Development of Lithium-ion Battery Deterioration Diagnosis Technology

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Deterioration of lithium-ion batteries is observed after repeated charge/discharge cycles or long term storage. The deterioration often appears as a decrease in capacity or increase in internal impedance of the batteries. Measuring alternating-current resistance (ACR) using a frequency response analyzer (FRA) is a well-known method for battery deterioration analysis. This paper introduces a newly developed Yokogawa technology for estimating ACR through any waveforms. This technology implies the possibility of in-situ battery deterioration diagnosis. To verify the feasibility for vehicles, actual voltage and current waveforms of running vehicles were used.

INTRODUCTION

Yokogawa has been aiming at providing total battery solutions not only in the areas of research and development of batteries, but also in newly expanded areas such as their production, operation, secondary use, and recycling. Since 2011, these results have been provided for battery manufacturers and users as battery measurement solutions.

Recently, reflecting safety issues, battery monitoring technology during operation is attracting attention. At present, monitoring of voltage and temperature of battery cells is an essential function. Yokogawa considers that monitoring battery deterioration will also come to be an important function, and Yokogawa is continuing research and development on related technologies.

This paper introduces a core technology achieved by Yokogawa's research and development teams and the feasibility of the deterioration diagnosis of in-vehicle batteries, clarified through joint research with Honda R&D Co., Ltd. (hereafter referred to as Honda).

BACKGROUND

It is known that lithium-ion batteries deteriorate after repeated charge/discharge cycles or long term storage, resulting in decreases in capacity or increases in internal impedance of the batteries. Thus, many studies using alternating-current resistance (ACR) characteristics measured by a frequency response analyzer (FRA) as a method to analyze the deterioration have been reported [(1)].

However, at the site where batteries are operating, it is difficult to expect an ideal measurement environment similar to that in laboratories. For example, measuring their alternating-current response for analysis while suspending their operations is not practical when considering the cost and operation for the measurement.

To resolve this problem, Yokogawa has developed a new technology that enables the estimation of the ACR from the waveforms during operation of batteries, without performing measurement for diagnoses requiring battery operation suspension. Assuming the use of this technology in vehicles, its feasibility has been verified by using vehicle running patterns derived from acceleration control assumed for a town area with acceleration control [(2)].

ACR ESTIMATION TECHNOLOGY USING THE SIGNAL WAVEFORMS OF OPERATING BATTERIES

Usually, in ACR measurement, a response to an alternating signal at a desired frequency is measured, and then ACR is calculated from it by using the discrete Fourier transform (DFT) or the fast Fourier transform (FFT).

The newly developed technology uses the inverse Laplace transform to estimate ACR from any signal waveforms of batteries under operation. This method can eliminate such decrease in calculation accuracy as seen when using the DFT or FFT, which is caused by the discontinuity of data at both ends of the selected interval of a waveform for integration.

The waveform data obtained is divided into step responses at appropriate time intervals. This processing makes it easier to perform a calculation using the inverse Laplace transform, allowing fast calculation while keeping estimation accuracy. The divided waveform data is used to decide the constants of a pre-defined equivalent circuit model for batteries, and then the estimated ACR at an intended frequency is calculated from the obtained circuit constants.

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Thus, this method can theoretically calculate ACR from any response waveform. Figure 1 shows the flow of this processing.

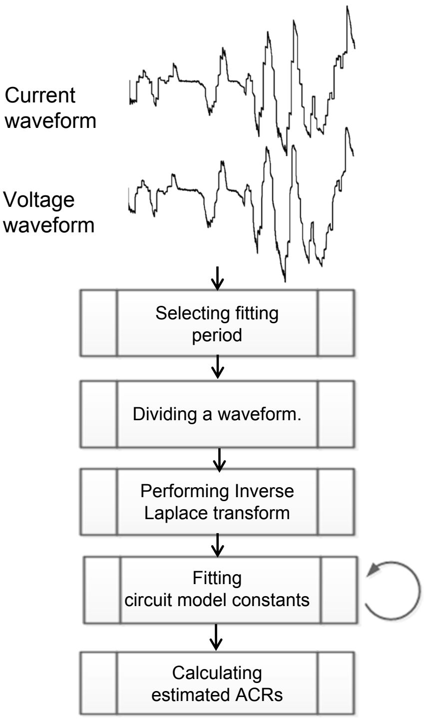

Figure 1 Flow of calculation processing for ACR estimation

OVERVIEW OF VERIFICATION TEST

In this verification test, the waveforms obtained from batteries in a vehicle running pattern assumed for a town area were used. All of the seven battery cells under the test are those for automotive application. One of them is almost new, and the other six differ in degrees of deterioration, with capacity retention ranging from 57.2 to 85.4%. Note that temperatures of all battery cells are controlled in a thermostat chamber. Figure 2 shows the measurement system. The measured voltage and current data are sent to the PC for measurement. The calculation for estimating ACR is also performed in this PC.

Figure 3 shows the equivalent circuit model for the batteries used. For example, when the current is applied following a unit step function u(t), 0 A when t < 0 and 1 A when t >= 0, the voltage waveform in response is expressed by the following equation:

$$v(t) = \left(R_1 + \sum_{n=2}^{3} R_n \left(1 - e^{-\frac{t}{R_n C_n}} \right) + \frac{T_4 t^{P_4}}{\Gamma(P_4+1)} + R_5 e^{-\frac{R_5}{L_5}t} \right) u(t)$$

In this equation, R_1, R_2, C_2, R_3, C_3, and CPE_4 (P_4 and T_4) are the constants to be decided through fitting for estimating ACR using the vehicle running pattern. CPE_4 is a constant phase element (CPE), and P_4 is a CPE exponent, and T_4 is a CPE constant. CPE_4 is used to express the diffused resistance part of the batteries. Because R_5 and L_5 mainly depend on the internal structure of the battery, and are not affected by its deterioration, they are regarded as fixed constants, which are obtained through separate fitting by using regular alternating signals.

In addition, ACRs are measured by an impedance analyzer using regular alternating signals for reference under various conditions of temperature and state of charge (SOC).

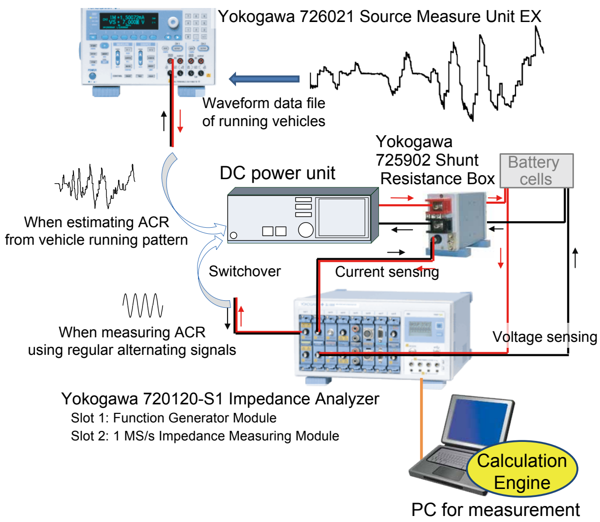

Figure 2 Measurement system for the verification test

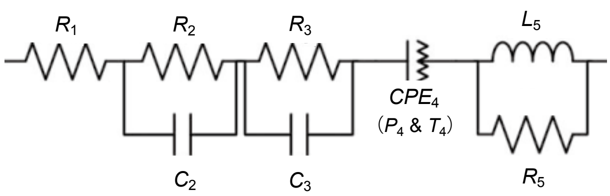

Figure 3 Equivalent circuit model used for fitting

TEST RESULTS

Under various measurement conditions, the differences between the measured ACRs and those estimated from the vehicle running pattern were confirmed for the seven battery cells.

Under the conditions of 25 °C temperature and 50% battery SOC, as shown in Figure 4, the differences in absolute values of impedance between the measured and estimated ACRs are less than ±5% in the range from 0.1 Hz to 1 kHz, except for the most deteriorated cell (no. 7) with 57.2% of capacity retention. Figure 5 shows the comparison of the measured and estimated ACRs using Nyquist diagrams.

Under these conditions, the ACRs estimated from the vehicle running pattern indicate the characteristics close to the measured ACRs.

This means that the deteriorated state of batteries in vehicles during operation can be monitored by keeping the ACR deterioration characteristic of batteries, which are obtained in a laboratory, in the vehicles for reference.

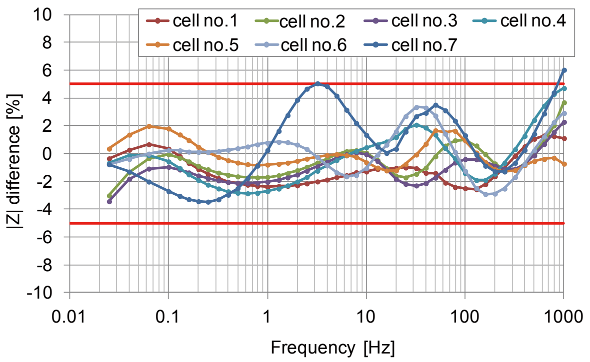

Figure 4 Differences in the absolute value of impedance between the measured ACRs and estimated ACRs

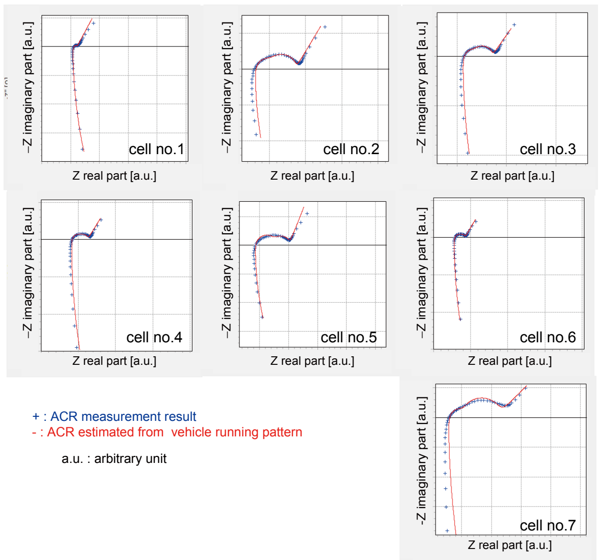

Figure 5 Comparison of the Nyquist diagrams of the measured and estimated ACRs

Meanwhile, under the conditions of low temperatures of -10 °C or low battery SOC of 10%, relatively large differences between the measured and estimated ACRs are seen.

We consider that these differences are due to the difference of both static and dynamic characteristics. It can be said that the measurements of ACR measure static characteristics by using stable simple harmonic oscillation signals, and that the ACR estimated from the vehicle running pattern estimates dynamic characteristics by using signals dynamically fluctuating at a high current rate, with no periodicity and under the conditions of relatively large-scale self-heating and SOC fluctuation.

We supposed that the large differences had arisen because the ACRs to be obtained were easily affected by these characteristics, especially under the conditions of low temperature or low SOC.

To validate this assumption, we compared the actual pulse response with the simulated response estimated from the ACR measurement. The former represents the actual dynamic characteristics, and the latter represents the simulated dynamic characteristics derived from the static characteristics. The voltage drop five seconds after the pulse application was compared.

Figure 6 shows the measurement and simulation results for cell no. 1 at 50% of SOC and 25 °C temperature. The difference of the results between them is approximately 4%. Figure 7 shows the results for the same cell at 10% of SOC and –10 °C of temperature. In this case, the difference is approximately 17%.

Consequently, it was confirmed that remarkable differences in internal impedance of batteries arise depending on whether static or dynamic characteristics are measured.

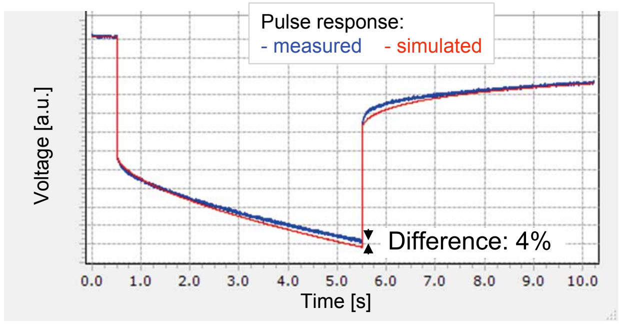

Figure 6 Measured pulse response and its simulation for cell no. 1 at 50% of SOC and 25 °C temperature

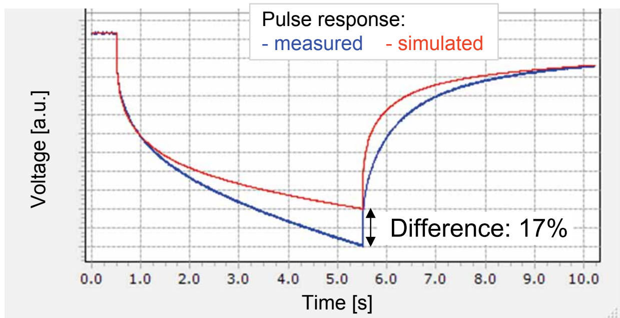

Figure 7 Measured pulse response and its simulation for cell no. 1 at 10% of SOC and –10 °C temperature

PROBLEMS TO BE RESOLVED

We were able to successfully verify the feasibility of the newly developed technology to be applied to batteries in vehicles. However, it became clear that this technology requires technological improvement, because the characteristics of the batteries significantly fluctuated when the SOC or temperature was low. In addition, the verification considering the effects of noise is also necessary because the waveform data used in this test does not include electrical noises emitted in running vehicles.

RESIDUAL LIFETIME PREDICTION FOR BATTERIES

So far, many types of battery deterioration models have been reported. Most of them uniquely predict the residual lifetime of a battery according to its capacity retention.

However, Honda is focusing on the fact that battery cells with the same capacity retention may have different deterioration states, appearing as differences in ACR, which eventually lead to different capacity deterioration trends afterwards [3].

This implies that predicting the residual lifetime of a battery using the ACR characteristics is feasible, although the residual lifetime varies depending on its use history. Figures 8 and 9 show the test results indicating the above phenomenon.

Yokogawa, with the background of these study results, is aiming at monitoring and predicting the deterioration degree of batteries during operation.

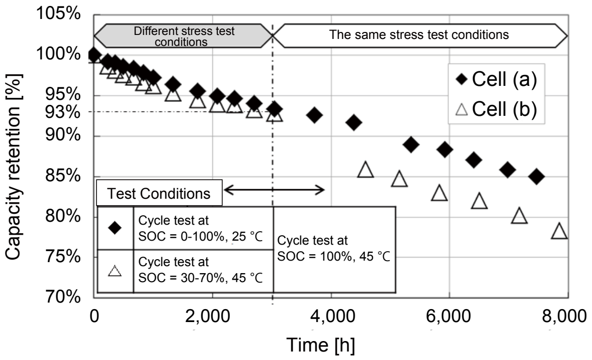

Figure 8 Capacity retention characteristics of battery cells with different use histories

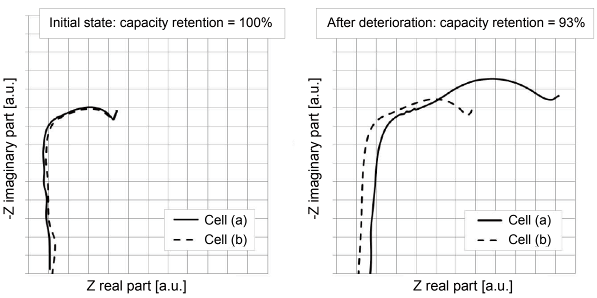

Figure 9 Impedance characteristics of battery cells at initial stage and after deterioration

BATTERY MEASUREMENT BOARD

Yokogawa has been engaged in the development of a battery measurement board with an ACR estimation function supposing an in-situ verification test. Figure 10 shows a prototype of the battery measurement board and a configuration example of a battery measurement system including the board.

This battery measurement board incorporates all functions required for measurement and calculation. This board enables drastic reduction in size and cost compared with the test system configuration shown in Figure 2

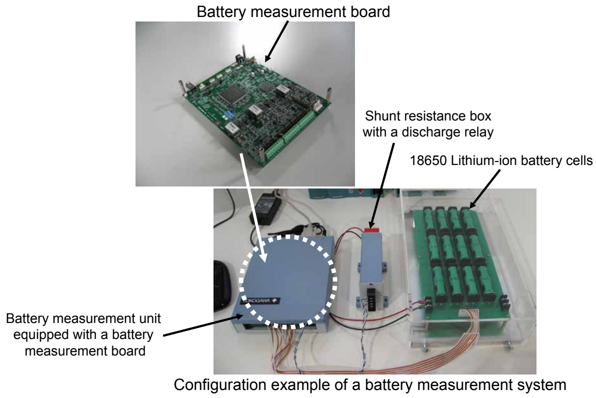

Figure 10 Battery measurement board and a configuration example of a battery measurement system

CONCLUSION

Yokogawa has developed a new technology for in-situ ACR estimation of battery cells. Applying this technology, Yokogawa has conducted technological verification tests assuming application to a deterioration diagnosis of in-vehicle batteries, and has proved its feasibility. Meanwhile, it has been confirmed that this technology requires technological improvement in some points. Subsequently, Yokogawa intends to pursue the development of an energy management system including stationary batteries, while working on the technical problems revealed in the verification tests.

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