consequently, resulting in the sharp decrease of the current

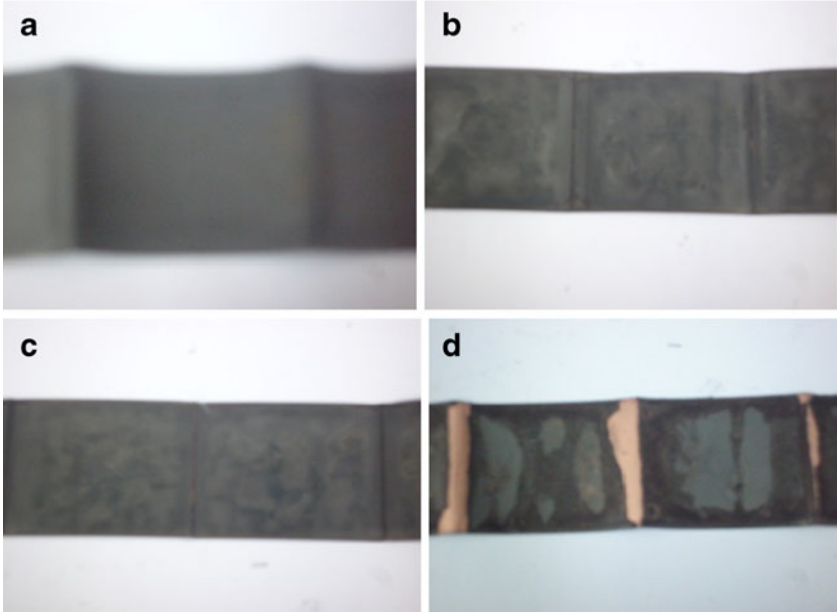


Fig. 6 Anode strips of the lithium ion batteries after the charge process at 1,800 mA and the following full discharge process. The width of each strip is 4.3 mm. **a** Good lithium ion battery (A), **b**–**d** defective lithium ion batteries with zero open-voltage after aging, marked as (B), (C), and (D), respectively

and the sharp increase of the voltage, and the charge current decreased rapidly from 1,800 to 6 mA, the voltage increased suddenly from 1.4 to 6.0 V, and the surface temperature declined at 440 s.

Same results were obtained when we repeated the whole experiments several times with several batches of zero open-voltage lithium ion batteries and good ones, indicating that the results mentioned above were not contingent. The voltages of the defective batteries could all reach the maximum voltage of 5.0 V or more, and some even close to 6.0 V at the over-charge current of 1,800 mA (corresponding to 3 C), while the maximum voltages of the good lithium ion batteries were located at about 4.7 V. It is known that when the voltage of a lithium ion battery is above 4.6 V, it can lead to unsafe events due to the use of lithium metal oxides as their cathodes [5]. So rapid charge process was much more dangerous to the zero open-voltage lithium ion batteries, and different temperature behavior could be observed. Compared with the temperature rises of the good lithium ion batteries, all zero open-voltage batteries had much higher increases in the temperature, and the differences between the two species were above 10 °C. This indicated that defective batteries with micro short-circuit could be distinguished from good ones during rapid charge process in combination with in situ thermal imaging camera.

Conclusion

In this paper, we manufactured some lithium ion batteries, whose voltages would appear to be zero and about 3.8 V after aging. The former ones belonged to defective lithium ion batteries, while the latter, good ones. Their charge and discharge behaviors as well as initial cycling at 0.2 C did not show any difference. However, when the charge rate was changed to 3 C, they presented great differences in the charge voltages, charge currents, and also surface temperatures. It was also confirmed from the changes of the cathode strips, separators, and anode strips after the charging process at 3 C and the following full discharge process. The above results proved that the technique of charge at high current in combination with in situ temperature measurement is effective to find defective lithium ion batteries of micro short circuits which could not be differentiated by normal charge and discharge methods.

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