An Aging Experimental Study of Li-ion Batteries for Marine Energy Power Station Application

Mingyi Chen, Liqiang Zhang, Fan Yu, Liqin Zhou
Department of Automation and Measurement, College of Engineering
Ocean University of China
Qingdao 266100, China
ZLQ @ ouc.edu.cn

***Abstract*—In order to study the aging laws and mechanism of Li-ion batteries under accelerated aging power profile, a cyclic aging experiment is designed to obtain the health characteristics of the battery, such as the capacity and resistance. The EIS and ICA methods are also used to analyze the reasons of aging. Aging around higher SOC will cause more obvious capacity fade. The results may further help to improve the reliability and safety of the energy storage system in marine energy power station.**

Keywords-Li-ion battery; aging test; EIS; ICA; marine energy

I. Introduction

The Marine Energy Power Station (MEPS) uses the batteries as the main energy storage system component. The safety, reliability and economy of the MEPS are affected by the health status of the batteries, which must be taken seriously. At present, the lead-acid batteries are widely used in MEPS, while the Li-ion batteries have rarely reported. Li-ion batteries are well researched in the field of hybrid vehicles and pure electric vehicles. Many methods and techniques have been developed to estimate and predict the remaining useful life (RUL) and state of charge (SOC) of power batteries [1,2]. However, there are few studies in the field of marine energy. Therefore, as the energy storage device of the MEPS, the aging of the Li-ion battery under typical working conditions is worth exploring.

Electrochemical Impedance Spectroscopy (EIS) is an effective method to obtain battery health characteristics. It is widely used in battery aging analysis and battery RUL prediction. Researchers measured the EIS and identified parameters of the equivalent circuit model and the fractional order model to evaluate the ohmic resistance and predict RUL [3,4]. Incremental Capacity Analysis (ICA) is a useful method that converts the voltage curve of a battery during charging and discharging into a capacity increment concerning voltage (dQ/dV). By comparing the peak height of the IC curves, the aging mechanism of the battery could be obtained. The capacity fade of li-ion battery is mainly due to two types of degradation mechanisms: the Loss of Lithium Inventory (LLI) and the Loss of Active Material (LAM) [5]. In this paper, the EIS and ICA methods will be used to analyze the experimental results.

The purpose of this paper is to explore the aging law of Li-ion batteries as the energy storage device in MEPS. The aging experiment design based on accelerated power profile is introduced in Section 2. Section 3 presents the test results and the aging law via EIS and ICA. Conclusions of this paper are presented in the final section.

II. Experimental Setup

The BTS-4000-5V20A battery testing system (Shenzhen Neware, China) has been used to charge/discharge for batteries. The highest current of the equipment is 20A, and the voltage range is 0~5V. Both the current and voltage are recorded at a frequency of 10Hz. The experimental setup is shown as Fig.1. Batteries are installed in four-wire clamps and connected to battery testing system. The room temperature is in the range of 15-20℃, and the average temperature is 18℃. The type of experimental Li-ion battery is LR1865SK (Tianjin Lishen, China), and its nominal capacity is 2600mAh.

The long-term typical working conditions provided by our previous work is simplified as an accelerated aging power

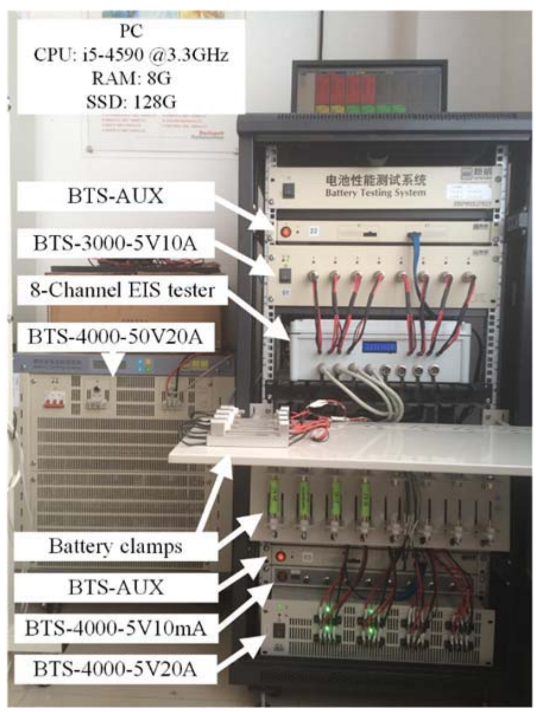


Figure 1. The battery testing system in the laboratory.

978-1-7281-0860-5/19/$31.00 ©2019 IEEE

profile [6]. It has 19 steps, and three of the steps (one discharge step and two charge steps) are over 25W. Considering that the highest discharging current 3C (7.8A) and nominal voltage 3.7V, the highest power is limited to 25W. The power profile of the accelerated aging tests can be obtained as Fig. 2 at last.

A set of cyclic aging test has been designed, including the accelerated aging test, the characteristic test, and the EIS test, Shown as Fig.3. The capacity test and dynamic stress test (DST) are contained in the characteristic test, and the EIS test is performed at SOC=0.

The accelerated aging power profile shown as Fig.2 is carried out for 30 times at room temperature, which is defined as the accelerated aging test. Four LR1865SK batteries are selected (labeled SK08, SK14, SK15, and SK16) for studying the battery's aging law around different SOC. Firstly, SK08, SK14, SK15, and SK16 batteries are discharged to certain SOC of 0.2, 0.4, 0.6 and 0.8 respectively. Then, those batteries are aged by the accelerated aging power profile (shown as accelerated aging test part of Fig. 4).

After the accelerated aging test, all batteries are charged to 4.2V by constant-current and constant-voltage (CC-CV) method. The constant current is 0.5C, and the constant voltage is 4.2V. The cutoff current at constant voltage charging stage is 0.05C. Then, batteries are discharged to 2.75V with a current of 0.5C in the capacity test. After a 30min rest, the batteries are charged by CC-CV. Those processes are shown in Fig. 4 as the CC-CV charge part and the capacity test part.

Discharge resistance and charge resistance are defined as $Rd=dU1/dI1$ and $Rc=dU2/dI2$ respectively.

The current pulse sequence for DST is custom, containing 7 current levels of -0.25C, -0.5C, 0.25C, 0, 1C, 0.5C and -0.625C. Batteries are discharged to 2.75V with a current of 0.5C in the last step, as shown as the DST part in Fig. 4.

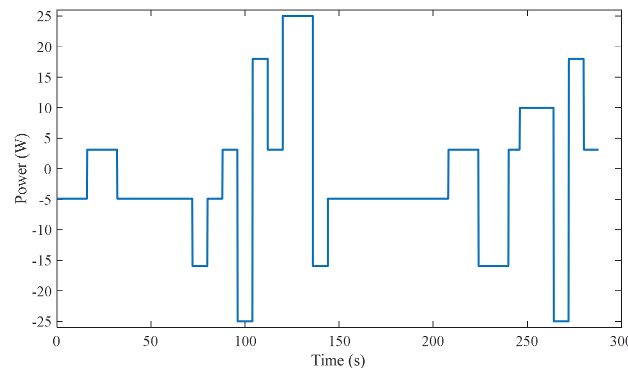


Figure 2. Power profiles of the accelerated aging tests.

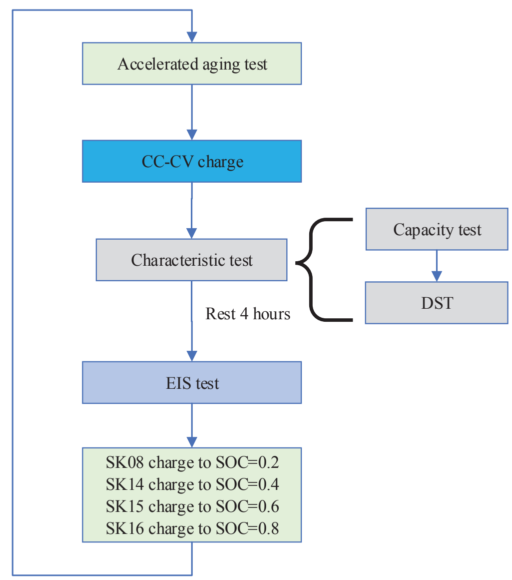


Figure 3. Schedules of the cyclic aging test.

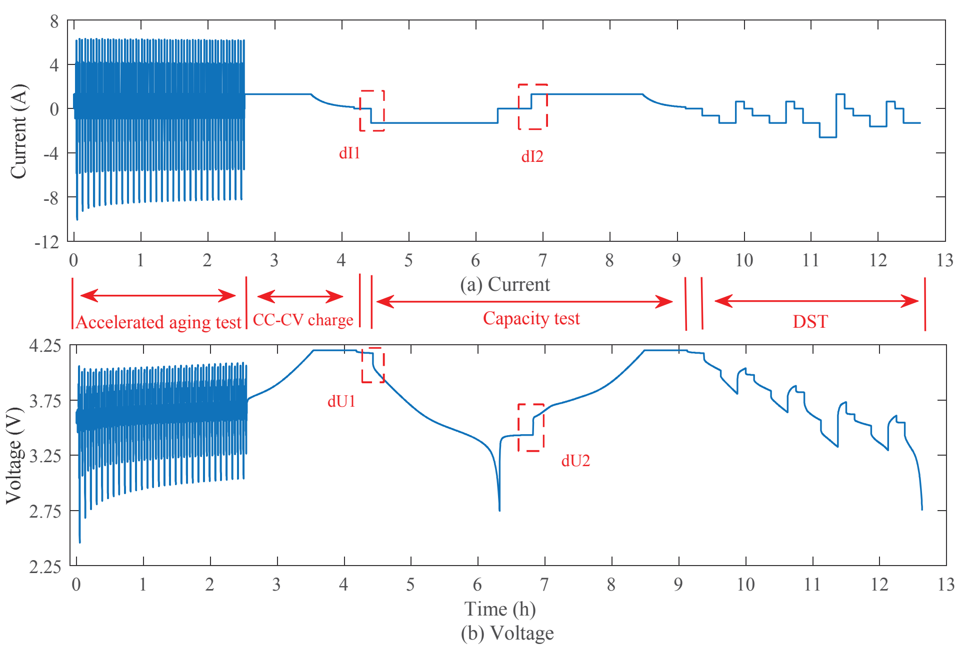


Figure 4. Current and voltage profiles of SK14 in the cyclic aging test.

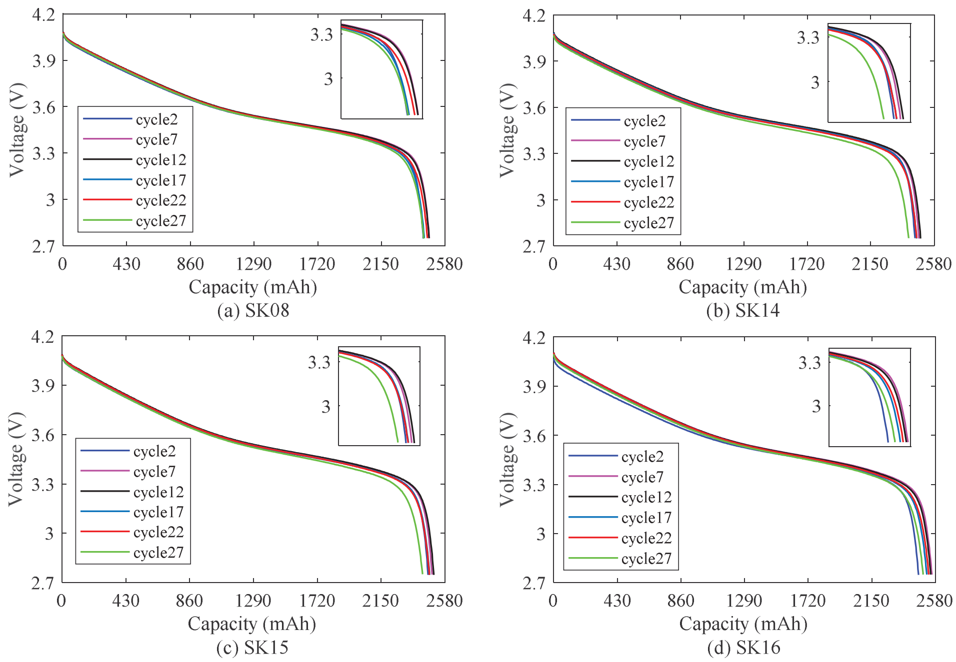


Figure 5. Standard discharging voltage-capacity curve.

III. RESULTS AND DISCUSSION

A. *Discharge Curves*

The relationship between voltage and capacity of the four batteries is shown in Fig. 5. During the aging progress, the End-of-Discharge (EoD) points slowly move to the left after 12 cycles, indicating that the capacity is decreasing.

B. *Capacity Fade*

The discharge capacity of the batteries is shown in Fig.6. The capacity change in a range of 120 mAh. The capacity increase in the first 12 cycles, possibly due to the activation of batteries. The batteries have been stored for over two years before this experiment. After that, the overall capacity decreases a little. Especially, the SK16 battery may be overcharged during the accelerated aging process, so in the capacity test, more capacity losses compare to other batteries.

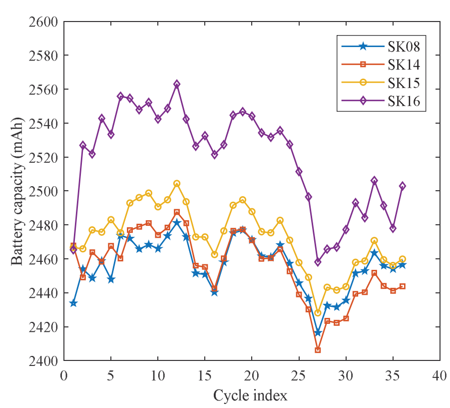


Figure 6. Capacity fade of the batteries.

C. *Internal Resistance*

The charge resistance Rc and the discharge resistance Rd are investigated with the Curve Fitting toolbox in MATLAB, using the exponential function. The results are shown in Fig. 7~10.

The resistance curves of the four batteries have the same form. The Rc and Rd of the first 12 cycles are reduced. After 12th cycle, the internal resistance increase monotonically. The resistance changes of the SK08, SK15, and SK16 batteries are almost the same, while the SK14 battery changes faster and has a larger range than others.

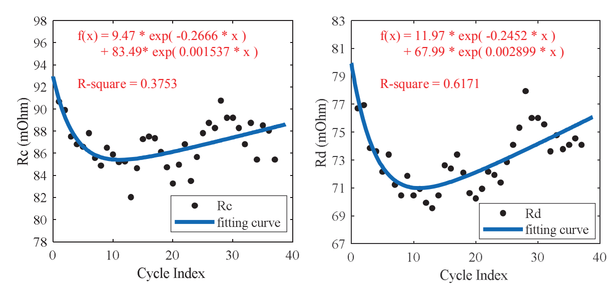


Figure 7. Rc and Rd Fitting results of battery SK08.

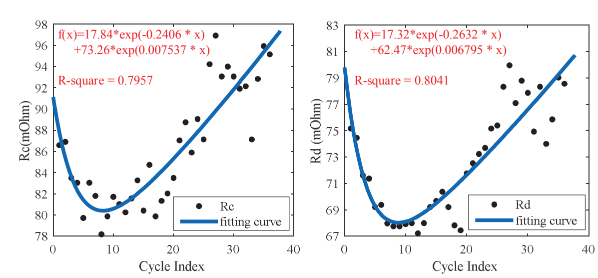


Figure 8. Rc and Rd Fitting results of battery SK14.

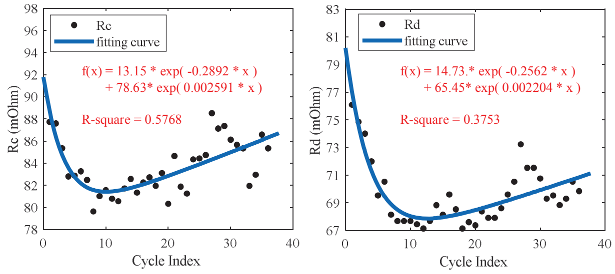


Figure 9. Rc and Rd Fitting results of battery SK15.

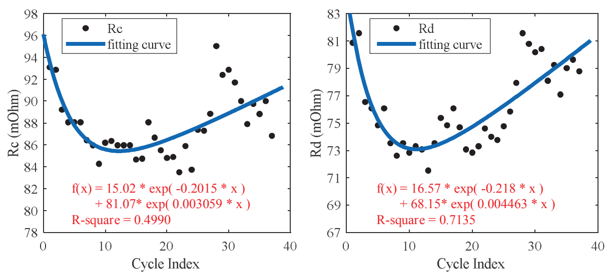


Figure 10. Rc and Rd Fitting results of battery SK16.

D. *EIS Curves*

The EIS test is performed after the characteristic test and 4 hours' rest, and the frequency range is 0.01Hz-1kHz. Eight of the EIS curves of each battery are selected, as shown in Fig.11.

During the aging process, the EIS curves generally showed a tendency to move to the upper right of the Nyquist plane, except for SK14. The radius of the small circle hardly changed while the radius of large circle increased. The intersection of the EIS curve and the x-axis of the Nyquist plot indicates the ohmic resistance of the cell. The results show that the ohmic resistance of the four cells increases during aging. The small arc in the EIS curve indicates the resistance of the solid electrolyte interphase (SEI) film on the electrode surface. The radius of the small arc remains constant, indicating that the SEI film is stable. The large arc is related to charge transfer, and the increase in arc radius indicates that the charge transfer resistance may be greater. SK14 shows a faster rise in internal resistance when aging around SOC=0.4, while the reason is currently unknown and will be discussed in future research.

E. *Incremental Capacity Analysis*

The incremental capacity analysis was respectively performed to CC discharge and charge by using the capacity test data in Fig. 4. The discharge IC curves are shown in Fig. 12.

As can be seen from the curves, the peak height gradually decreases with the cycle. It shows that the discharge capacity on the voltage platform reduces. The reason for capacity fade will be specifically analyzed by the charge IC curves as shown in Fig. 13.

It is showing that the height of peak ① is almost constant, and so are the shape and size. This phenomenon indicates that the lithium ion released from the positive electrode at the initial stage of the reaction is relatively sufficient, which means there is no LAM in the positive electrode. The height decrease of peak ② of battery is mainly attributed to the LLI [7].

From Fig.13, it can be seen that in the different aging cases of SOC=0.2~0.8, the changes in peak ② are more obvious. When the batteries are aging around higher SOC, the height of peak ② moves downwards more obviously. It shows that aging with higher SOC will cause more LLI. When SK16 is cycled around SOC=0.8, partial charge peak may cause overcharge. The voltage of the battery even goes higher than 4.5V in this

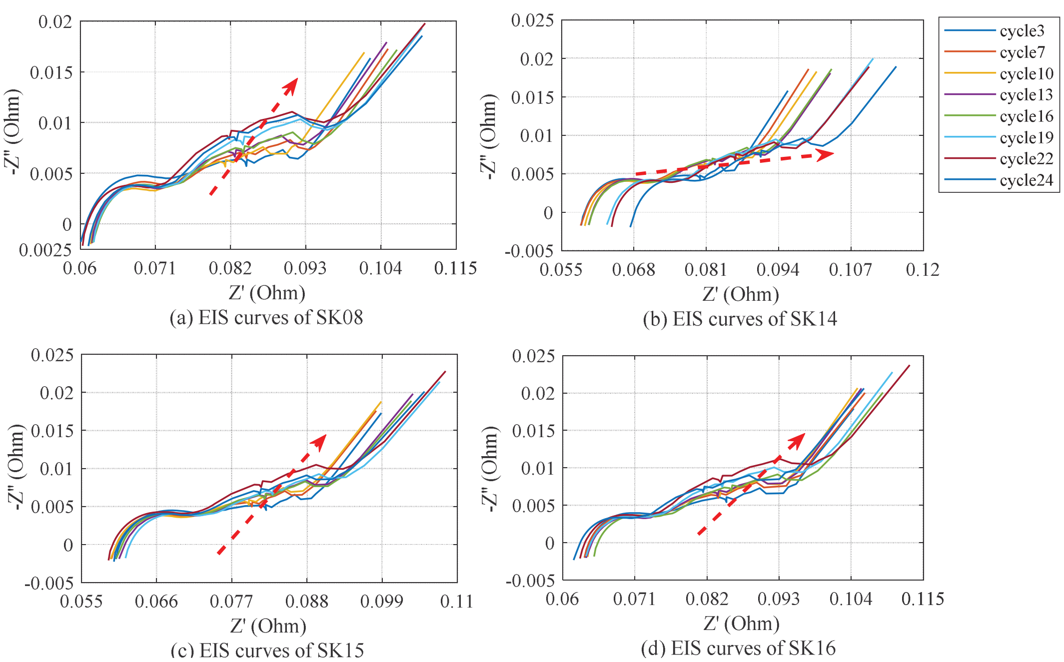
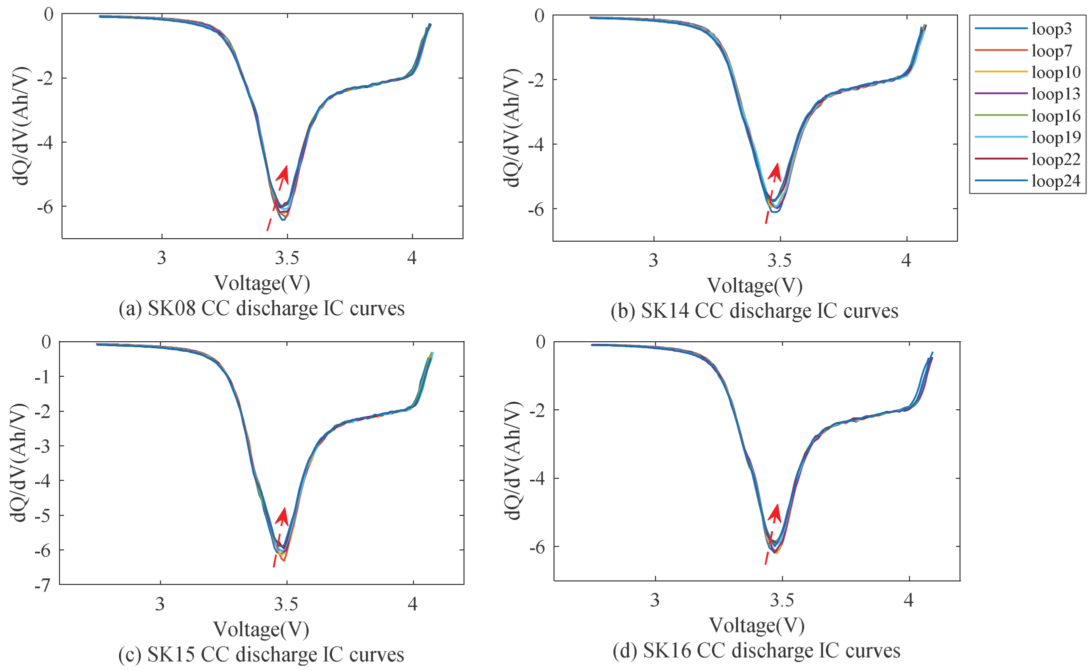
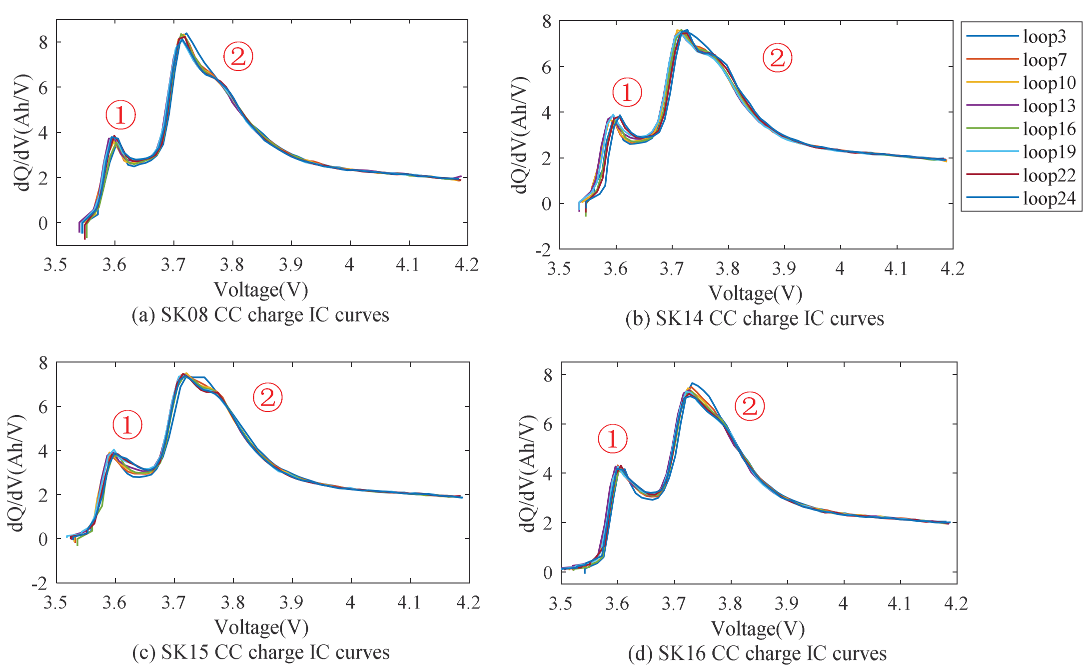


Figure 11. The EIS curves of the batteries.



(a) SK08 CC discharge IC curves
(b) SK14 CC discharge IC curves
(c) SK15 CC discharge IC curves
(d) SK16 CC discharge IC curves

Figure 12. IC curves of CC discharge.



(a) SK08 CC charge IC curves
(b) SK14 CC charge IC curves
(c) SK15 CC charge IC curves
(d) SK16 CC charge IC curves

Figure 13. IC curves of CC charge.

case, and it may have a great impact on the health of the battery.

Till now, we found that the batteries began to age, but the aging phenomenon is not obvious. On the one hand, a few cycles of aging have been done, the experiments should be continued. Some more obvious aging phenomenon may be obtained from a long term experiment. On the other hand, the accelerated aging test proposed in the literature [6] is obtained from large-scale battery packs. The average rate of charge and discharge is small, compared to the battery capacity. The batteries are cycled in a small SOC range, so they are aged slowly.

However, the construction and maintenance costs of large battery packs are very high. If a smaller battery pack is used, it is necessary to consider the overcharge or over-discharge caused by the peak power in actual operating conditions. So supercapacitors could be installed with Li-ion battery pack in future. In order to find a balance between cost and aging of the energy storage system, the aging laws and much more aging mechanism should be studied and used for optimizing.

IV. Conclusions

In this paper, the cyclic aging test was designed by using an accelerated aging power profile. The aging test of commercial Li-ion battery LR1865SK was carried out. Battery health characteristics such as the capacity, internal resistance, EIS and IC curves were obtained. It is found that the battery capacity first increases and then decreases, and continues to decrease during aging. While the internal resistances show opposite phenomenon. The ohmic impedance and the transfer impedance of the battery slightly increase, while the SEI film hardly changes from EIS results. The quantity of material in the positive electrode has no obvious loss, and the change of peak heights of the IC curves may mainly cause by LLI process. Aging around higher SOC will cause more obvious aging. Much more data will be obtained by this proposed experiment in further, and the aging laws and mechanism of Li-ion battery may be discussed in details. It can be very beneficial for the PHM study of Li-ion batteries, and will have further help to improve the reliability and safety of the energy storage system in MEPS.

Acknowledgment

This research was financially supported by the National Natural Science Foundation of China (NSFC Grant 51607167 and 51761135014). We are also grateful to all anonymous reviewers for providing useful comments and suggestions that resulted in the improved quality of this paper.

References

[1] X. Li, X. Shu, J. Shen, R. Xiao, W. Yan, Z. Chen,et al, "An on-board remaining useful life estimation algorithm for lithium-ion batteries of electric vehicles," Energies, vol. 10, p. 691, 2017-01-01 2017.

[2] S. Huang, K. Tseng, J. Liang, C. Chang, and M. Pecht, "An online SOC and SOH estimation model for lithium-ion batteries," Energies, vol. 10, p. 512, 2017-04-10 2017.

[3] K. Goebel, B. Saha, A. Saxena, J. Celaya, and J. Christophersen, "Prognostics in battery health management,". vol. 11 New York: IEEE, 2008, pp. 33-40.

[4] L. De Sutter, Y. Firouz, J. De Hoog, N. Omar, and J. Van Mierlo, "Battery aging assessment and parametric study of lithium-ion batteries by means of a fractional differential model," Electrochimica Acta, vol. 305, pp. 24-36, 2019.

[5] X. Han, M. Ouyang, L. Lu, J. Li, Y. Zheng, and Z. Li, "A comparative study of commercial lithium ion battery cycle life in electrical vehicle: aging mechanism identification," Journal of Power Sources, vol. 251, pp. 38-54, 2014.

[6] L. Zhang, J. Lin and M. Li, "Research on the typical working condition of energy storage batteries for a wave energy converter," in The 2nd IEEE International Power Electronics and Application Conference and Exposition, 2018, pp. 1-6.

[7] T. Wang, L. Pei, T. Wang, R. Lu, and C. Zhu, "Capacity-loss diagnostic and life-time prediction in lithium-ion batteries: Part 1. Development of a capacity-loss diagnostic method based on open-circuit voltage analysis," Journal of Power Sources, vol. 301, pp. 187-193, 2016.