

# Comments on Internal Alternating Current Resistance Test Standard and Methods of Lithium-Ion Batteries

ZHANG Ya-li<sup>1,2\*</sup>, XIN Sen<sup>1</sup>, GUO Yu-guo<sup>1\*</sup>, WAN Li-jun<sup>1</sup>

(1. *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China;*

2. *Weifang Wina Green Power Co., Ltd., Shouguang 262705, Shandong, China*)

**Abstract:** The sustainable development of energy and environment is one of the most influential issues of this century. Batteries, especially secondary batteries, are important for powering our daily life. However, in many practical applications, such as in electric vehicles and hybrid electric vehicles, batteries should be used in packs and the performance consistency of each battery in the pack should be taken into consideration. As one of the performance parameters being used to characterize the battery consistency, internal resistance is of great importance to the industrial fabrication and the use of batteries. Currently, internal resistance tests of secondary batteries, such as lithium-ion batteries are usually performed in accordance with the International Electrotechnical Commission (IEC) Standard 61960 (2003). This comment addresses the problematic issues in the standard, both from its theoretical basis and its practical use in internal resistance testers, for providing instructional views on new standard setting of the entire battery industry, and hoping it definitely promote the development of sustainable energy devices as well as electric vehicles.

**Key words:** lithium-ion batteries; internal resistance; electrochemical impedance spectroscopy; internal alternating current resistance test standard

**CLC Number:** TM912.9

**Document Code:** A

Batteries, since the beginning of their inventions, are destined to become one of the most important electronic components and power in people's daily life<sup>[1-3]</sup>. Currently, technological improvements in energy industry have been driven by an ever-increasing demand for batteries with high performance. Extensive studies have been focused on further improving the performance of Li-ion batteries<sup>[4-8]</sup>. Internal resistance is an essential performance index for both lithium-ion batteries and batteries of any other types. For battery modules and stacks, which obtain high voltages through the series connection of many batteries, the consistency of each single battery is of great importance<sup>[9]</sup>. Yet the internal resistance is one of

the most important criteria for characterizing the consistency of each single battery. There are two methods to measure the battery internal resistance, namely, the d.c. internal resistance method and the a.c. internal resistance method. The a.c. internal resistance method is fast in measurement and has a small influence on the batteries. Therefore, most battery manufacturers have adopted the a.c. internal resistance method in their production testing. However, there are ignorant problems in the standard, the method and the test instrument of a.c. internal resistance measurement currently used, and the measured internal resistance data are far from the actual values. In spite of this, the situation has lasted for many years,

Received:2011-11-30, Revised:2012-03-23 \* Corresponding author, E-mail: ylzhang@iccas.ac.cn, ygguo@iccas.ac.cn

This work was supported by MOST (No. 2012AA110407, No. 2011CB935700), National Natural Science Foundation of China (No. 21073205, No. 21121063) and the Chinese Academy of Sciences

which is rarely seen in the industrial production. In this paper, we have discussed the present test standard and test method for the a. c. internal resistance of Li-ion battery based on the test result of battery's a. c. internal resistance. Problems in both the standard and the test instrument have been addressed, and the approach for establishing a new test standard for the a. c. internal resistance of battery has been proposed. We hope this paper can provide instructional views on new standard setting of the entire battery industry, and promote the development of sustainable energy devices as well as electric vehicles.

### 1 Comparison Between the Battery Internal Resistance Test Results Obtained by Both the Electrochemical Impedance Spectroscopy and the Internal Resistance Tester

Electrochemical impedance spectroscopy (EIS) and a commercial a. c. internal resistance tester (IRT) have been employed to test the internal resistances of two groups of Li-ion batteries (ten batteries in each group), and their test results are summarized in Fig. 1.  $R_{in}$  represents the data measured by the IRT, and  $Z_{in}$  represents the data measured by EIS method. Obviously, these results obtained from the two methods are far different from each other. Tab. 1 and Tab. 2 compare the results of the two groups of

batteries obtained by the two methods. It can be seen that, for 423450-type rectangular cells, the results acquired by the two methods have a maximum deviation of 8.1 times, and a minimum deviation of 3.2 times. On the other hand, results of 18650-type cylindrical cells have a maximum deviation of 3.8 times, and even the minimum deviation can achieve 2.0 times.

Since there are significant differences between the results obtained by the two methods, one method is sure to be wrong, while the other method could be either correct or wrong. In other words, the problem lies in which method is more convincing, or both methods are problematic.

It is well-known that EIS is one of the most important analysis methods in electrochemical research. This method has application histories of more than 100 years in scientific research and around 70 years in electrochemical research. Since the method has already matured in theories, practices and instruments<sup>[10-14]</sup>, it is reasonably believed that the data measured by EIS method should be true and reliable, and can objectively reflect the actual value of the battery internal resistance. In other words, the data measured by the commercial battery IRT are wrong. In order to find out the origins of these problems, one must examine the test standard, test method and test instrument.

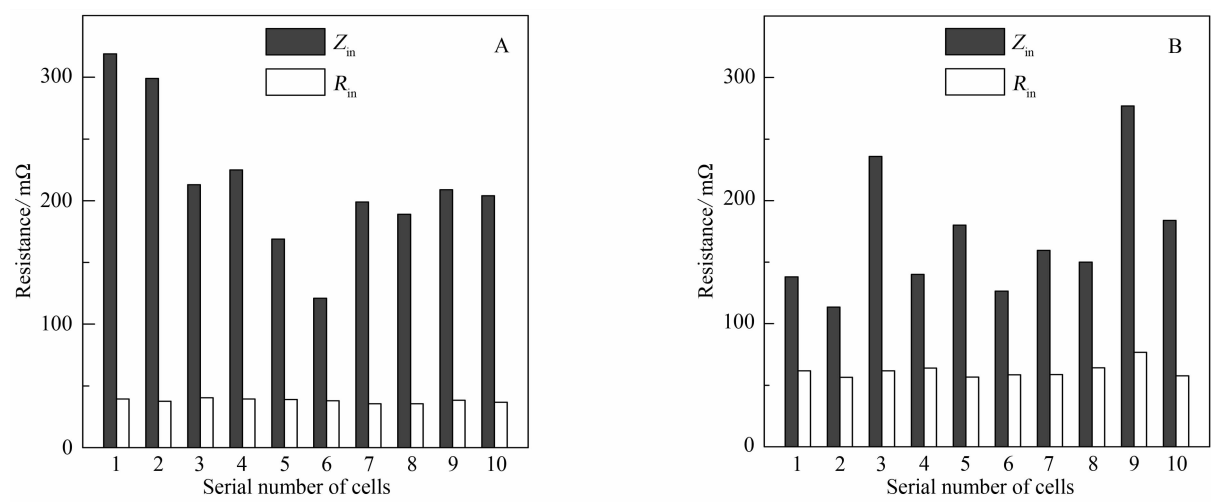


Fig. 1 Comparison between the internal resistance test results of 423450-type batteries (A) and 18650-type batteries (B)  $R_{in}$  is the data obtained with a battery IRT and  $Z_{in}$  is the data obtained by EIS method

Tab.1 Battery IRT test results ( $R_{in}$ ) and EIS test results ( $Z_{in}$ ) of 423450-type rectangular cells

Cell No.	$R_{in}/m\Omega$	$Z_{in}/m\Omega$	$Z_{in}/R_{in}$
1	39.3	319	8.1
2	37.6	299	8.0
3	40.3	213	5.3
4	39.4	225	5.7
5	38.9	169	4.3
6	37.9	121	3.2
7	35.5	199	5.6
8	35.6	189	5.3
9	38.4	209	5.4
10	36.7	204	5.6

Tab.2 Battery IRT test results ( $R_{in}$ ) and EIS test results ( $Z_{in}$ ) of 18650-type cylindrical cells

Cell No.	$R_{in}/m\Omega$	$Z_{in}/m\Omega$	$Z_{in}/R_{in}$
1	61.8	138.0	2.2
2	56.4	113.5	2.0
3	61.8	236.0	3.8
4	63.9	140.0	2.2
5	56.6	180.0	3.2
6	58.5	126.5	2.2
7	58.6	159.5	2.7
8	64.2	150.0	2.3
9	76.7	277.0	3.6
10	57.7	184.0	3.2

2 Standard and Method for Battery  
A. C. Internal Resistance Test

The test standard of battery a. c. internal resistance is established according to the IEC 61960 (2003) Standard, i. e. , *Secondary Cells and Batteries Containing Alkaline or Other Non-Acid Electrolytes-Secondary Lithium Cells and Batteries for Portable Applications*, which is established by the IEC.

According to the IEC 61960 (2003) Standard,

the test method of batteries' internal a. c. resistance is as follows:

1) Apply an alternating root mean square (r.m.s.) current,  $I_a$ , at the frequency of 1.0 kHz, to the battery, for a period of 1 s to 5 s. The alternating current applied on the battery should be selected such that the peak voltage is less than 20 mV.

2) Measure the alternating r.m.s. voltage response.

And the a.c. internal resistance of the battery,  $R_{ac}$ , is given by the following formula,

$$R_{ac} = \frac{U_a}{I_a}(\Omega)$$

(1)

Wherein,  $U_a$  is the alternating r.m.s. voltage;  $I_a$  is the alternating r.m.s. current.

To further discuss the above-mentioned test method and calculation formula, one should first look at the background knowledge concerned with the alternating current.

A sine-wave alternating current can be expressed as,

$$I = I^0 = \sin(\omega t)$$

(2)

Wherein,  $I$ ,  $I^0$ ,  $\omega$  and  $t$  respectively denote the alternating current, the amplitude, the angular frequency and the time.

After the sine-wave alternating current has been applied onto a circuit component, the voltage response is still a sine-wave, while its phase may change,

$$V = V^0 \sin(\omega t + \varphi)$$

(3)

for a pure resistor  $R$ ,  $\varphi = 0$ , i. e. , there is no phase change; for a pure capacitor  $C$ ,  $\varphi = -\pi/2$ , i. e. , the voltage lags the current by  $90^\circ$ ; for a pure inductor  $L$ ,  $\varphi = \pi/2$ , i. e. , the voltage leads the current by  $90^\circ$ ; and for a circuit composed of resistor(s) and capacitor(s),  $0 > \varphi > -\pi/2$ .

However, when coming to the r.m.s. values of an alternating current, things may be different. The r.m.s. voltage is the effective value of an alternating voltage, i. e. , the voltage value with the same effectiveness as the d.c. voltage. The sine-wave a.c. voltage is a function of time and frequency,

$$V(t) = V^0 \sin(\omega t)$$

(4)

Wherein,  $V(t)$  is the voltage value at the moment of  $t$ ,  $V^0$  is the peak value or the amplitude, and  $\omega$  is the angular frequency,  $\omega = 2\pi f$ , where  $f$  is the frequency.

Then the r.m.s. voltage  $V_{\text{rms}}$  is,

$$V_{\text{rms}} = V^0 / \sqrt{2}$$
 (5)

The r.m.s. current has the same form.

Therefore, in Eq. (1) of the IEC 61960 (2003) Standard, whether the voltage  $U_a$  and the current  $I_a$  adopt their peak values or r.m.s. values, the calculation results should be the same.

However, a battery is a complex system, and its equivalent circuit usually contains both resistor(s) and capacitor(s). Therefore, the voltage response towards the sine-wave current applied during the battery internal resistance test is a sine-wave with different phase from that of the current. At this time, the resistance of the battery is,

$$Z = \frac{V^0 \sin(\omega t + \varphi)}{I^0 \sin(\omega t)} = \frac{V^0}{I^0} \cdot \frac{\sin(\omega t + \varphi)}{\sin(\omega t)} = \frac{V^0}{I^0} \cos\varphi + j \frac{V^0}{I^0} \sin\varphi$$
 (6)

And it is a complex impedance rather than a pure resistance.

In the calculation formula Eq. (1) of the IEC 61960 (2003) Standard, the resistance is obtained simply by the division of the r.m.s. values (or the amplitudes) of the response voltage and the disturbance current. However, in consideration of the phase difference, Eq. (1) is only suitable for the pure resistance system, and may not be applied to the actual battery system. From what has been discussed above, it is clear that Eq. (1) means nothing but a computing formula taken for granted. Since the test method is theoretically unwarranted and paradoxical, its results have no specific physical significance, thus can not mirror the actual internal resistance of the battery.

3 Analysis of the A. C. Voltage Response in the A. C. Internal Resistance Test of Li-Ion Batteries

Fig.2 shows a typical electrochemical a. c. impedance spectrum of a rectangular Li-ion battery

(Type: 423450), which is similar to the a. c. impedance spectra of other types of Li-ion batteries. Wherein, the horizontal axis is the real part of the impedance, and the vertical axis is the imaginary part.

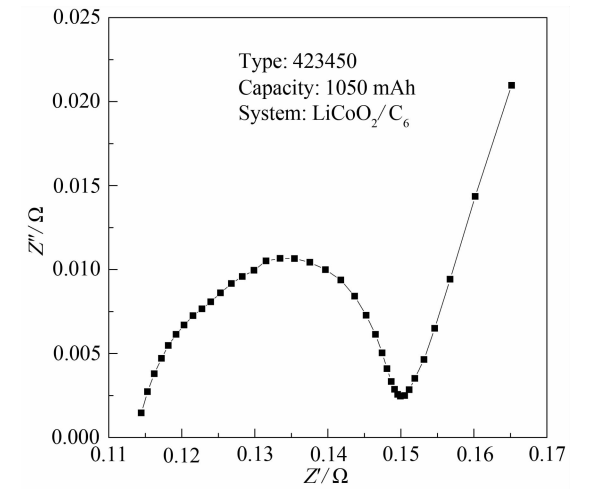


Fig.2 A. C. impedance spectrum of a Li-ion battery

From the understanding to the electrode process of a Li-ion battery, in combination with the a. c. impedance spectrum in Fig. 2, a Li-ion battery can be expressed as the following simplified equivalent circuit (Fig. 3).

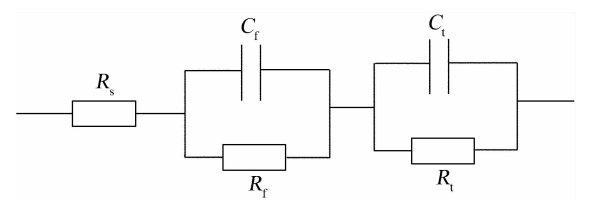


Fig.3 Simplified equivalent circuit of a Li-ion battery

Wherein,  $R_s$  represents the ohmic internal resistance,  $R_t$  represents the resistance of the surface film,  $C_t$  represents the geometric capacitance of the surface film,  $R_i$  represents the charge transfer resistance, and  $C_i$  represents the electrochemical double-layer capacitance.

Given the alternating current applied on the battery is

$$i = I^0 \sin\omega t$$
 (7)

Wherein,  $I^0$  is the module of the alternating current,  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ,  $f$  is the frequency), and  $t$  is the time.

Given the total alternating voltage applied on the circuit is  $U$ , the voltage on  $R_s$  is  $U_s$ , and the voltages on the parallel units  $C_f R_f$ , and  $C_t R_t$  are  $U_f$  and  $U_t$ , respectively, the following formulas are obtained:

$$U = U_s + U_f + U_t \quad (8)$$

$$U_s = R_s I^0 \sin(\omega t) \quad (9)$$

The voltage applied at both ends of  $C_f$  and  $R_f$  are the same, while the current flowing through the two components are  $i_{C_f}$  and  $i_{R_f}$ , respectively, and their sum is  $i$ .

$$i_{R_f} = \frac{U_f}{R_f} \quad (10)$$

$$i_{C_f} = C_f \frac{dU_f}{dt} \quad (11)$$

$$i_{R_f} + i_{C_f} = i = I^0 \sin(\omega t) \quad (12)$$

That is

$$\frac{dU_f}{dt} = -\frac{1}{R_f C_f} U_f + \frac{I^0}{C_f} \sin(\omega t) \quad (13)$$

The solution to above differential equation can be expressed as

$$U_f = \exp\left(-\int \frac{dt}{R_f C_f}\right) \left\{ K + \int \left[ \frac{I^0}{C_f} \sin(\omega t) \right] \cdot \exp\left(\int \frac{dt}{R_f C_f}\right) dt \right\} \quad (14)$$

Where  $K$  is the integral constant.

After transformation, the solution can be expressed as

$$U_f = \frac{I^0}{\omega C_f} \exp\left(-\frac{\omega t}{\omega R_f C_f}\right) \int \sin(\omega t) \cdot \exp\left(\frac{\omega t}{\omega R_f C_f}\right) d(\omega t) \quad (15)$$

And  $U_f$  may be solved as

$$U_f = \frac{R_f I^0}{1 + (\omega R_f C_f)^2} [\sin(\omega t) + \omega R_f C_f \cos(\omega t)] \quad (16)$$

Similarly,  $U_t$  may be solved as

$$U_t = \frac{R_t I^0}{1 + (\omega R_t C_t)^2} [\sin(\omega t) + \omega R_t C_t \cos(\omega t)] \quad (17)$$

The alternating voltage response on the battery is the sum of the three parts:

$$U = U_s + U_f + U_t = R_s I^0 \sin(\omega t) + \frac{R_f I^0}{1 + (\omega R_f C_f)^2} [\sin(\omega t) + \omega R_f C_f \cos(\omega t)] +$$

$$\frac{R_t I^0}{1 + (\omega R_t C_t)^2} [\sin(\omega t) + \omega R_t C_t \cos(\omega t)] \quad (18)$$

Wherein,  $U_s$  is the voltage on the ohmic internal resistance, and the voltage  $U_p$  on the polarized internal resistance is the sum of the last two terms, that is

$$U = U_s + U_p = U_s + (U_f + U_t) \quad (19)$$

It is not hard to prove that above analysis remains valid for more complex equivalent circuits, which are simulated for actual Li-ion batteries (see appendix).

The voltage response on the battery may be expressed as a more common form,

$$U = A(\omega) \sin(\omega t + \varphi) \quad (20)$$

Its module  $A$  relates to  $\omega$ ,  $I^0$ ,  $R_f$ ,  $R_t$ ,  $C_f$ , and  $C_t$ , and has a phase difference of  $\varphi$  with the alternating current.

Eq. (18) can be transformed as

$$U = I^0 \sqrt{a^2 + b^2} \left[ \sin(\omega t + \arcsin \frac{b}{\sqrt{a^2 + b^2}}) \right] \quad (21)$$

Wherein,

$$a = R_s + \frac{R_f}{1 + (\omega R_f C_f)^2} + \frac{R_t}{1 + (\omega R_t C_t)^2} \quad (22)$$

$$b = \omega \left[ \frac{R_f}{1 + (\omega R_f C_f)^2} R_f C_f + \frac{R_t}{1 + (\omega R_t C_t)^2} R_t C_t \right] \quad (23)$$

When compared with Eq. (20), the following formulas are obtained:

$$A(\omega) = I^0 \sqrt{a^2 + b^2} \quad (24)$$

$$\varphi = \arcsin \frac{b}{\sqrt{a^2 + b^2}} \quad (25)$$

Both of them are the functions of the angular frequency  $\omega$ . That is to say, although the same alternating current has been applied onto the battery, the module and the phase difference for the voltage response of the battery may change as the current frequency has changed.

Fig. 4 is a schematic diagram in accordance with Eq. (18) and Eq. (19). The ohmic internal resistance and the applied voltage have the same phase, while the polarized internal resistance has certain

phase difference, and the total voltage on the battery is the sum of the two.

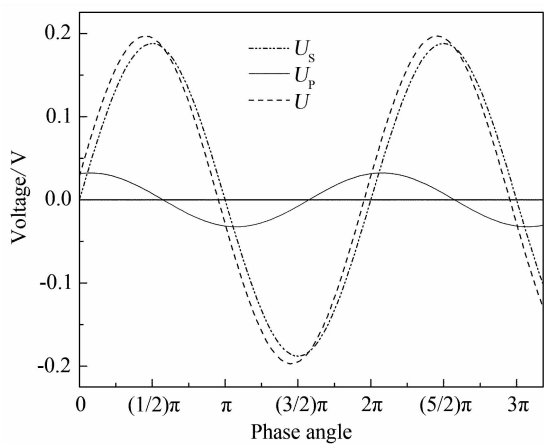


Fig. 4 Alternating voltage responses during the a. c. internal resistance test of a Li-ion battery, in which  $U_s$  is the voltage on the ohmic internal resistance,  $U_p$  is the voltage on the polarized internal resistance, and  $U$  is the total voltage

#### 4 The Internal Resistance Test of the Battery IRT

According to the IEC 61960 (2003) Standard, the battery a. c. IRT obtains the internal resistance of the battery by measuring the r. m. s. value of the response voltage, and dividing the value by the r. m. s. value of the set known current. As mentioned above, the standard is theoretically incorrect. Therefore, the internal resistance value measured by the battery IRT according to such standard is far from the actual value.

The a. c. impedance of the battery should be the ratio of Eq. (21) and Eq. (7), that is,

$$Z_{in} = \frac{U}{I} = \frac{I^0 \sqrt{a^2 + b^2} \sin(\omega t + \varphi)}{I^0 \sin(\omega t)} = \sqrt{a^2 + b^2} \cdot \frac{\sin(\omega t + \varphi)}{\sin(\omega t)} \quad (26)$$

However, the result obtained from the measurement based on the IEC 61960 (2003) Standard is

$$R_{in} = \sqrt{a^2 + b^2} \quad (27)$$

While the actual result should be

$$Z_{in} = \sqrt{a^2 + b^2} \cdot \frac{\sin(\omega t + \varphi)}{\sin(\omega t)} \quad (28)$$

The ratio of the real internal resistance of a battery and the internal resistance measured by a commercial battery a. c. IRT is related to the phase difference of the a. c. current applied. It can be concluded from Eq. (22), Eq. (23) and Eq. (25) that, in case of a selected frequency, the phase difference is related to  $R_f$ ,  $R_t$ ,  $C_f$  and  $C_t$ . Since a battery is a complex system, it may not be either a pure resistor or a pure capacitor, the phase difference  $\varphi$  should lie between  $0 \sim \pi/2$ . It can be seen from Eq. (28) that, when  $\varphi = 0$  (in case of pure resistor),  $Z_{in} = R_{in}$ , when  $\varphi \neq 0$ , the difference between the two will increase with the increase of the phase difference. From the data actually measured on the 423450-type rectangular cells and the 18650-type cylindrical cells, the differences can be  $2 \sim 8$  times.

When measuring, a commercial alternating IRT will apply an alternating current to the battery, and detect its alternating voltage response. However, no description has been made in the specification about the sampling method for the voltage response of battery. It is clear that most of a. c. IRTs carry out com-

Tab. 3 Parameters of a battery IRT obtained from Hioki E. E. Corporation

Sampling	Ex. Fast	Fast	Medium	Slow
$\Omega V$ (50 Hz)	7 ms	23 ms	83 ms	258 ms
(60 Hz)			69 ms	251 ms
$\Omega$ (50 Hz)	4 ms	12 ms	42 ms	157 ms
(60 Hz)			35 ms	150 ms
V (50 Hz)	4 ms	12 ms	42 ms	157 ms
(60 Hz)			35 ms	150 ms

mutations on the voltage responses first, then obtain the a. c. internal resistances by measuring the d. c. voltage after commutation (i.e., the so called r.m.s. voltage), and dividing it with the r.m.s. value of a known a. c. current.

For example, when measure the a.c. voltage responses of a battery, the battery IRT (Hioki E. E. Corporation) test samples according to the following sampling periods (see Tab. 3)<sup>[15]</sup>.

The sampling method of the response voltage was not explained in the specification. If according to the method of the IEC 61960 (2003) Standard, the r. m. s. value of the response voltage should be taken, that is, measuring the effective value of the corresponding voltage within the sampling period. In that case, the same analysis as above-mentioned one will be applicable. If the response voltage is sampled at a given time, the following analysis may be applied.

The phase angle of the ohmic voltage  $U_s$  is  $2\pi ft$ , since  $f = 1000$  Hz, the phase angle is  $2000\pi t$ . In the minimum sampling period of 4 ms, the phase angle at sampling is  $8\pi$  while in the maximum sampling period of 258 ms, the phase angle at sampling is  $516\pi$ , which are all at the phase of  $n\pi$ . At this phase,  $U_s = 0$ , and the result detected by the IRT excludes the measurement of the voltage on the ohmic internal resistance. In other words, the measured result does not include the contribution from the ohmic internal resistance. Besides,  $U_p$  generally does not reach its peak value. Therefore, the result given by the a. c. IRT may not reflect the actual internal resistance of the battery.

## 5 Looking for New Industrial Standard and Measurement Method for Battery A. C. Internal Resistance Test

The foregoing analysis has shown that, the IEC 61960 (2003) Standard and its method can not correctly measure the internal resistance of the battery. Therefore, a new standard must be established, and new methods must be found to measure the internal resistance of battery.

The use of a. c. impedance spectroscopy (electrochemical impedance spectroscopy, EIS) can not only obtain the actual internal resistance of the battery, but distinguish the ohmic internal resistance from the polarized internal resistance as well. The ohmic internal resistance represents the sum of the resistance of the metallic conductor in the battery, the resistance at the welding joint or the rivet joint, and other types of the contact resistances. However, the polarized resistance represents the difficulty of the electrochemical process in the battery, and the two resistances are completely different in their natures. In view of analyzing and improving the battery products, the separation of the two types of resistances is beneficial. Besides, considering the criteria for the consistency of batteries, and especially the consistency for long-term operations of batteries, the use of the ohmic internal resistance and the polarized internal resistance has a larger superiority than the use of the total resistance.

In view of taking EIS as the method for the battery internal resistance test, there are no problems in establishing the test standard and test method. There will also be no problems in the development of specified detecting equipments. Current techniques on microelectronics, computers and software are sufficient for designing and manufacturing the detecting instrument with a comparable price to current battery IRT. To sum up, we hope a new standard and its corresponding method can be established to lead the industry, and new testers in accordance with the standard should be manufactured. Solving these challenges will require a wide collaboration from both scientific research and industry in the International Electrotechnical Commission, and their success will definitely promote the developments of sustainable energy devices as well as electric vehicles.

## 6 Appendix

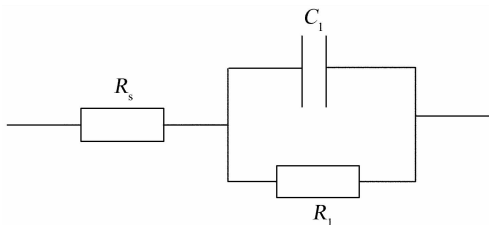
### Deductions Associated with Circuit Transformation and Mathematical Reasoning

Internal resistance ( $R_i$ ) is a concept that helps to model the electrical consequences of the complex chemical reactions inside a battery. In a typical lithi-

um-ion battery, it can usually be expressed as the combination of the following two parts: the ohmic internal resistance ( $R_{\text{ohm}}$ ) and the polarized internal resistance ( $R_f$ ), as seen in Eq. S(1):

$$R_i = R_{\text{ohm}} + R_f \quad \text{S(1)}$$

Generally,  $R_{\text{ohm}}$  is a kind of physical resistance related to the electronic and ionic conductions, and obeys the Ohm's law; while  $R_f$  is often associated with the electrochemical process in the battery, i. e. the process in which electric charges migrate through the phase interface. In the simplest case, a lithium-ion battery can be expressed as the following equivalent circuit:



Scheme S1 Simplified equivalent circuit sketch of a lithium-ion battery

As can be seen in Scheme S1,  $R_s$  denotes the ohmic internal resistance,  $R_1$  denotes the polarized internal resistance, and  $C_1$  denotes the capacitor corresponding to it. Given the alternating current applied on the battery is:

$$i = I^0 \sin \omega t \quad \text{S(2)}$$

Where  $I^0$  is the module of alternating current,  $\omega$  is the angular frequency ( $\omega = 2\pi f$ , and  $f$  is the frequency), and  $t$  is the time.

Given the total alternating voltage applied on the circuit is  $U$ , the voltage on  $R_s$  is  $U_s$ , and the voltage on parallel units  $C_1$  and  $R_1$  is  $U_1$ , and the following two equations are obtained:

$$U = U_s + U_1 \quad \text{S(3)}$$

$$U_s = R_s I^0 \sin(\omega t) \quad \text{S(4)}$$

It can be seen from Scheme S1 that the voltages on  $C_1$  and  $R_1$  are of the same value. Given the currents flow through these two components are  $i_{C_1}$  and  $i_{R_1}$ , respectively, and their sum is  $I$ , Eq. S(5) to Eq. S(7) can be established:

$$i_{R_1} = \frac{U_1}{R_1} \quad \text{S(5)}$$

$$i_{C_1} = C_1 \frac{dU_1}{dt} \quad \text{S(6)}$$

$$i_{R_1} + i_{C_1} = i = I^0 \sin(\omega t) \quad \text{S(7)}$$

that is,

$$\frac{dU_1}{dt} = -\frac{1}{R_1 C_1} U_1 + \frac{I^0}{C_1} \sin(\omega t) \quad \text{S(8)}$$

Solution to the above differential equation with regard to  $U_1$  (Eq. S(8)) can be expressed as:

$$U_1 = \exp\left(-\int \frac{dt}{R_1 C_1}\right) \left\{ K + \int \left[ \frac{I^0}{C_1} \sin(\omega t) \cdot \exp\left(\int \frac{dt}{R_1 C_1}\right) dt \right] \right\}, \text{ where } K \text{ is the integral constant.}$$

After the transformation, the solution can be expressed as

$$U_1 = \frac{R_1 I^0}{1 + (\omega R_1 C_1)^2} \left[ \sin(\omega t) + \omega R_1 C_1 \cos(\omega t) \right] \quad \text{S(9)}$$

According to Eq. S(3), the total alternating voltage on the battery is the sum of  $U_s$  and  $U_1$ . Therefore, Eq. S(4) and Eq. S(9) can be substituted into Eq. S(3), and the following deduction is established:

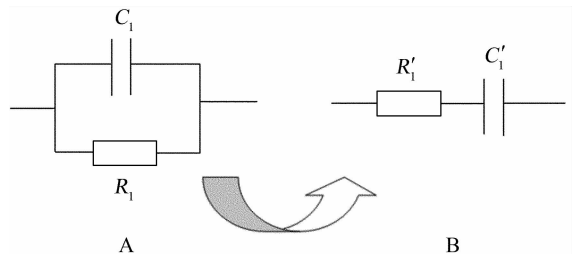
$$U = U_s + U_1 = R I^0 \sin(\omega t) + \frac{R_1 I^0}{1 + (\omega R_1 C_1)^2} \left[ \sin(\omega t) + \omega R_1 C_1 \cos(\omega t) \right] \quad \text{S(10)}$$

It is also noteworthy that the expression of  $U_1$  can be solved through the following method, which can be more convenient since no differential equation is required to solve.

The parallel circuit, as shown in Scheme S2 A, can be converted into the series circuit in Scheme S2 B, hence the following two equations are obtained, where  $Z$  denotes the total impedance of circuit (A), whereas  $Z'$  denotes the total impedance of circuit (B):

$$Z = \frac{1}{\frac{1}{R_1} + j\omega C_1} = \frac{R_1}{1 + (\omega R_1 C_1)^2} - j \frac{\omega R_1^2 C_1}{1 + (\omega R_1 C_1)^2} \quad \text{S(11)}$$

$$Z' = R'_1 - j \frac{1}{\omega C_1} \quad \text{S(12)}$$



Scheme S2 Simplified circuit sketches of (A) the parallel circuit and (B) the series circuit

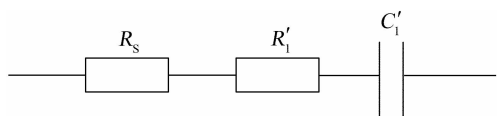
The two circuits are equivalent, i. e.,  $Z = Z'$ ; therefore,  $R'_1$  and  $C'_1$  can be respectively expressed as:

$$R'_1 = \frac{R_1}{1 + (\omega R_1 C_1)^2} \quad S(13)$$

$$C'_1 = \frac{1 + (\omega R_1 C_1)^2}{\omega^2 R_1^2 C_1} \quad S(14)$$

As long as above substitutions are conducted, these two circuits are equivalent to each other. In this way, the circuit in Scheme S1 can be transformed to the following circuit as shown in Scheme S3.

Since all the components are series-connected in the above circuit, it can be much easier to solve the voltage on the battery after the alternating current is applied, wherein voltage on  $R_s$  ( $U_s$ ) can be related to the ohmic internal resistance, and voltage on series-connected  $R'_1$  ( $UR'_1$ ) and  $C'_1$  ( $UC'_1$ ) can be related to the polarized internal resistance.



Scheme S3 Simplified circuit sketch equivalent to the one in Scheme S1

$$U_s = R_s I^0 \sin(\omega t) \quad S(15)$$

$$U_{R'_1} = R'_1 I^0 \sin(\omega t) \quad S(16)$$

$$U_{C'_1} = \frac{1}{C'_1} \int i dt = -\frac{1}{\omega C'_1} I^0 \cos(\omega t) \quad S(17)$$

Since  $U_1$  is the combination of  $UR'_1$  and  $UC'_1$ ,

$$U_1 = U_{R'_1} + U_{C'_1} = R'_1 I^0 \sin(\omega t) + \frac{1}{\omega C'_1} I^0 \cos(\omega t) \quad S(18)$$

After substituting Eq. S(13) and Eq. S(14) into Eq. S(18), Eq. S(9) will also be obtained:

$$U_1 = \frac{R_1 I^0}{1 + (\omega R_1 C_1)^2} [\sin(\omega t) + \omega R_1 C_1 \cos(\omega t)] \quad S(9)$$

Based on the above analysis, any circuit, no matter how complicated it is, can be finally converted to a simple series circuit.

## Acknowledgments

The authors thank Dong-Dong Fan for providing the internal resistance test results of 423450-type battery and 18650-type battery.

## References:

- [1] Armand M, Tarascon J M. Building better batteries[J]. Nature, 2008, 451(7179): 652-657.
- [2] Maier J. Nanoionics: Ion transport and electrochemical storage in confined systems[J]. Nature Materials, 2005, 4(11): 805-815.
- [3] Whittingham M S. Lithium batteries and cathode materials[J]. Chemical Reviews, 2004, 104(10): 4271-4302.
- [4] Arico A S, Bruce P, Scrosati B, et al. Nanostructured materials for advanced energy conversion and storage devices[J]. Nature Materials, 2005, 4(5): 366-377.
- [5] Balaya P. Size effects and nanostructured materials for energy applications[J]. Energy & Environmental Science, 2008, 1(6): 645-654.
- [6] Bruce P G, Scrosati B, Tarascon J-M. Nanomaterials for rechargeable lithium batteries[J]. Angewandte Chemie International Edition, 2008, 47(16): 2930-2946.
- [7] Guo Y G, Hu J S, Wan L J. Nanostructured materials for electrochemical energy conversion and storage devices[J]. Advanced Materials, 2008, 20(15): 2878-2887.
- [8] Li H, Wang Z, Chen L, et al. Research on advanced materials for Li-ion batteries[J]. Advanced Materials, 2009, 21(45): 4593-4607.
- [9] Berdichevsky G, Kely K, Straubel J, et al. The tesla roadster battery system. Tesla Motors. 2006: 1-5.
- [10] Barsoukov E, Macdonald J R. Impedance spectroscopy: Theory, experiment and applications[M]. 2nd Ed. Hoboken: John Wiley & Sons, Inc., 2005: 1-616.
- [11] Orazem M E, Tribollet B. Electrochemical impedance spectroscopy[M]. Hoboken: John Wiley & Sons, Inc., 2008: 1-525.
- [12] Maier J. Physical chemistry of ionic materials: Ions and electrons in solids[M]. Chichester: John Wiley & Sons, Ltd, 2004: 1-537.

- [13] Bard A J, Faulkner L R. Electrochemical methods: Fundamentals and applications [M]. 2nd Ed. New York: John Wiley & Sons, Inc., 2000: 1-856.
- [14] Lee J S, Jamnik J, Maier J. Generalized equivalent circuits for mixed conductors; Silver sulfide as a model system [J]. Monatshefte für Chemie/Chemical Monthly, 2009, 140(9): 1113-1119.
- [15] HIOKI E. E. Corporation. Product Catalog of 3561 Battery HiTESTER [EB/OL]. [http://www.hioki.com/product/pdf/3561E1-56E-05U\\_web.pdf](http://www.hioki.com/product/pdf/3561E1-56E-05U_web.pdf).

## 对工业电池交流内阻测量的讨论

张亚利<sup>1,2\*</sup>, 辛 森<sup>1</sup>, 郭玉国<sup>1\*</sup>, 万立骏<sup>1</sup>

(1. 中国科学院化学研究所, 北京 100190; 2. 潍坊威能环保电源有限公司, 山东 寿光 262705)

**摘要:** 能源和环境的可持续发展是本世纪最重要的问题之一。二次电池是具有重要意义的高效储能器件, 在电动汽车及混合动力汽车等实际应用中, 经常会用到电池组, 此时需要考虑电池组中每一个单体电池性能的一致性。内阻作为用于表征电池一致性的性能参数之一, 对电池的工业制造和使用非常重要。目前, 锂离子电池等二次电池的内阻测试都是按照国际电工委员会第 61960 号标准(2003)来进行的。本文从该标准的理论基础和其在内阻测试仪中的实际应用等方面出发, 分析并指出了该测试标准中的问题, 希望能为电池行业新标准的建立提供一定的指导, 并有助于可持续能源设备及电动汽车用动力电池的开发。

**关键词:** 锂离子电池; 内阻; 电化学阻抗谱方法; 交流内阻测试标准