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Electrochemical impedance spectra for lithium-ion battery ageing considering the rate of discharge ability

Jiuchun Jiang[a,b], Zhisong Lin[a,b], Qun Ju[c], Zeyu Ma[a,b,]*, Caihui Zheng[d], Zhanguo Wang[a,b]

[a]*National Active Distribution Network Technology Research Center, Beijing Jiaotong University, Beijing, 100044, China*
[b] *Collaborative Innovation Center of Electric Vehicles in Beijing, Beijing Jiaotong University, Beijing, 100044, China*
[c]*Supervision And Test Center For Lithium Battery Product Quality, Zaozhuang, 277000, China*
[d]*Changchun Railway Vehicles Co.,Ltd., Jilin, 130062, China*

Abstract

The state of health (SOH) of lithium-ion battery is a critical index for the characteristic of the batteries. It is important to evaluate the SOH of lithium-ion cells to avoid dangerous operating conditions and to extend the useful life. The study about the electrochemical impedance characteristics plays an important role for diagnosing the ageing cells. After electrochemical impedance spectra (EIS) tests and the rate of discharge ability tests at various temperatures following cycle life tests, the relation between the electrochemical impedance and the capacity of the ageing batteries is presented in this paper. The batteries experience the same ageing process, but the available capacities at high discharge rate present evident differences while they are similar at low discharge rate. Considering the characteristic demanded in practical applications such as the rate of discharge ability, both impedance and the available capacity of the battery should be taken into account in the evaluation of SOH.

Keywords: Lithium-ion battery; State of health; Ageing; Electrochemical impedance spectra; the rate of dischargeablility

1. Introduction

Lithium-ion batteries have experienced a growing interest in automotive, stationary and hybrid energy production systems [1-6] because of the high power density, energy density and long lifetime. It is

* Corresponding author. Tel.: +86-010-82481744; fax: +86-010-82481744.
E-mail address: zeyuma@bjtu.edu.cn.

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important to evaluate the state of the batteries, especially SOH of lithium-ion cells, to avoid dangerous operating conditions and to extend the useful life. Some research has been done on investigating the electrochemical impedance characteristic of ageing batteries. Reference [6] analyzes the impedance spectra at different state of charge (SOC) to study the ageing mechanisms through the EIS. The impedance characteristic of over the battery life time is investigated on a 40Ah lithium-ion cell with nickel manganese cobalt oxide (NMC) cathode material as an example [2]. There is not discussion about the impact of the impedance and the available capacity on the estimating the SOH of the battery considering the characteristic demanded in practical applications, such as the rate of discharge ability. For this purpose, the characteristic of the battery electrochemical impedance with different rate requirement is performed in different ageing states using EIS in this paper.

2. EIS for battery impedance characterisation

EIS is a kind of electrochemical measurement method that the small amplitude sine wave voltage (or current) disturbance signal is imposed on the electrochemical system. The impedance modulus and phase angle of different frequencies in a frequency domain are presented by changing the frequency of the sine wave. EIS wields little influence over the state of the system and can present more information about the dynamics and structure of the electrode interface than other conventional electrochemical methods.

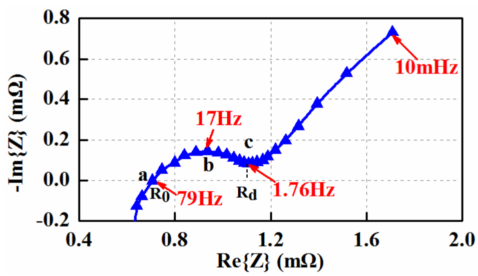

Fig. 1. The EIS of #1 cell at 25°C and 50% SOC

As shown in Fig. 1, the three feature points, a, b and c, describe the dynamic characteristic of the battery. Point a, the intersection of the semicircle and the horizontal axis, represents the ohm resistance R_0 of the battery. Point b, the peak of the semicircle, represents the dynamic response characteristic of the voltage driven by the changing current. The real part of the impedance, R_0, is represented as the intersection of the diagonal and the semicircle, point c. The semicircle, between R_0 and R_d, is associated with the charge transfer reaction on the battery interface, approximate to the charge transfer resistance R_{ct}. Then R_{ct} can be calculated:

$$R_{ct} = R_d - R_0 \tag{1}$$

Using complex numbers to represent the sinusoidal voltage ($\tilde{u}(f)$) and the current ($\tilde{i}(f)$), the complex impedance of the battery at the given frequency f can be calculated [7]:

$$\tilde{z}(f) = \tilde{u}(f) / \tilde{i}(f) \tag{2}$$

The dynamic characteristics of the battery can be described by the parameters: the value of $\tilde{z}(f)$, the real part $Re[\tilde{z}(f)]$, imaginary part $\mathrm{Im}[\tilde{z}(f)]$,absolute value $|\tilde{z}(f)|$ and the phase angle $\varphi(f)$.Given frequency f_x, they can be calculated:

$$Re\left[\tilde{z}\left(f_x\right)\right]=\left|\tilde{z}\left(f_x\right)\right|\cos\left[\varphi\left(f_x\right)\right],x\in\left[1,2,\cdots,n\right] \tag{3}$$

$$\mathrm{Im}\left[\tilde{z}\left(f_x\right)\right]=\left|\tilde{z}\left(f_x\right)\right|\sin\left[\varphi\left(f_x\right)\right],x\in\left[1,2,\cdots,n\right] \tag{4}$$

$$\varphi\left(f_x\right)=\tan^{-1}\left\{-\mathrm{Im}\left[\tilde{z}\left(f_x\right)\right]/\mathrm{Re}\left[\tilde{z}\left(f_x\right)\right]\right\},x\in\left[1,2,\cdots,n\right] \tag{5}$$

$$\left|\tilde{z}\left(f_x\right)\right|=\sqrt{\mathrm{Re}\left[\tilde{z}\left(f_x\right)\right]^2+\mathrm{Im}\left[\tilde{z}\left(f_x\right)\right]^2},x\in\left[1,2,\cdots,n\right] \tag{6}$$

3. Test and result

3.1. Test platform and scheme

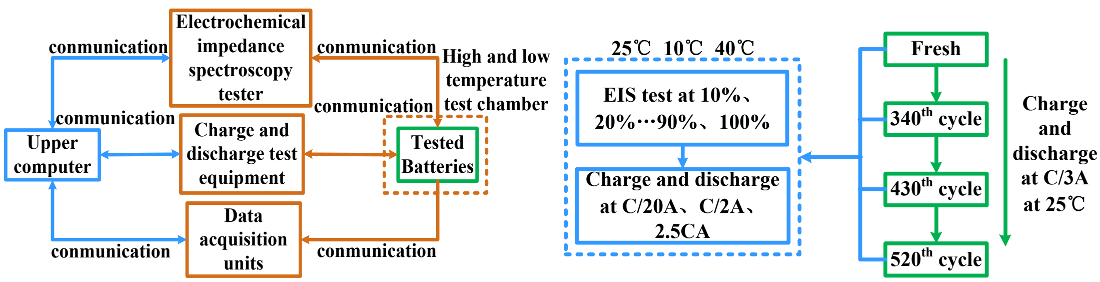

Fig. 2. (a) The battery test platform; (b) The battery test scheme

As shown in Fig. 2. (a), the experiment platform consists of the upper computer, charge and discharge test equipment, EIS tester, high and low temperature test chamber and two tested batteries. In this paper, the tested batteries use a positive electrode (PE) active material comprising $\{LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2 + LiMn_2O_4\}$ composite and a negative electrode (NE) made of graphite. Nominal capacity is 35 Ah and nominal voltage is 3.7 V.

The ageing cycle test is going with C/3A current and the batteries are placed in a high and low temperature test chamber at a temperature of 25 ℃. A series of performance tests are done on the fresh batteries and the same tests are done after the 340th cycle, 430th cycle and 520th cycle ageing test as well. The test program is shown in Fig. 2. (b).

3.2. Result

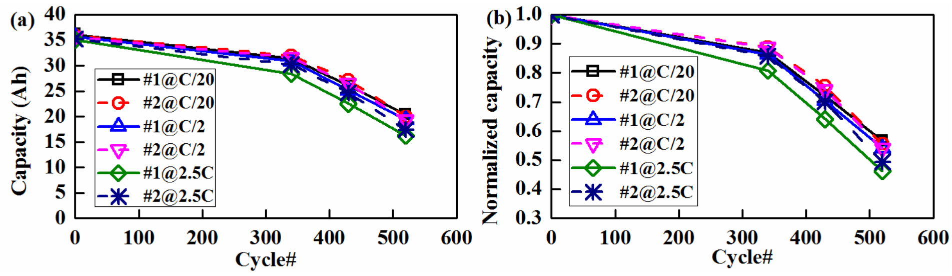

Fig. 3. (a) Capacity variations with different rates discharge current; (b) Normalized capacity with different rates discharge current

The discrepancy of the capacities with different rates measured at 25℃ of #1 and #2 cell is shown in Fig. 3, after cycled at 25℃ and 2C rate. As the batteries ageing, the capacities decrease with the increase of the batteries impedance. These changes affect the external characteristic of the batteries directly, especially the reserve capacity and power. The initial maximum available capacity of #1 cell is 36.17Ah while that of #2 cell is 35.96Ah. As the batteries ageing, the curves of the capacities measured with the C/20 and C/2 rates are consistent. The origin and the end of the curves with 2.5C rate are similar, but the middle sections of the two curves are apparent separated. Although the two batteries experience the same ageing progress which causes the similar capacity fade, the increase of the impedance is obviously different.

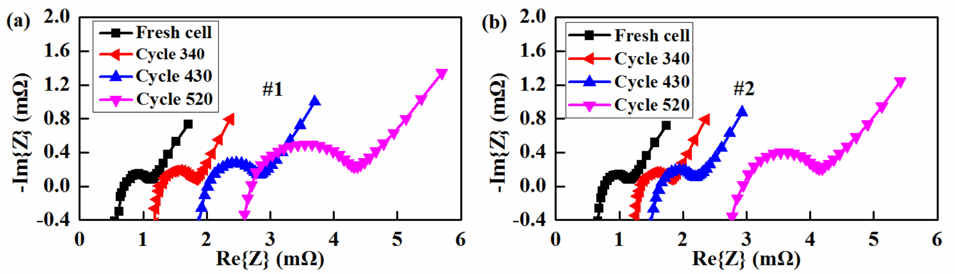

Fig. 4. (a) The EIS of #1 cell in different ageing states; (b) The EIS of #2 cell in different ageing states

Fig. 4.(a) and (b) show the different changing process of the EIS of #1 and #2 cell at 50% SOC. As the cycle increases, the ohm resistance of #1 cell presents linear increment. The increase of the ohm resistance of #2 cell between the 340th cycle test and the 430th cycle test is minor, but it increases rapidly after the 430th cycle as well as the semicircle of the medium frequency.

4. Discussion

Fig. 5 presents the curves of the real part of the impedance, ohm resistance and the charge transfer resistance of the three feature points mentioned in section 2 of this paper. The evolution process of these three parameters is divided into two stages, the first stage of steady increase and the stage of speed-up increase. The #1 cell goes into the second stage earlier than #2 cell while the impedance of #2 cell increases faster than that of #1 cell as a whole. As a result, the fade process of the maximum available capacity of the two cells is similar, but the increase process of the impedance is not the same which affects the capacity of the batteries with high-rate current. It indicates that both impedance and the available capacity of the battery should be taken into account in the evaluation of SOH especially in the high-rate discharge current required applications.

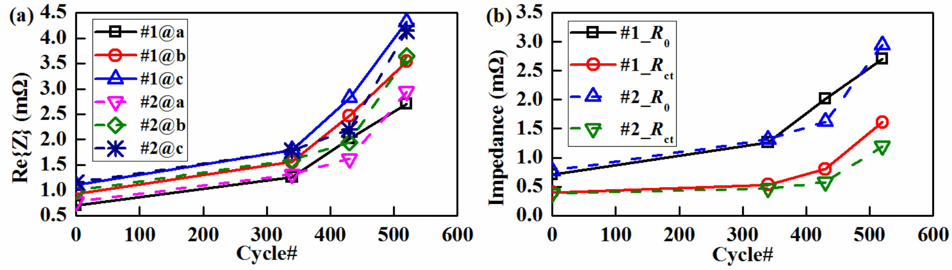

Fig. 5. (a) The real part of battery impedance at 25℃ and 50%SOC in different ageing stages; (b) The ohm resistance and the charge transfer resistance of batteries at 25℃ and 50%SOC in different ageing stages

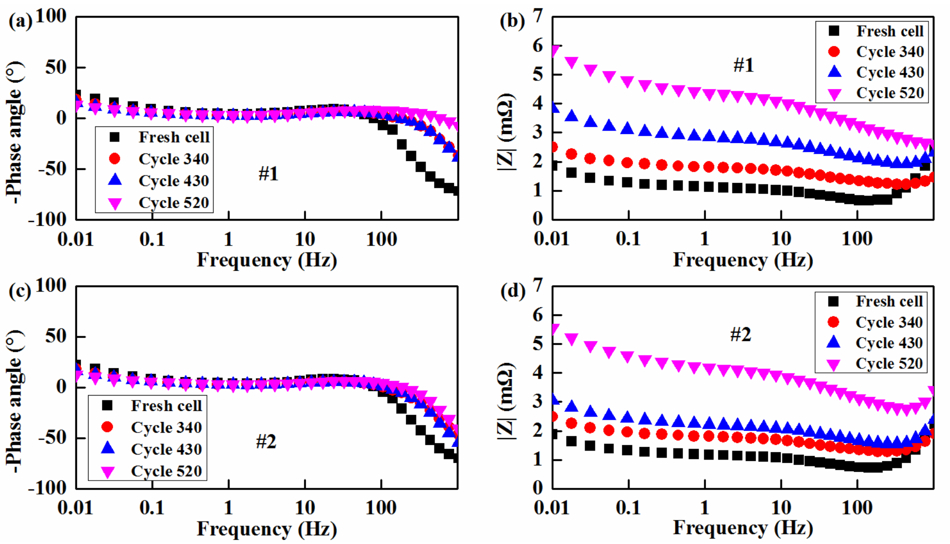

Fig. 6. (a) The negative phase angle of #1 cell in different ageing stages; (b) The absolute value of #1 cell impedance in different ageing stages; (c) The negative phase angle of #2 cell in different ageing stages; (d) The absolute value of #2 cell impedance in different ageing stages

The phase angle and the absolute value of the battery impedance in different ageing stages with the temperature of 25 ℃ at 50%SOC are shown in Fig. 6. The ageing of the batteries has a significant impact on the impedance characteristic. In low frequency region in which the frequency is less than 100Hz, the phase angles of impedance in different ageing stages are similar. When the frequency is higher than 100Hz, there is a significant difference between the phase angles of different ageing impedance. The absolute value of the impedance increases constantly with the batteries ageing and different batteries present different increase regularity. Therefore the same ageing process may cause the different changes of the impedance.

5. Conclusion

- The electrochemical impedance experiments and the available capacity tests in different ageing stages are done. And other performance experiments of the batteries are also accomplished.
- The electrochemical impedance characteristic of the batteries in different ageing stages is analyzed considering the rate of discharge ability. The same ageing process may cause similar capacity fade but different changes of the impedance. It indicates that both impedance and the available capacity of the battery should be taken into account in the evaluation of SOH especially in the high-rate discharge current required applications.
- More battery characteristics that affect the evaluation of SOH can be further investigated in the future.

6. Copyright

Acknowledgements

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He is currently working toward the Ph.D. degree from Beijing Jiaotong University, Beijing, China. His research interests include battery management system, battery modeling and state estimation, battery diagnosis and prognosis for electric drive vehicle and energy storage system applications.