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Diagnosis technology for lithium ion battery degradation

- A battery pack of EV can be analyzed by square-wave current EIS -

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ABSTRACT: Electrochemical impedance spectroscopic (EIS) analysis is used as the most effective tool in the design and development process of batteries and the related materials. However, its weak-point is the long measurement time, making it difficult to apply to operational battery systems such as Electric Vehicle (EV) and Stational Battery Storage System (BESS). We have developed a square-current wave EIS method, which has succeeded in shortening the measurement time by 1/10. Furthermore, by generating a square- current wave using an inverter installed into a quick charger, we have succeeded in detecting the internal impedance of EVs.

KEY WORDS: battery, impedance, EIS, square-wave, EV, BESS, degradation, diagnosis

1. INTRODUCTION

Electrochemical impedance spectroscopic (EIS) analysis was firstly reported for use in electrochemical electrodes by Osaka and Naoi about 40 years ago[1)], where this method involves inputting a weak sinusoidal voltage waveform to a battery cell while sweeping the frequency, measuring the responded current waveform from the battery cell, and drawing a Nyquist figure by performing complex analysis (also called a Cole-Cole plot). This method has been widely used in the design and development mission of battery cells and the development of battery materials for 40 years, and it can be said that it has been established today as the most powerful tool for analyzing the internal state of a battery cell.

Regarding to electric vehicles (EVs) and stationary battery energy storage systems (BESSs), hundreds to tens of thousands of battery cells are connected in a multi-series and multi-parallel configuration. It is possible to use this EIS method to analyze the internal state of these operational battery systems, however the weakness of this method is that the measurement time takes several minutes to several tens of minutes, therefore, the conventional EIS method is not suitable to the real battery systems such as EVs and BESSs in operation.

We proposed a square-current wave electrochemical impedance spectroscopy (SC-EIS)[2,3)]. This method can reduce the measurement time to a minute or less, making it possible to apply it to EVs and BESSs on-site because the square wave includes not only the fundamental frequence but also many higher harmonic waves (Fig.1).

In addition, by replacing the input signal to a current waveform from voltage one, it is possible to detect the signal with good S/N ratio even in the case of battery systems with quite low internal resistance.

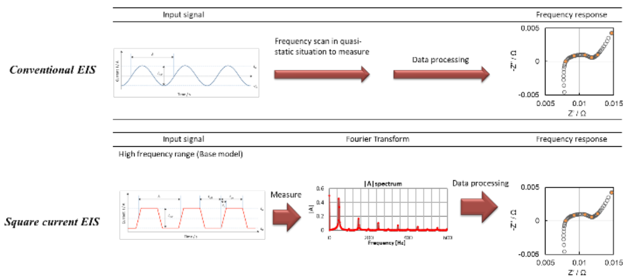

Fig. 1 Comparison between the conventional EIS and SC-EIS

2. SQUARE-CURRENT WAVE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (SC-EIS)

A square-current waveform is generated using a power source capable of generating waveforms, and applied to the battery cell or battery pack/system. The current strength is determined taking into consideration the capacity of the battery cell and pack, the value of the combined internal resistance, the surrounding noise environment, etc., but is around 0.01C. The fundamental frequencies of square wave is selected between 0.1 and 10Hz. The waveform generation time is about 10 seconds to 1 minute, but is determined taking into consideration the noise environment in which the battery system is placed and the accumulated measurement time.

The square wave current generated in this way is applied to the battery pack/system. At this time, the current waveform and the voltage response waveform returned from the battery pack/system are measured with a high-performance measuring device, and the data is accumulated. The accumulated current and voltage waveform data are subjected to Fourier analysis and complex analysis to draw Nyquist figures.

3. EXPERIMENTAL

We here carried out the field-test in which we measured the internal state of both battery pack or lack installed in an EV and a BESS using SC-EIS method.

3.1. Measurement for EV

EVs can be charged with a CHAdeMO type of quick charger. We attempted to incorporate SC-EIS measuring function into this quick charger shown in Figure 2.

Fig.2 Photo of field-test that EV was diagnosed by SC-EIS method installed into the CHAdeMO charger

The quick charger has a built-in inverter that generates the charging current and necessary voltage for the EV. We modified part of the control software for this inverter to make it possible to superimpose a square-current wave (AC) with the frequency: 0.1, 1 and 10Hz on the DC charging current, Figure 3 shows the configuration of this experimental system which EIS measurements are concurrently performed while charging an EV using this modified quick charger.

Regarding to the terminal voltage of the battery pack, which basically shows the OCV of the battery pack in accordance with the State of Charge (SoC) change associated with charging, but there is a slight voltage fluctuation due to the input of the square-current wave. Both current and voltage are measured with a high-performance measuring instrument, then a complex analysis was performed after Fourier-Transform analysis of the current and voltage waveforms. The three EVs did not shut down and could be driven normally after this measurement.

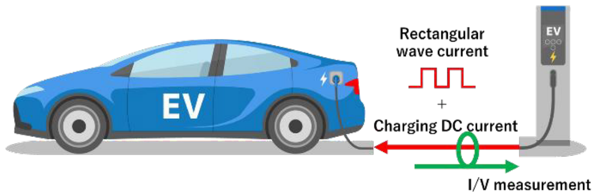

Fig. 3 Schematic configuration of SC-EIS measurement

Fig.4 Photo of BESS installed SC-EIS function and assembled battery module

3.2. Measurement for BESS

A commercial type of BESS intalled by Toshiba Corporation was used with 50 kW power controllers and the lithum ion battery unit of 11KWh composed of series connected 10 battery modules, in which 2P12S battery cells was assembled, as shown in Figure 4. The total cells are 240cells with 2P120S configuration. For SC-EIS function, the power controller was remodeled to generate a square-current with a frequency of up to 50 Hz using only software modifications. The amplitude current from zero to peak was 10 A without use of an offset current. The frequencies of the current input waves were 50 Hz, 5 Hz, 0.5 Hz, and 0.05 Hz. The overall average of measurement were taken 5 times.

The high-accuracy data logging system (Yokokawa Electronics Corporation, 720120-S1_Impedance Analyzer: the sampling rate was 100 kHz) was connected to the battery unit in BESS to monitor the main-circuite voltage between the end terminals of battery unit. This logger was also connected to monitor the coltage difference between the terminals of battery modules, therefore the internal status of not only the whole battery unit but also each of battery modules can be simultaneously diagnosed.

4. RESULTS AND DISCUSSION

4.1. Data of EVs

The resulting Nyquist diagram (Cole-Cole plot) of impedance response is shown in Figure 5. The semicircle shape are generally observed in the case of lithium ion batteries. In the case of OEM A's EV which has been in use for more than five years, the data plot also showed a part of semicircle shape and are positioned to the lefthand side of the center of this figure, suggesting that the internal impedance of this battery pack was maintained at a relatively lower level. OEM B's EV is a new car equipped with a large battery pack. A part of the semicircle was also observed, indicating that it is in a relatively good initial condition. Company C's EV is an early model that has been in use for more than five years. The plot is located to the righthand side of the center of the graph, and the semicircle shape seems to be distorted, indicating that the battery is deteriorating.

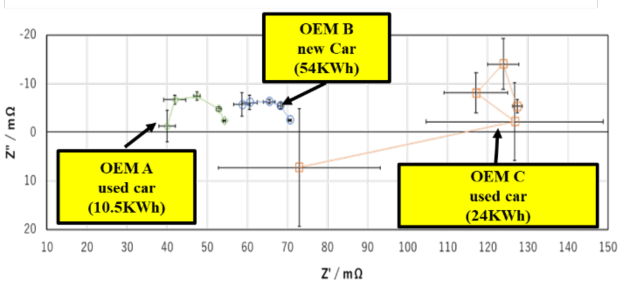

Fig. 5 Naiquist plots of impedance data measured at three types of EVs

To diagnose an installed battery pack in EV in detail, the battery data-base would be needed, where the impedance behavior of single battery cell assembled in the pack should be analyzed in advance from initial to degraded situation with applying various cyclic charging and discharging processes at various temperature condition. The impedance data measured as the above will be compared with the prior battery data-base, then a so-called battery diagnosis chart can be created to be reported to the EV owner.

Even unless a specific battery cells assembled in a pack on EV are obtained, the data-base about battery pack level, so-called big data, can be prepared by monitoring many set of new EVs from the beginning.

4.2. Data of BESS

Figure 6 shows the Nyquist diagram of impedance response for frequencies up to 2 kHz of the 11kWh battery unit composed of these10 modules in the dedicated BESS. The frequency region of the present system was 50 m Hz – 2 kHz, which is sufficient for battery analysis. Thus, the results indicate that this system enables the use of high-accuracy impedance responses in BESSs. Using this system, not only one unit but also ten modules could be analyzed simultaneously, but the result will be explained in the next.

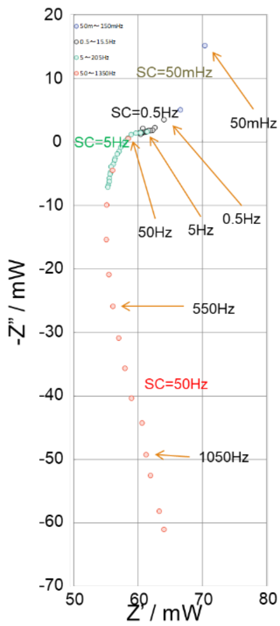

Fig. 6 Nyquist plots of impedance data at BESS battery unit

4.3. Detection of degradation of BESS

In order to assess the extent of degradation of LIBs in a BESS, one battery module was replaced by a degraded one. In other words, the battery whole unit in the BESS included one degraded battery module and nine original existing modules. The degraded module was prepared until the State of Health (SoH) of the module was reduced up to 80% remaining-capacity by applying cyclic charging & discharging process at relatively higher temperature condition. Figure 7 shows the Nyquist plots of the impedance responses about the degraded module comparing with a new one. Specifically, the semicircle diameter was much larger than that of the existing modules, also showing the larger resistance value.

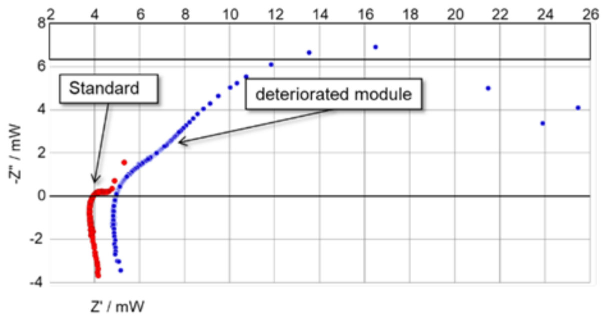

Fig.7 Nyquist plots of degraded module (blue) with new one (red)

Figure 8 shows the Nyquist plots of the impedance responses about the partly degraded battery unit including one degraded LIB module at the total SOC of 50% comparing with the normal battery unit composed of ten existing modules. Apparently, the semicircle diameter of partly degraded battery unit became larger than that of the normal unit, which suggests that BESS would be deteriorated either partly or totally.

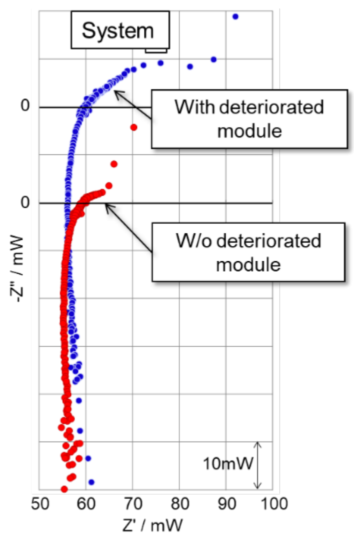

Fig.8 Nyquist plots of the partly degraded battery unit (blue) and normal unit (red)

Figure 9 shows the respective impedance responses of 10 modules installed in the partly degraded battery unit. The impedance responses of 9 modules: from No.1 to No.9 indicated the semicircle shape similar to the new one and also resistance level similar to the new one shown in Figure6, however single module: No.10 obviously showed the larger diameter of semicircle shape and resistance level which were similar to those of degraded module shown in Figure 7. It can be easily identified which module is degraded how much, because the voltage response of each module can be simultaneously picked up by accessing it's electrical terminals.

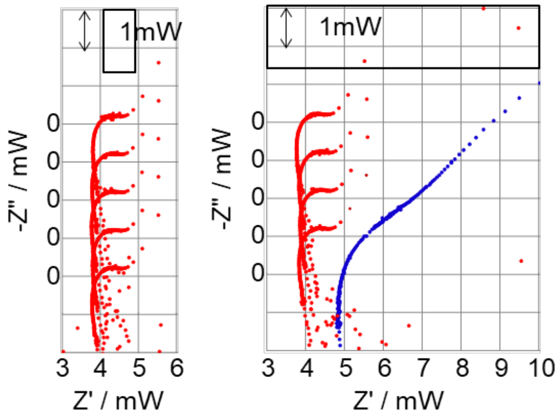

Fig.9 Nyquist plots of impedance data of respective modules in the partly degraded battery unit. The data of module No1 to N.5 (red) in the lefthand graph, and those of module No.6 to No.9 (red) and that of No.10 (blue) in the righthand graph

This result strongly indicates that SC-EIS method is powerful tool to monitor and diagnose a degradation level of battery system.

4.4 Problems to be improved

There remain still several issues to be improved.

1. The internal impedance depends on the SoC and temperature of the battery pack. It is particularly sensitive to the temperature, and it is necessary to identify a function that normalizes the data measured under various conditions.

2. The first concern for EV owners regarding battery degradation would be State of Health (SoH). In order to estimate SoH, it is necessary to find a correlation between the internal impedance and the degradation of SoH.

3. The materials and technologies of lithium ion battery are constantly evolving, and it is necessary to investigate the relationship between impedance and degradation anew.

Nevertheless, when considering the obligations to reuse and recycle of batteries that will be required in near future, we believe that this method, which can measure the detailed deterioration state of onboard battery packs in a short period of time, will be an effective tool in the EV industry.

5. FUTURE BUSINESS PLAN

Based on the results of these field-tests, we are considering the service business model to provide a diagnostic chart of battery to both EV owners and BESS operator as shown in Figure 10. In the case of EVs, through collaboration with charger manufacturers or their operators, the chargers equipped with SC-EIS measurement functions should be widely deployed. When a EV owner uses the quick charger, it will send the measured data via a IT-cloud to a battery diagnostic server, and the server analyses them and will return a diagnostic chart to the EV owner via the cloud. EV owners can utilize these diagnostic chart and it's historical record, for example, when they sell their EVs as used cars. An used-car buyer can refer to these record to apprise the used EV. This would be helpful for keeping the price of used EV in an appropriated level, whereas the prices of used EVs seem to be significantly underestimated less than those of used ICE cars in the used-car market.

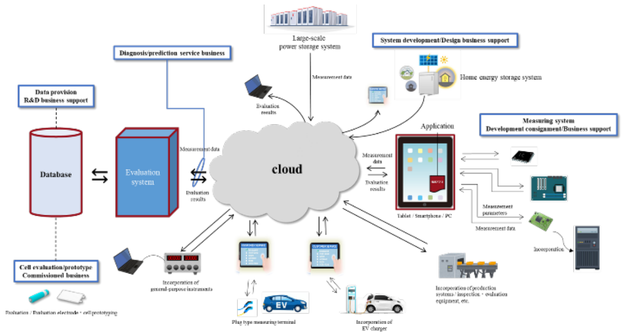

Fig.10 Schematic business model for battery diagnosis service

6. CONCLUSION

Measurement function about the square-current wave electrochemical impedance spectroscopy (RC-EIS) was installed into the inverter inside of CHAdeMO charger and power-controller in BESS, then SC-EIS was applied to analyze the internal battery status of both battery pack in EV and battery unit in BESS. It is indicated that SC-EIS method is a powerful and available tool to monitor the internal status of installed battery pack and unit in the system.

ACKNOWLEDGMENT

This field-test was carried out in collaboration with Toshiba Corporation.

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