E3S Web of Conferences **299**, 03004 (2021) https://doi.org/10.1051/e3sconf/202129903004
EDEP 2021

Microanalysis of the Substances in Positive and Negative Electrodes of a $LiMn_2O_4$ Battery for Road Vehicles under Over-charge and Over-discharge

Hongwei Wang[1,*], *Jun* Liu[2], *Zhengjian* Gu[3], *Haiqing* Xiao[1], *Yusong* Zhu[4] and *Qing* Zhang[1]

[1]Institute of Industrial and Consumer Product Safety, Chinese Academy of Inspection and Quarantine, No. 11, Ronghua South Road, Yizhuang, Daxing, Beijing, 100176, China
[2]Beijing Petrochemical Engineering Co., Ltd. Beijing, 100107, China
[3]Wuxi Institution of Supervision and Inspection on Product Quality, Wuxi, 214028, China
[4]Nanjing Tech University, Nanjing, Jiangsu Province, 211816, China

Abstract. With an 11Ah $LiMn_2O_4$ battery as the object of study, through disassembling the battery after normal charge and normal discharge as well as over-charge and over-discharge, and using such methods as x-ray diffraction and scanning electron microscope, this study explores the micro-changes that happened to the material for the anode and cathode of this lithium battery after over-charge and over-discharge, and provides the measures to prevent batteries from charge and discharge, so as to avoid potential safety problems during the use of lithium batteries.

1 Introduction

With the popularization of lithium-ion batteries, their safety issues become more pressing, and under existing technical conditions, the over-charge and over-discharge of lithium-ion cells is inevitable. At present, a lot of research has been conducted into the thermal behavior of lithium batteries towards over-charge and over-discharge, as well as failure mechanism and electric resistance changes [1-7]. Based on precedents, this study looks at the substances in anodes and cathodes from a micro-perspective after the experiment on $LiMn_2O_4$ batteries through normal charge and normal discharge as well as over-charge and over-discharge.

2 Experiment

IMP18/66/133-11HA type; Rated voltage: 3.7V; Rated capacity: 11Ah. 2) Composition of two sets of batteries: $LiMn_2O_4$ as the active material for the anode; graphite as the active material for the cathode; LiPF6, EC (Ethylene carbonate), DMC (Dimethyl carbonate), and celgard 2325 film as the main components of electrolyte. 3) Six sets of samples going through: over-charge, over-discharge, respectively.

[*] Corresponding author: wanghw@caiq.org.cn

In order to more accurately analyse the relevant performance of the battery, and to reduce the impacts from other factors, all the samples are chosen from the same batch of batteries.

Ambient temperature: 15~35°C, relative humidity: 25%~75% RH; atmospheric pressure: 86kPa.

Experimental instruments: table-type scanning microscope 86kPa; diffractometer system (128FOUCS) Hitachi scanning electron microscope (S-4800).

Experimental procedures: with 11Ah $LiMn_2O_4$ power batteries in over-charge and over-discharge at 20°C ± 5°C temperatures as the objects of experiment, through disassembling batteries, and using such analytical means as x-ray diffraction and scanning electron microscope, this experiment has explored the micro-changes that happened to the anodes and cathodes under over-charge and over-discharge.

3 Test results and analysis

3.1 Overview of the experiment

With the 11Ah $LiMn_2O_4$ lithium batteries in different states (the batteries on which the experiment is performed through the processes of charging, discharging, over-charging and over-discharging at different temperatures) as the objects of the experiment, by disassembling the batteries, and using such analytical methods as x-ray diffraction (XRD for short), scanning electron microscope (SEM for short) and energy dispersive spectrum (EDS for short), this experiment has explored the possibilities of the potential safety problems caused by the lithium batteries during the processes of charging, discharging, over-charging, and over-discharging at different temperatures.

The experimental samples are in the states as shown in the Table 1.

Table 1. States of experimental samples

Designation of early test	**Sample No.**		
	Anode	**Cathode**	**Procedures for the tests in early stages**
Over-charge	OC+	OC-	a) Charge the battery b) The experiment can be conducted in two ways of charging: 1) Charge with the current at $3I_3$(A) until the voltage of the storage battery has reached 5V or until the duration of charging has lasted 90min, whichever occurs first will cause the test to stop; 2) Charge with the current at $9I_3$(A), and stop the test immediately after the voltage of the storage battery has reached l0V.
Over-discharge	ODC+	ODC-	a) Charge the battery b) Discharge the storage battery at a temperature of 20°C±5°C, with the current at $1I_3$(A) (if there are any electronic protection circuits, such electronic protection circuits for the process of discharging should be temporarily removed), until the voltage of the storage battery has reached 0V, and stop the test.

3.2 Analysis of the results from the experiment

Disassembling of a lithium battery.

A lithium battery in a normal state is disassembled as follows:

1. Remove the 3luminium cover

Fig. 1. A lithium battery.

2. Internal electrodes (the left picture shows a cathode "-", while the right one shows a anode "+")

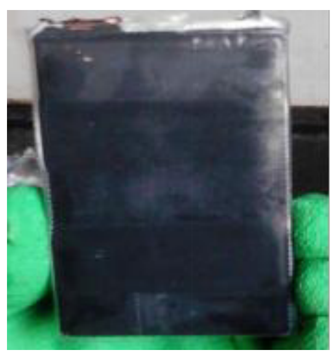


Fig. 2. Disassembled battery

3. Randomly choose two sets of anodes and cathodes from the "+" and "-" electrodes, with one set from the both ends of the battery while the another set is chosen from the middle part of the battery at the time of experiment, and draw samples from these two sets separately, to provide the final experimental samples.

4. Separately immerse all the samples in DMC (dimethyl carbonate) solution for 4-5 hours, so as to remove electrolyte from the surfaces of the samples and to reduce the effect of electrolyte on follow-up experimental analyses and studies, finally take out the samples, and make them dry and sealed.

3.3 Contrastive analysis of the performance under over-charge, under over-discharge and in normal condition

1. Charge and discharge under normal conditions

A lithium-ion battery requires the voltage to be highly accurate, with a tolerance of less than 1%. Currently, it is the batteries with a rated voltage of 3.7V that are in relatively popular use, for which the end-of-charge voltage is 4.2V, thus with a tolerance of 0.042V.

Charging a lithium-ion battery usually falls into the pattern of from constant current to constant voltage. The beginning of a charging process is at the constant-current stage, with the battery at a lower voltage, and during this stage, the charging current is stable without change. As the charging process goes on, the voltage of the battery gradually rises to 4.2V, and then, the charger should immediately change to the constant voltage stage. The fluctuation in charging voltage should be limited to less than 1%. The charging current decreases gradually. When the current has decreased to a certain value, the trickle charge stage is reached. The trickle charge is also called maintenance charge, under which, a charger continues charging a battery at a certain charging rate until the battery is sufficiently charged.

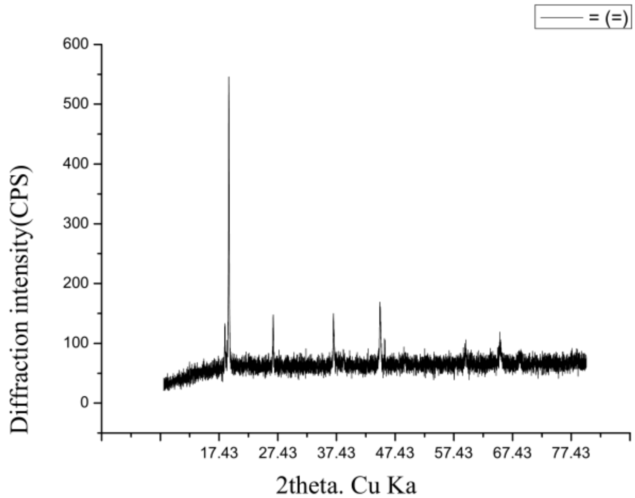
When a lithium battery is discharged, first, the discharging current should not be too high, because a too high current will cause the temperature inside to rise, resulting in permanent damage; second, the voltage of the battery should not be lower than the end-of-discharge voltage, because that, if the discharging process is continued, it well lead to over-discharge, which also can cause permanent damage to the battery. At different discharging rates, the changes in the voltage of the battery are very different. The higher discharging rate, the lower the voltage of the battery corresponding to the remaining capacity will be.

2. Effects of over-charge and over-discharge on batteries

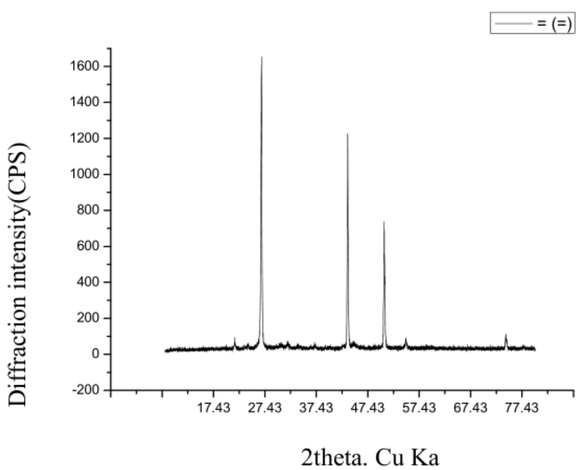
Over-charge refers to the practice of continuing charging a battery after it has been fully charged through a certain charging process. Since the capacity of a cathode is designed to be higher than that of an anode, the gas produced by the anode will pass through the film and combine with the cadmium produced by the cathode. Therefore, generally, the pressure inside the battery will not significantly increase. However, if the charging current is too high, or the duration of the charging process is too long, the oxygen produced cannot be consumed in time, causing the pressure inside to increase, resulting in battery deformation, liquid leakage, as well as the remarkable deterioration of its electric performance.

Over-discharge refers to the practice of forcefully continuing discharging a lithium battery after it has been so discharged that its voltage has dropped to a certain value. If discharging a battery is continued after the electricity stored inside it has been totally discharged and its voltage has reached a certain value, it will lead to over-discharge. Usually, an end-of-discharge voltage is determined according to the discharging current. The process of 0.2C-2C discharge is usually set at 1.0V/unit, while the process of above 3C discharge, e.g. 5C or 10C, is set at 0.8V/unit. Over-discharging a battery may cause the battery to take disastrous consequences. Especially, over-discharge at a higher current or repeated over-charge will have a stronger effect on the battery. Generally speaking, over-discharge will cause the pressure inside a battery to increase, destroying the reversibility of the active substances in its anode and cathode, which can only be partly recovered even if the battery is charged, and the capacity will be significantly weakened as well.

3. The OC, ODC, C in Figure 1 are the XRD images of the anode and cathode under over-charge, over-discharge, and normal charge and discharge, respectively.



The cathode under over-charge



The cathode under over-discharge

Fig. 3. The XRD images of the anode and the cathode

It can be seen from the Figure 3 that, as compared with normally charging the battery, the amounts and varieties of the elements contained in the anode and cathode of the battery after over-charge and over-discharge are all more than those after normal charge and discharge. Over-charge and over-discharge has caused irreversible destructive changes to all the amounts of the elements in the material for the battery's anode and cathode.

Figure 4 shows the SEM (with a magnification of 9000) images of the anode and cathode under over-charge, over-discharge, and normal charge and discharge.

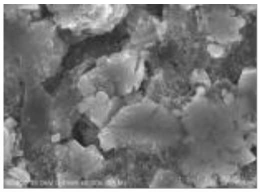
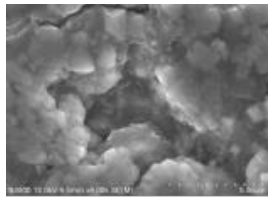
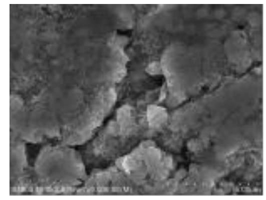
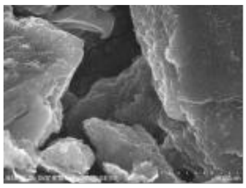
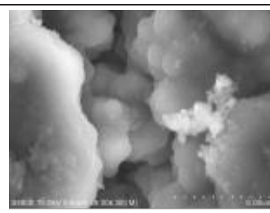
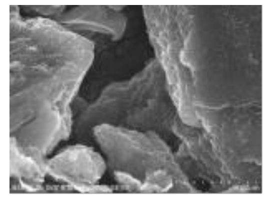
Electrode	Over-charge	Over-discharge	Normal charge and discharge
Anode			
Cathode			

Fig. 4. The SEM images of the anode and cathode

It can be easily seen from the Figure 4 that the anode and cathode have been structurally crystallized with fractures in varying degrees after the battery is over-charged and over-discharged.

Therefore, in order to prevent a battery from over-charge, the end of charge needs to be controlled. When a battery is fully charged, there will be some special information that can used to decide whether the end of charge is reached. Generally, there are following six methods to prevent a battery from over-charge:

- Peak voltage control: decide the end of charge through testing for the peak voltage of the battery.
- dT/dt control: decide the end of charge by testing the battery for the changes in peak temperatures;
- T control: the difference between the temperature of the battery and the ambient temperature will reach the maximum when the battery is fully charged;
- V control: after the battery is fully charged and reaches one of the peak voltages, its voltage will drop to a certain value;
- Duration control: control the end of charge by determining the duration of charge. Generally, the duration will enable a charge equal to 130% of nominal capacity;
- TCO control: avoid charging at a high temperature (except for high-temperature batteries) for the sake of the safety and characteristics of the battery. Therefore, stop charging when the temperature of the battery is higher than 60 °C.

4 Conclusion

For the lithium batteries in this experiment, by comparison with normal charge and discharge, the amounts and varieties of the elements in the anodes and cathodes of the batteries after over-charge and over-discharge are all more than those under normal charge and discharge. Over-charge and over-discharge has caused irreversible destructive changes to all the amounts of the elements contained in the material for the battery's anode and cathode, and the anode and cathode of the battery have been structurally crystallized with fractures in varying degrees after over-charge and over-discharge. Therefore, during the use of lithium batteries, over-charge and over-discharge should be avoided.

5 Acknowledgment

The authors would like to acknowledge the financial support provided for this research work by Fund: National key R & D program of China (2017YFF0210703) and (2018YFF021550103).

References

[1] Dunn B, Kamath H, Tarascon J M. Electrical energy storage for the grid: a battery of choices[J]. Science, 2011, 334(6058): pp 928-935

[2] Schweikert N, Hofmann A, Schulz M, et al. Suppressed lithium dendrite growth in lithium batteries using ionic liquid electrolytes: Investigation by electrochemical impedance spectroscopy, scanning electron microscopy, and in situ 7Li nuclear magnetic resonance spectroscopy[J]. Journal of Power Sources, 2013, 228: pp 237-243

[3] LeijenPeter, KularatnaNihal. Developing a monitoring system for Toyota Prius battery-packs for longer term performance issues[A]. 2013 IEEE International Symposium onIndustrial Electronics (ISIE)[C]. IEEE, 2013: pp 1-6

[4] Henschel J, Horsthemke F, Stenzel Y P, et al. Lithium ion battery electrolyte degradation of field-tested electric vehicle battery cells-A comprehensive analytical study[J]. Journal of Power Sources, 2020, 447, 227370

[5] Siguang, L., Chengning, Z. Study on battery management system and lithium-ion battery [J]. Computer and Automation Engineering, 2009. ICCAE'09. International Conference on, pp 218-222