

Study of the State of Charge for Lithium-ion Batteries Based on Real-time Electrochemical Impedance Spectroscopy

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Abstract. The state of charge (SOC) prediction of Li-ion batteries is always a tough topic. Many methods such as current integration, open circuit voltage etc have been widely used in industry. The dynamic impedance $|Z|$ and the phase angle θ , what contain not only the internal resistance but also the electrochemical and concentration polarization if perturbation frequencies are appropriate. In this paper, the 10Ah lithium-ion phosphate (LiFePO₄) battery was used for the real-time electrochemical impedance spectroscopy (EIS) research without statics during charge/discharge. EIS analysis results indicated that the θ and $|Z|$ have a strong relevance with SOC especially at the frequencies of 0.025Hz and 1Hz when charging and discharging, respectively. This provides a technical reference for SOC prediction of Li-ion batteries.

1. Introduction

Li-ion batteries have been widely used on mobile phones, digital products, electrical vehicles and large-scale energy storage, etc. Battery management system plays an important role on cell safety and energy conversion efficiency. Therefore, the research on battery management system is becoming more and more important. The exact estimation of SOC is the key to premise to sound operation of battery management [1]. Various techniques that already been applied in industry such as current integration, DC internal resistance, open circuit voltage are always imprecise [2]. To this, a reliable and accurate SOC algorithm under real user conditions has not been proposed successfully but urgent.

Compared with those of other Li-ion batteries, the voltage range of the discharge platform of LiFePO₄ batteries is relatively small. Therefore, the open circuit voltage measurement is seldom used. In addition, the ampere integral method cannot accurately estimate the initial SOC and the cumulative effect of coulomb efficiency on the error [3]. Through analyzing the working principle of Li-ion batteries and EIS measurement in detail, the advantages of EIS measurement over DC internal resistance method are obvious, that EIS analysis can provide full information of electrochemical interface, providing in-situ and non-destructive electrochemical reaction mechanism inside the batteries. The measurement of EIS contains a series of AC signals at different frequencies, which can reflect many electrochemical characteristic parameters of the battery and kinetic information of the related reactions [4]. Thus, the EIS measurement will be more accurate to estimate the SOC of a battery.

In normal case, establishing equivalent circuit to fit the impedance spectroscopy is usually adopted [5]. The SOC prediction model is established though analyzing the electrochemical parameters, for example the ohmic internal resistance R_{ohm} , the charge transfer resistance R_{ct} and double-layer capacitance C_{dl} , the Warburg impedance caused by concentration polarization and so on. In this paper, the dynamic impedance $|Z|$ and the phase angle θ are introduced. $|Z|$ is a complex impedance, whose square equals to the sum of squares of the real and imaginary parts. θ starts from the origin of the coordinate axis to the slope of each point in the frequency domain, whose tangent equals to the ratio of the imaginary part to the real part. $|Z|$ and θ can reflect the change of ohmic and polarization resistance inside the battery during charging and discharging. This paper mainly focuses on the change of dynamic impedance $|Z|$ and phase angle θ in the low frequencies region ($<1\text{Hz}$).

2. Experiment

The experimental battery is a commercial LiFePO_4 battery produced by Narada. Model: FE10A, Nominal voltage/capacity: 3.2V/10Ah. In order to obtain the dynamic impedance at different SOC, the 5V/5A LANHE equipment and 24V/10A Modulab-Xm (Solartron) electrochemical workstation are used to conduct 0.2C charge-discharge experiment and dynamic impedance analysis respectively.

The standard charge test will not only affect the real-time impedance, but also increase the error of SOC estimation. To address this problem, the charge and discharge capacity of this battery are checked out for three times to take the average under 0.2C current density by nominal capacity (10A), as shown in Table 1.

Table 1. The charge-discharge capacity in three times.

	1st	2nd	3rd	Average	$0.2C_4$
Charge capacity/mAh	12032	11779	11823	11878	2376
Discharge capacity/mAh	11676	11594	11656	11642	2328

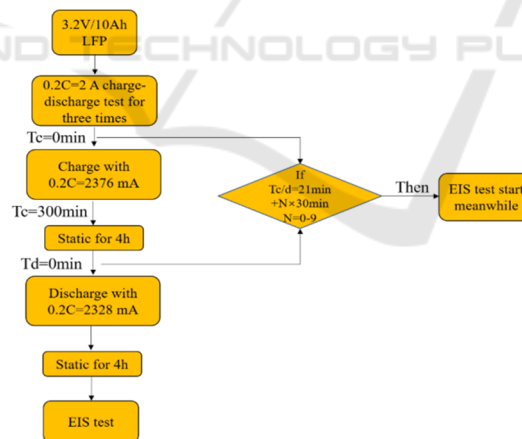


Figure 1. The flow chart of experiment test.

Many tests have been studied repeatedly to find the relationships between electrochemistry parameters and SOC, such as placing different statics times, different charge/discharge current or temperature [4]. However, in this experiment the LANHE machine and Modulab-Xm are used for charging and discharging with no statics times and EIS analysis for every 10% SOC during charging and discharging process simultaneously. There is 4h for standing between charge and discharge processes to ensure that the battery is completely depolarized. 5mV potential disturbance and the test frequency of 10K-0.01Hz are used in the EIS analysis. The accuracy of the test is guaranteed by

setting the cut-off point of each impedance analysis as the cut-off point of each 10% SOC during charge-discharge. Results show that the impedance analysis lasts about 9 minutes in this frequencies domain. Inevitably, the impedance data at 100% SOC (Charge) and 0% SOC (Discharge) may not be accurate because of the distinction from the time required for each EIS analysis at different SOC. Here, we utilize the floating mode (L0) of the Modulab-Xm workstation to reduce and eliminate the interference of alternating current (AC) signals during charging and discharging. The flowchart of the whole experiment is shown in Figure 1.

3. Results and discussion

3.1. EIS analysis during charge

The Nyquist semicircle in Figure 2(A) indicate that the charge transfer resistance of 0% SOC/100% SOC is maximum/minimum respectively. Figure 2(B) shows the different EIS diagrams when the SOC cuts off from 90% to 10% during charge. Generally, the impedance is higher in full/empty charge of battery than other states. In addition, the relevance between frequency and phase angle are very strong when the frequency change from 1Hz to 0.01Hz. Figure 3 and Figure 4 show the variation of phase angle with SOC at different frequencies during charge.

Research suggests that the smaller the disturbance frequency is, the more obvious the phase angle responds to SOC [5-6]. After analyzing the SOC- θ graph at frequencies of 0.1Hz, 0.025Hz and 0.01Hz, we find that the linear relationship between them is the most obvious at the frequency of 0.025Hz. Therefore, when using the phase angle to predict SOC during charge, 0.025Hz is researched as the key.

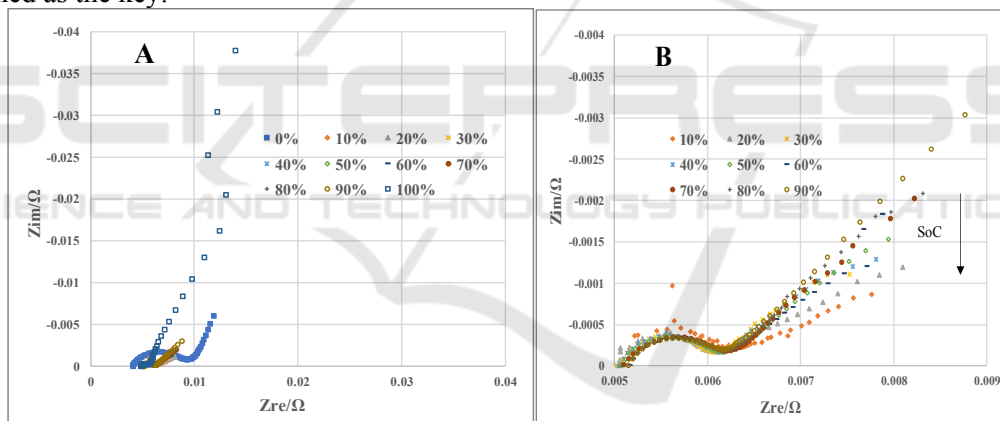


Figure 2. The EIS diagrams for different SOC during charge.

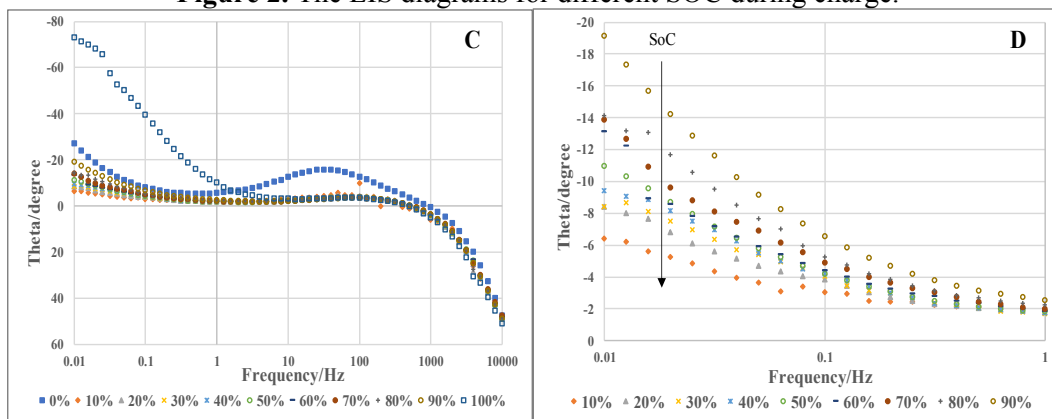


Figure 3. The Frequency-Phase angle diagrams for different SOC during charge.

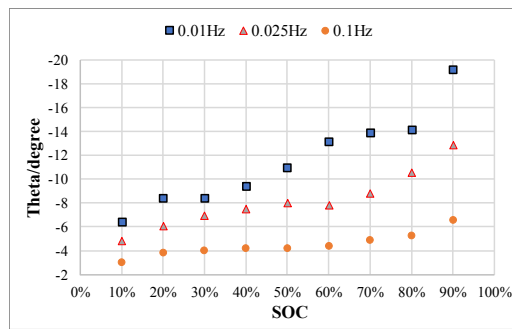


Figure 4. The variation of phase angle with SOC at different frequencies.

3.2. EIS analysis during discharge

Figure 5 and Figure 6 show the EIS diagrams and the Frequency $-|Z|$ for different SOC during discharge, which the $|Z|$ represents the dynamic total impedance in the EIS analysing. Due to the time required to complete the EIS analysis in this frequency domain are inconsistent at different SOC, the impedance test in low frequencies is inaccurate when charging to 100% SOC or discharging to 0% SOC. Unlike charging, the impedance of discharging at 0% SOC is the highest and no significant relationships between the SOC and θ . However, the relevance between SOC and $|Z|$ is strong in low frequencies. Figure 7 shows the variation of dynamic impedance with SOC at above three frequencies.

The results show that the dynamic $|Z|$ impedance increase accordingly when the SOC reduce from 90% to 10% in a certain frequency range. The linear relationship between $|Z|$ and SOC is the strongest especially at the frequency of 1Hz.

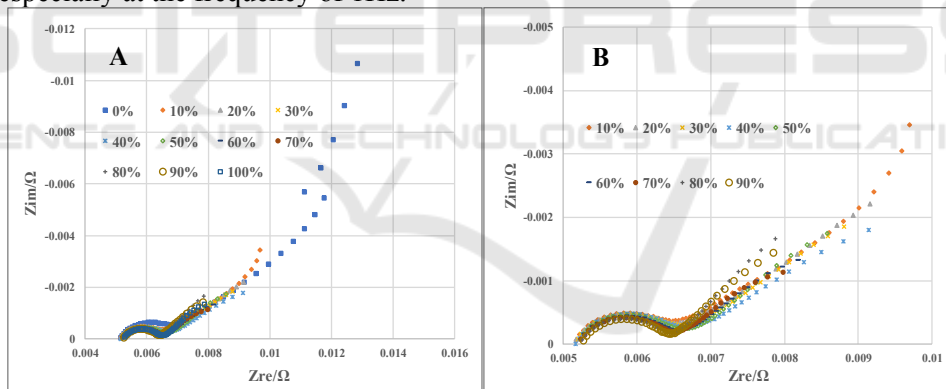


Figure 5. The EIS diagrams for different SOC during discharge.

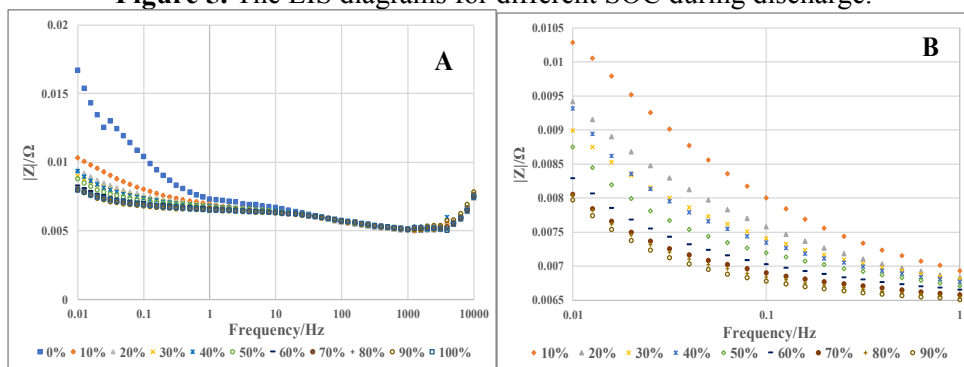


Figure 6. The Frequency- $|Z|$ for different SOC during discharge.

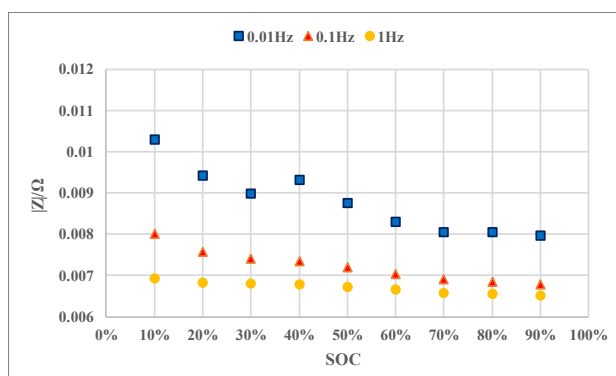


Figure 7. The variation of dynamic impedance with SOC at different frequencies.

3.3. The study on the variation of EIS parameters with SOC

The equivalent fitting circuit is set up according to the EIS diagram in the charging/discharging process as shown in Figure 8. The ohmic internal resistance R_{ohm} includes the connection and contact internal resistance, the resistance of cathode/anode, separator and electrolyte. Both the charge transfer resistance R_{ct} and the Warburg impedance Z_w caused by concentration polarization belong to the polarization internal resistance. The electrochemical polarization is caused when the electrode reaction cannot keep up with the charge accumulation speed, the larger the current density is, the faster the charge accumulates, and the value of R_{ct} will be greater. The Warburg impedance Z_w is related to the solid-state diffusion of Li-ions in the active material particles, which reflects the Warburg diagonal in low frequency section. The double-layer capacitance C_{dl} belongs to the interfacial capacitance, the parallel connection of R_{ct}/C_{dl} represent the Nyquist semicircle.

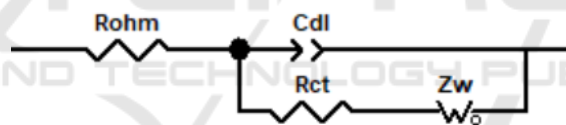


Figure 8. The corresponding equivalent fitting circuit based on the EIS diagram.

The EIS plot is fitted by the equivalent circuit which established above. The changes of different EIS parameters with SOC during charge-discharge are exhibited as Table 2 and Figure 9. When removing the two points of 0%/100% SOC, we can find that the R_{ohm} and C_{dl} increase as the augmentation of SOC. However, the linear relationships between R_{ohm} and SOC are the strongest.

Table 2. The different impedance parameters obtained by equivalent circuit fitting.

	SOC	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
R_{ohm}	Charge	3.95	5	5.05	5.1	5.11	5.14	5.21	5.17	5.21	5.2	4.81
	Discharge	5.25	5.17	5.19	5.2	5.21	5.22	5.23	5.24	5.25	5.28	5.29
R_{ct}	Charge	5.52	0.97	0.87	0.86	0.92	0.9	0.91	0.96	0.87	0.9	0.89
	Discharge	1.21	1.25	1.17	1.24	1.29	1.28	1.21	1.14	1.15	1.07	1.09
C_{dl}	Charge	6.28	2.2	4.17	4.8	5.29	5.17	5.66	6.3	5.22	5.87	8.25
	Discharge	2.3	5.51	4.6	5.2	5.67	6.15	5.83	5.8	6.72	5.82	5.39
Z_w	Charge	41	3.52	3.31	4	3.61	4.48	6.11	5.42	6.21	8.37	86.1
	Discharge	23.8	16.7	13.6	11.1	5.12	5.4	4.27	3.53	5.25	3.9	4.49

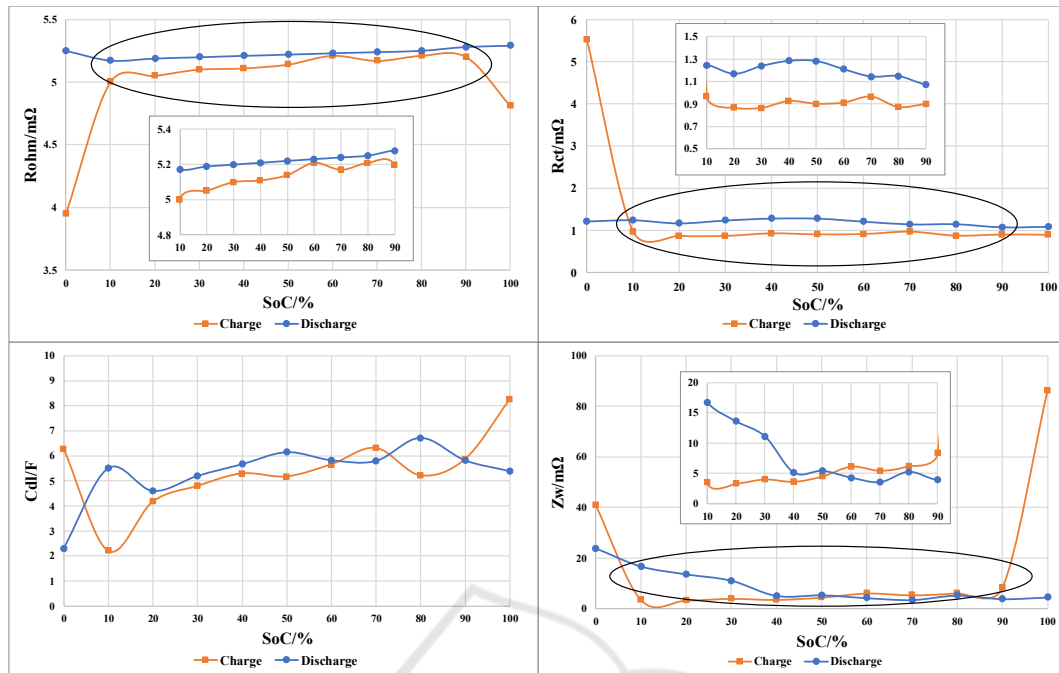


Figure 9. Changes of different EIS parameters with SOC.

The results indicate that it is the most accurate and reliable to predict SOC through the phase angle θ and the dynamic impedance $|Z|$ especially at 0.025Hz and 1Hz when charging and discharging.

4. Conclusions

In normal case, establishing equivalent circuit to fit the electrochemical impedance spectroscopy is usually adopted. The method of analyzing the variation of dynamic total impedance and different electrochemical parameters with SOC have been used in this paper. During this process, the 3.2V/10Ah LiFePO₄ battery has been used in charge and discharge state without static. This method not only fits the actual conditions well but also can reduce the error caused by fitting, thus increasing the reliability of the prediction. EIS analysis results show that the phase angle and the dynamic impedance is proportional/inversely proportional to SOC in a certain frequency domain when charging/discharging respectively. This provides a technical reference for SOC prediction of Lithium ion batteries in varied dynamic conditions.

Acknowledgements

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References

- [1] Pop V, Bergveld H J, Danilov D and et al. 2008 *Springer Netherlands* **181-220** 9.
- [2] Asakura K, Shimomura M and Shodai T 2003 *Journal of Power Sources* **119-121** 902.
- [3] Bergveld H J, Kruijt W S and Notten P H L 2008 *Springer Netherlands* **9-30** 86.
- [4] Mingant R, Bernard J, Moynot V S and et al. 2011 *Ecs Transactions* **41-53** 33.
- [5] Xie C J, Liu J B and Zhao H B 2013 *Advanced Materials Research* **509-512** 823.
- [6] Brandell D, Srivastav S and Lacey M 2015 *Meeting of the International Society of Electrochemistry in Taipei* **55-61** 56.