Electrochemical Impedance and Statistical Voltage Analysis

– Marine Use Application: Energy Storage Life Cycle

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AA-size Nickel-Metal Hydride (Ni-MH) secondary (rechargeable) batteries can be used to replace primary (disposable) batteries on portable electric devices for marine use such as wireless LAN voice call apparatus. This study investigates the extent to which AC impedance response analysis can verify battery deterioration during its life cycle. Verification of battery deterioration levels using this analysis has been confirmed under small scale conditions with AB5 alloy structure type Ni-MH batteries but not with super lattice alloy structure type Ni-MH batteries. Using the terminal voltage during cycle mode experiments and the statistical analysis of Mahalanobis distance, evaluation of battery deterioration levels of super lattice alloy type batteries was conducted. This study's goal is to verify whether the AC impedance method can be applied to check the state of health (SOH) of on-board batteries under operating conditions.

1. Introduction

Penlight size energy storages are installed on electric power equipment and devices for marine use. The energy source battery has a chemical degradation with cycle and preservation lifetime. This study investigates a possibility extent that an AC impedance response analysis is able to verify the battery deterioration in progress of lifetime cycle. The battery is focused on a Ni-MH battery. A general purpose secondary battery which is widely used in marine use electric power equipment and devices can be replaceable from primary (disposable single-use) battery [1]. Major battery deterioration parameters are enumerated a battery load rate and cumulative energy amount, a battery state of charge (SOC) and a battery temperature. A discharge capacity test and a high rate discharge test are most popular measurement methods to verify the battery deterioration level precisely on a laboratory scale. These methods have to do with large scale equipment. AC impedance response analysis is the other method which can be detected

easily to measure the battery deterioration level on a small scale condition [2],[3]. The study final object is a verification of the battery AC impedance method which is applied to check a battery state of health (SOH) on an on-board battery under operating conditions.

2. Experimental Method and Apparatus

2.1 Principle of Battery Equivalent Circuit

A battery impedance spectrum plots on a complex plane which is a notational system. The battery AC impedance has two parts which are a real part Z' on a horizontal axis and an imaginary part Z'' on a vertical axis respectively. The plotted figure is generally called a Nyquist diagram. Figure 1 shows battery chemical impedance on equivalent circuit elements both with a resistor component R and with a capacitance component C . Equation (1) shows the battery chemical impedance Z in Fig. 1 [4] and [5].

$$Z = R_{sol} + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}} \quad (1)$$

$$Z = Z' - jZ'' \quad (2)$$

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Eq. (1) consists of a real part Z' and an imaginary part Z'' shown in Eq. (2).

$$Z' = R_{sol} + \frac{R_{ct}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} \quad (3)$$

$$Z'' = \frac{\omega R_{ct}^2 C_{dl}}{1 + \omega^2 R_{ct}^2 C_{dl}^2} \quad (4)$$

Eq. (3) is the real part impedance Z' and Eq. (4) is the imaginary part impedance Z'' .

$$\left(Z' - R_{sol} - \frac{R_{ct}}{2} \right)^2 + Z''^2 = \left(\frac{R_{ct}}{2} \right)^2 \quad (5)$$

The battery chemical impedance makes a circle equation both with a resistor component R and with a capacitance component C of equivalent circuit elements shown in Eq. (5).

Herewith

R_{sol} : battery electrolyte resistance
 R_{ct} : charge transfer resistance
 C_{dl} : electric double layer resistance

Fig. 1 Fundamental battery chemical impedance model with RC circuit components

2.2 Experimental Battery

Experimental batteries are commercial model of Ni-MH secondary batteries in two types. One of which is the most popular AB5 alloy type and the other is a super lattice alloy type. Herewith, the AB5 alloy type is called “AB5” in short and the super lattice alloy type is called “SL” in short. The specific battery capacity is 1900mAh both AB5 alloy type and SL alloy type. The AB5 battery has the name of EVOLTA (type; HHR-3MWS) manufactured by Panasonic Co., Ltd. The “SL” battery has the name of Eneloop (type; HR-3UTGB) also manufactured by Panasonic Co., Ltd. The examination is carried out with the brand-new battery after activation under both charged and discharged within 10 cycles.

2.3 Experimental Method

The experimental test condition is as follows; a charge-discharge electrical load to the experimental battery is set by load control unit (type; HJ0610SD8Y) manufactured by Hokuto Denko Co., Ltd. The experimental battery temperature is set in a thermostatic chamber (type; LU-113) manufactured by Espec Co., Ltd. The experimental battery AC impedance response with sweeping frequency is measured by a chemical impedance analyzer (type; IM3590) manufactured by Hioki Co., Ltd. The battery cycle examination load is applied on the basis of JC08 mode (the verification mode for vehicle fuel consumption and exhaust gas emission certified by Japanese government). The JC08 mode consists of zero speed part which simulates an engine idling condition. The battery cycle examination load which deleted the zero speed data. The battery cycle examination mode profile on the basis of JC08 mode deleted zero speed data is shown in Fig. 2 (a). The battery examination load profile is shown in Fig. 2(b).

(a) Mode profile

(b) Load profile

Fig. 2 Experimental battery cycle examination profile (JC08 mode, zero speed deleted data)

The actual load current profile scales down to the experimental battery load rate. The

experimental battery load amount sets from 60% SOC to 40% SOC. The battery experiment one cycle consists of JC08 load for 20% discharge and a constant current 950mA (0.5C) load back for 20% charge. The experimental battery AC impedance measurement has done when the experimental cycle to reach in each check point cycle. The measurement has carried out after the following conditioning. The experimental battery is charged to a full capacity level and then preserved for 12 hours to reach a steady condition of the battery. The experimental battery connected to a measurement wire harness where is attached to solder pieces of metal which prevents a voltage drop of the contact resistance [6], [7] and [8]. This is because the battery impedance is so small which level is a few milli-ohm, and necessary to reduce any ohmic loss during the battery AC impedance measurement. The experimental battery AC impedance measurement connects the measurement wires, which connected both battery terminal with solder, insert a test fixture (type: IM3590) manufactured by Hioki Co., Ltd. The measurement has taken three times to acquire an appropriate data.

The battery AC impedance response is measured at a different frequency to apply the battery. The AC impedance measurement is done from 1000Hz to 0.1Hz, on the frequency range from 1000Hz to 100Hz in each 100Hz step, on the frequency range from 100Hz to 10Hz in each 10Hz step, on the frequency range from 10Hz to 1Hz in each 1Hz step and on the frequency range from 1Hz to 0.1Hz in each 0.1Hz step. It is necessary to verify that the battery AC impedance response from 1000Hz to 0.1Hz can evaluate below 40 points measurement data. For the verification, we measured the battery AC impedance response of 800 points with a decrease that follows an exponential function from 1000Hz to 0.1Hz. Fig. 3 shows the electrochemical impedance response in different of the measurement points. The zero cross impedance Z' ($Z''=0$) is 750 Hz in the verification experiment which makes a little low number of the verification data. Fig. 3 shows 34 points measurement data plot on the line of 800 points measurement data and the 34 points measurement data connected line traces the 800 points measurement data connected line closely. The

verification results shows that the below 40 points measurement data can evaluate the battery AC impedance response.

Fig. 3 Differentiation of electrochemical impedance response of measurement points, AB5 type battery

The results of the AC impedance measurement reveals both battery impedance components of the real part Z' and of the imaginary part Z'' . After the measurement, the experimental battery is discharged with a constant current 950mA (0.5C) to an empty capacity level 1.0V. Then the experimental battery is charged with a constant current 950mA (0.5C) for two hours to a full capacity level. A battery voltage curve nearly traces CC-CV (constant current – constant voltage) curve of standard charge method.

3. Experimental Study

3.1 AC Impedance Response in Durability Cycles

Fig. 4 Electrochemical impedance response in durability cycles, AB5 type battery

Figure 4 shows the experimental battery AC impedance measurement results of AB5 alloy type, which is called Nyquist diagram. The AC impedance measurement has done on a brand new battery activated at first and then measured when the durability cycles reaches to each check point

cycle of 100, 400, 700, 1000, 1300 and 1600 respectively. The experimental battery AC impedance measurement result shows the AB5 alloy type battery increases the real part impedance along with durability cycles.

Fig. 5 Electrochemical impedance response in durability cycles, SL type battery

Figure 5 shows the experimental battery AC impedance measurement results from the super lattice alloy type. The AC impedance measurement has done on a brand new battery activated at first and then measured when the durability cycles reaches to each check point cycle of 100, 400, 700, 1000, 1300 and 1600 respectively. Though the measurement results of the super lattice alloy type battery almost plots on the same area.

Electrochemical impedance responses show in different plot figures between AB5 alloy type and super lattice alloy type in progress of durability cycles. The experimental results show that AC impedance measurement method is capable of being applied AB5 alloy type battery to verify the progress of battery deterioration. The super lattice alloy type battery is necessary to another method to verify the progress of battery deterioration.

4. Experimental Discussion

4.1 Statistical Analysis Method

Nyquist diagram for the electrochemical impedance response is verified with a method of Mahalanobis distance analysis [9], [10], [11] and [12]. The Mahalanobis distance analysis is as follows; Data u_{ij} is defined both a number of events i ($i=1$ to n) and of components j ($j=1$ to m). In a component of the basic standard group, a means of the events is μ_i ; a variance of the events is σ_j^2 , Data u_{ij} is written at the unit space by standardizing U_{ij} .

$$v_{j1,j2} = \frac{1}{n} \sum_{i=1}^n (U_{i,j1} - \bar{U}_{j1}) \cdot (U_{i,j2} - \bar{U}_{j2}) \quad (6)$$

The basic standard group consists of a number of components. A covariance V is written between components.

$$V = \begin{bmatrix} 1 & v_{1,2} & \cdots & v_{1,m} \\ v_{1,2} & 1 & \cdots & v_{2,m} \\ \vdots & \vdots & \ddots & \vdots \\ v_{1,m} & v_{2,m} & \cdots & 1 \end{bmatrix} \quad (7)$$

$$D = \sqrt{\frac{1}{m} \begin{bmatrix} X_{1,1} & \cdots & X_{1,m} \\ \vdots & \ddots & \vdots \\ X_{k,1} & \cdots & X_{k,m} \end{bmatrix} \cdot V^{-1} \cdot \begin{bmatrix} X_{1,1} & \cdots & X_{1,m} \\ \vdots & \ddots & \vdots \\ X_{k,1} & \cdots & X_{k,m} \end{bmatrix}^t} \quad (8)$$

Mahalanobis distance d_{ij} to a data x_{ij} of verification group is determined to Eq. (8) matrix. The distance d_{ij} and the data x_{ij} is defined with both a number of events i ($i=1$ to k) and a number of components j ($j=1$ to m). Herewith the Mahalanobis distance matrix D is applied the following diagonal matrix elements to the verification. And the data x_{ij} is standardizing with the unit space.

$$D = \begin{bmatrix} d_{1,1} & - & \cdots & - \\ - & d_{2,2} & \cdots & - \\ \vdots & \vdots & \ddots & \vdots \\ - & - & \cdots & d_{k,k} \end{bmatrix}, \quad X_{i,j} = \frac{x_{i,j} - \mu_j}{\sqrt{\sigma_j^2}} \quad (9)$$

4.2 Statistical Analysis Examination [13] and [14]

The Mahalanobis distance analysis applies to the AC impedance measurement response from 1000Hz to 01Hz to evaluate between the 800 points measurement results to the 34 points measurement results. Fig. 6 shows Mahalanobis distance analysis of the AC impedance measurement response of the AB5 type battery shown in Fig.3. The standard space is defined in the 800 points measurement results of electrochemical impedance response of the AB5 type battery. The Mahalanobis distance shows the statistical distance between the standard space data group and the verification data group. Fig. 6 shows the 34 points measurement data connected line traces the 800 points measurement data connected line closely.

Fig. 6 Mahalanobis distance, the standard feature is 800 measurement points of electrochemical impedance response, AB5 type battery

Figure 7 shows the Mahalanobis distance distribution of the AB5 alloy type experimental battery shown in Fig. 6. The bold distribution line is the Mahalanobis distance from the standard feature of 800 points measurement results of the AB5 type battery electrochemical impedance response group to the verification group regressed on itself, draws a center line. Fig. 7 shows easy to verify that the distribution points which equal to or under the bold distribution line are the standard feature group in a zone range. The above solution makes easy to verify the each distribution point group which belongs to the standard feature group or not without considering the Mahalanobis distance. The Mahalanobis distance statistical analysis verifies that the 34 points measurement data can evaluate the battery AC impedance response without using the 800 points measurement data.

Fig. 7 Mahalanobis distance distribution from the standard feature of 800 points measurement results of the AB5 type battery electrochemical

impedance response group

4.3 Statistical Analysis Application

Figure 5 shows that the super lattice alloy type battery Nyquist diagram plots overlapping on the same area. The super lattice alloy type battery is necessary to another method to verify the progress of battery deterioration.

(a) 100th cycle

(b) 1600th cycle

Fig. 8 Experimental battery terminal voltage, SL type battery

The verification method which the battery terminal voltage of cycle mode experience is a subject of interest. Fig. 8 shows the battery terminal voltage during the experimental cycle mode. Fig. 8(a) shows the battery terminal voltage of 100th cycle mode experience. Fig. 8(b) shows the battery terminal voltage of which progressed in 1600th cycles. The verification load is shown in Fig. 2 which repeats three times to maintain the currently specified range from 60% SOC to 40% SOC.

The Mahalanobis distance analysis applies to the Experimental battery terminal voltage. The standard space is defined in the battery terminal voltage of the 100th cycle mode experience. Fig. 9 shows the Mahalanobis distance from the standard

feature group of the 100th cycle mode voltage. Fig. 9(a) shows the Mahalanobis distance from the standard feature group to the verification group regressed on itself. Fig. 9(b) shows the Mahalanobis distance from the standard feature group to the verification group of 1600th cycle mode voltage.

(a) 100th cycle

(b) 1600th cycle

Fig. 9 Mahalanobis distance from the standard feature of 100th cycle voltage, SL type battery

Figure 10 shows the Mahalanobis distance distribution of the super lattice alloy type experimental battery shown in Fig. 9. In Fig. 10, the center line which the Mahalanobis distance from the standard feature group of the battery terminal voltage of the 100th cycle mode experience to the verification group regressed on itself. The distribution plot points show the Mahalanobis distance from the standard feature group to the verification group of the 1600th cycle mode voltage. The Mahalanobis distance distribution of the verification group of the battery terminal voltage of the 1600th cycle mode experience shows much distance from the standard feature group. It is indeed that the actual battery deterioration is in progress with the cycle mode experience which can verify the Mahalanobis distance distribution of the

battery terminal voltage information.

Fig. 10 Mahalanobis distance distribution from the standard feature of 100th cycle voltage, SL type battery

Fig. 11 Battery capacity in the state condition check point of the cycles, SL type battery (The battery capacity measures which is to be charged 100% SOC with 0.5C, and discharged to 0% SOC with 0.5C)

Figure 11 shows the battery capacity of the super lattice alloy type experimental battery on the battery check points during the cycle mode experience. The battery capacity still maintain the initial stage of the 100th cycle in progress of the 1600th cycle. The Mahalanobis distance analysis applies to the Experimental battery terminal voltage reveals the battery deterioration in progress of the cycles which information can be achieved as appropriate control cannot lead to significant battery degradation or even to safety critical conditions.

5. Conclusion

This study verified two types of different alloy structure of Ni-MH battery with the durability cycle experiment and acquired following knowledge.

- (1) AB5 alloy type battery increases the real part impedance along with durability cycles. The AC impedance measurement method is capable of verifying AB5 alloy type battery in progress of deterioration.
- (2) Super lattice alloy type battery does not increase and still maintains the initial impedance Nyquist diagram along with durability cycles. The AC impedance measurement method is not capable of verifying the super lattice alloy type battery in progress of the deterioration.
- (3) The battery terminal voltage of cycle mode experience and the statistical analysis of the Mahalanobis distance can verify the super lattice alloy type battery deterioration which is an effective approach to the defective results mentioned above conclusion (2).

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