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Statistical Analysis Applied to Ni-MH Battery Impedance for Preservation Lifetime Experiment

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Abstract

Electric prime mover traction battery has a chemical degradation with cycle and preservation lifetime. The battery verification shall be done in both aspect of the battery cycle lifetime experiment and the battery preservation lifetime experiment. Though it is a fact that the most of the experiment which does not verify the battery preservation lifetime but the battery cycle lifetime prior to the battery mass production. Owing to an allowable research and development span, there is not enough time to verify the battery preservation lifetime experiment which makes hard to estimate the battery total life in actual usage. This study investigates a possibility extent that an AC impedance response analysis, which method is able to verify the battery deterioration condition in progress of cycle lifetime experiment which was previously reported, and also apply to verify the battery deterioration condition in progress of preservation periods and the estimation life time. The battery is focused on a Nickel-metal hydride (Ni-MH) battery which is widely used as traction energy storage in HEVs. The AC impedance response analysis is an appropriate method which can be detected easily to measure the battery deterioration level of an amount of the battery's self-discharge, a nominal type of Ni-MH battery called AB5 alloy type. The final objective of this study is verified that the AC impedance response with a statistical analysis is an effective method to verify the battery deterioration level in progress of preservation easily and to estimate the battery total life time.

Keywords: Automobile, Battery, Measurement, Voltage, Analysis

1. Introduction

Battery-powered prime mover vehicles, i.e., electric vehicles (EVs) and hybrid electric vehicles (HEVs), have on-board batteries installed that are intended to be used for more than a ten-year period. A vehicle traction battery undergoes a chemical degradation along with the cycle and preservation lifetime. A battery cycle lifetime experiment must be conducted prior to the mass production of a battery-powered prime mover in order to avoid problems with the battery cycle lifetime during the early stage of use, i.e., less than 1/3 of the design lifetime. A battery cycle lifetime experiment that concentrates on the durability periods using an Arrhenius equation expressing the chemical reaction rate has been proposed. However, a battery preservation lifetime experiment is a difficult way to concentrate on the durability periods. This difficulty makes a total battery lifetime experience represent both the battery cycle lifetime experiment and the preservation lifetime experiment, but it is indeed that the total battery lifetime experience consists of both the battery cycle lifetime experiment and the preservation lifetime expectation.

This study investigates the possibility of conducting an AC impedance response analysis to verify the battery deterioration level during the preservation periods. The study focuses on a nickel-metal hydride (Ni-MH) battery, which is widely used for traction energy storage in an HEV^[1]. A discharge capacity test and a high rate discharge test are the most popular

measurement methods for precisely verifying the battery deterioration level at a laboratory scale. These methods deal with large-scale equipment. An AC impedance response analysis is another method that can be used to easily measure the battery deterioration level under small-scale conditions^[2-3]. The final objective of this study is a verification of a battery AC impedance method that is applied to check the State of Health (SOH) of an on-board battery under the operating conditions.

2. Experimental method

2.1. Experimental Battery

There are two types of experimental batteries used for a commercial Ni-MH secondary batteries model. One, which is the most popular, is an AB5 alloy type, and the other is a super lattice alloy type. Herein, the AB5 alloy type is called AB5 for short, and the super lattice alloy type is called SL. The AB5-type battery studied is an HHR-3MWS EVOLTA (Panasonic Co., Ltd.) with a rated capacity of 1900mAh, whereas the SL-type battery is an HR-3UTGB Eneloop (Panasonic Co., Ltd.), also with a rated capacity of 1900mAh. The examination was carried out using brand-new batteries preserved for around two years at normal temperature.

2.2 Equivalent Circuit Theory

A battery impedance spectrum is plotted on a complex plane, which is a notational system. The battery AC impedance has two parts, i.e., a real part,

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Z' , on a horizontal axis, and an imaginary part, Z'' , on a vertical axis. The plotted figure is generally called a Nyquist diagram. Figure 1 shows the battery chemical impedance of equivalent circuit elements with both a resistor component, R , and a capacitance component, C . Equation (1) shows the battery chemical impedance, Z , of Fig. 1^[4-5].

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

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

Equation (1) consists of a real part, Z' , and an imaginary part, Z'' , from Eq. (2).

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

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

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

where

R_{sol} : solution resistance (electrolyte resistance)

R_{ct} : charge transfer resistance

C_{dl} : electric double layer capacitance

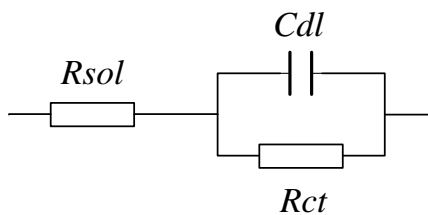


Fig. 1 Basic battery electrochemical impedance model with RC circuit components

2.3 Experimental Method

The experimental test conditions are as follows: a charge-discharge electrical load to the experimental battery is set by the load control unit (HJ0610SD8Y, Hokuto Denko Co., Ltd.). The experimental battery temperature is set in a thermostatic chamber (LU-113, Espec Co., Ltd.). The AC impedance response with a sweeping frequency of the experimental battery is measured using a chemical impedance analyzer

(IM3590, Hioki Co., Ltd.). The experimental battery is connected to a measurement wire harness attached to soldered pieces of metal preventing a voltage drop of the contact resistance^[6-8]. This is because the battery impedance is quite small, a few milli-ohm, and it is necessary to reduce any ohmic loss during the battery AC impedance measurement. The experimental battery AC impedance measurement is conducted using measurement wires soldered to both battery terminals with an inserted test fixture (IM3590, Hioki Co., Ltd.). The measurements were taken three times to acquire the appropriate data. The battery AC impedance response was measured at different frequencies. The AC impedance measurement was conducted from 0.1 to 1,000 Hz, within the frequency range of 100 to 1,000 Hz at 100-Hz steps, within the frequency range of 10 to 100 Hz at 10-Hz steps, within the frequency range of 1 to 10 Hz at 1-Hz steps, and within the frequency range of 0.1 to 1 Hz at 0.1-Hz steps. The results of the AC impedance measurement reveal the battery impedance components of both the real part, Z' , and the imaginary part, Z'' .

The first stage of the experimental battery AC impedance measurement was conducted three times under the battery condition when the preservation period was finished after around two years, which is indicated as “inactivation” in the following figures (Fig.5, Fig.6). The second stage of the experimental battery AC impedance measurement was conducted under full charged conditions for a total of three charge-discharge operations, which is indicated as “activation” in the figures. For the charge-discharge operations, the experimental battery was charged to full capacity and then preserved for 12 hours to reach a steady condition, and the experimental battery AC impedance was measured. After the measurement, the experimental battery was discharged at a constant current of 950 mA (0.5 C) to an empty capacity level of 1.0 V. The experimental battery was then charged with a constant current of 950 mA (0.5C) for two hours to full capacity, and then preserved for 12 hours to reach a steady condition. The battery AC impedance was then measured a second time. The above battery charge operation is one in which the battery voltage curve nearly traces the constant current-constant voltage (CC-CV) curve of a standard charge method. The third stage of the experimental battery AC impedance measurement was conducted three times under a condition in which the preservation period reaches the check time, which is indicated as “(x) days of time” in the figures. The fourth stage of the experimental battery AC impedance measurement was conducted under full charge conditions with a total of three charge-discharge operations, which is indicated as “reactivation” in the figures. For the charge-discharge operations, the experimental battery was charged to full capacity, and then preserved for 12 hours to reach a steady condition, at which point the battery AC impedance was measured. After the

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measurement, the experimental battery was discharged with a constant current of 950 mA (0.5 C) to an empty capacity level of 1.0 V. The experimental battery was then charged at a constant current of 950 mA (0.5 C) for 2 hours to a full capacity level and then preserved for 12 hours to reach a steady condition, at which the battery AC impedance was measured a second time. For the third measurement, the same operation is repeated. For the AC impedance measurements of the experimental battery, the first stage is investigating the effectiveness of a long preservation period, the second stage is investigating the recovery condition level after the long preservation period and the initialization of the following preservation period, the third stage is investigating the effectiveness of a short preservation period for each span, and the fourth stage is investigating the recovery condition after the short preservation period.

3. Experimental Study

3.1 Self-discharge Amount

Figures 2 and 3 show the residual capacity of the AB5- and SL-type batteries, respectively.

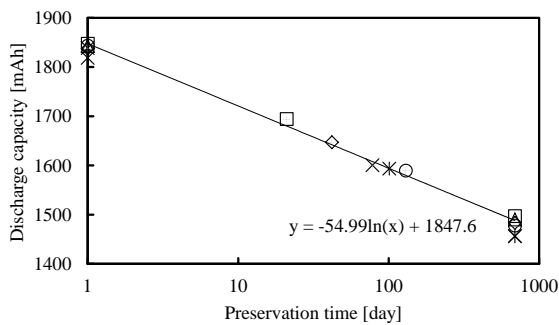


Fig. 2 Residual capacity by self-discharge, AB5 type battery

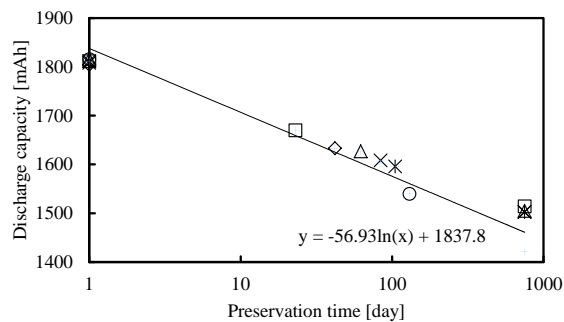


Fig. 3 Residual capacity by self-discharge, SL type battery

The preservation period around two years of which the battery had marked the year and month of manufactured date indication. The AB5 alloy type battery surpassed the manufacturer's indicated preservation period by 690 days, whereas the super lattice alloy type surpassed it by 750 days. The AC impedance measurements were conducted for AB5

alloy type batteries surpassing the expected preservation time by 21,42,64,78,101, and 130 days, and for the SL alloy type batteries surpassing the expected preservation time by 23, 42, 64, 84, 105, and 130 days. The residual capacity indicated during the preservation experiment, which is indicated as "(x) days of time," is in line with the battery condition when the preservation period finished after around two years, which is indicated as the "inactivation" period, and when the battery was fully charged after the two-year preservation period was finished, which is indicated as the "activation" period" Figures 1 and 2 indicate that the amount of battery self-discharge has a relationship with the preservation period.

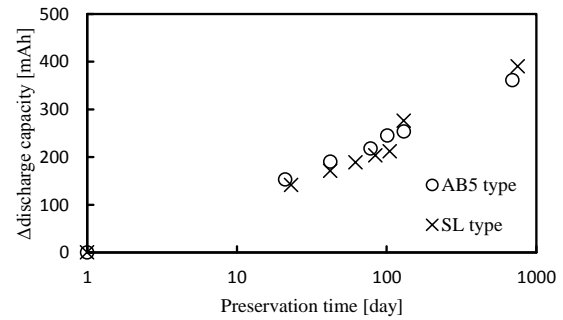


Fig. 4 Self discharging electrical quantity

Figure 4 shows the electrical discharge amount for both types of batteries. The experiment results show that the residual capacity through a self-discharge is the same for both the AB5 alloy type battery and the SL alloy type battery.

3.2 Self-discharge Amount

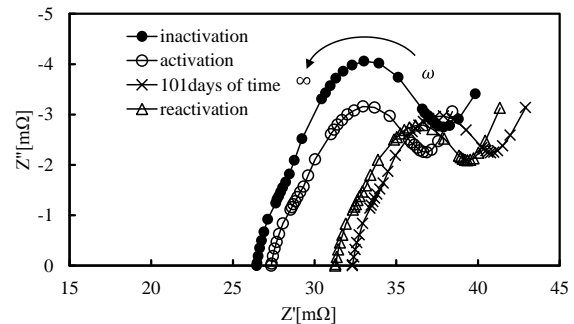


Fig. 5 Electrochemical impedance response in preservation period 101 days passed since activation, AB5 type battery

Figure 5 shows the AC impedance measurement results of the AB5 alloy type experimental battery, which surpassed 101 days of preservation from the "activation" operation after a long-term preservation period of 690 days. The AC impedance measurements were conducted for AB5 alloy type batteries surpassing the expected preservation time by 21,42,64,78,101, and 130 days. The results of the AC impedance measurement of the experiment samples show the same relation plots regardless of the number

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of preservation days surpassed. The real impedance of the zero cross point ($Z'' = 0$) increases the battery “inactivation,” “activation,” “reactivation,” and “(x) days of time” conditions in ascending order.

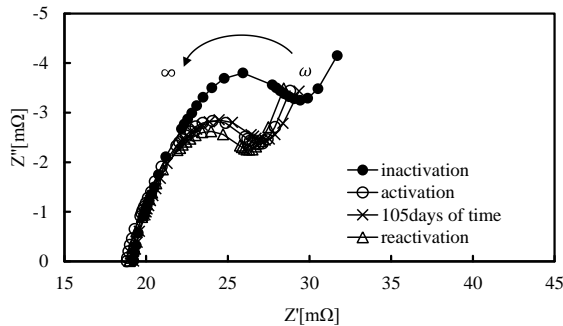


Fig. 6 Electrochemical impedance response in preservation period 105 days passed since activation, SL type battery

Figure 6 shows the AC impedance measurement results of a super lattice alloy experimental battery that surpassed the preservation period by 105 days from the “activation” operation after a long-term preservation period of 750 days. The AC impedance measurements were conducted for super lattice alloy type batteries surpassing the expected preservation time by 23, 42, 64, 84, 105, and 130 days. AC impedance measurement results of the experiment samples show the same relation plots regardless of the preservation days surpassed. The real impedance of the zero cross point ($Z'' = 0$) was not increased and maintains the initial value from the battery “inactivation,” “activation,” “reactivation,” and “(x) days of time” conditions in order.

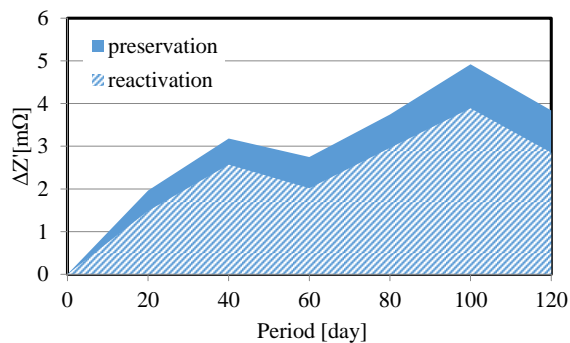


Fig. 7 Zero cross impedance increase rate $\Delta Z'$ ($Z'' = 0$) from activation, AB5 type battery

Figure 7 shows the real impedance of the zero cross point ($Z'' = 0$) of an AB5 alloy type battery surpassing 21, 42, 64, 78, 101, and 130 days of preservation from the “activation” operation after a long-term preservation period of 690 days. In addition, Fig. 7 also shows the real impedance of the zero cross point ($Z'' = 0$) of a reactivation after the “activation” operation. The real impedance of the zero cross point ($Z'' = 0$) in the experimental data is corrected to a 20-day span. The real impedance increases along with the

number of preservation days in spite of the position, which moves up or down. For a reactivation operation after “(x) days of time” have passed, the preservation of the battery is reduced in terms of the real impedance; however, the effectiveness of this is limited.

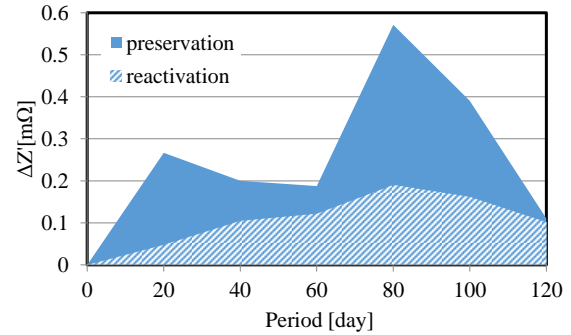


Fig. 8 Zero cross impedance increase rate $\Delta Z'$ ($Z'' = 0$) from activation, SL type battery

Figure 8 shows the real impedance of the zero cross point ($Z'' = 0$) of the super lattice alloy type battery surpassing 23, 42, 64, 84, 105, and 130 preservation days after the “activation” operation after a long-term preservation period of 750 days. The real impedance shows a slight increase based on the number of preservation days despite the position, either up or down. The reactivation operation after the battery has surpassed the preservation period by “(x) days of time” shows a reduction in the real impedance, but the effectiveness is also limited.

4. Conclusion

This study verified two types of different alloy structures for penlight sized Ni-MH secondary batteries, which have the same alloy structure, used in an actual HEV. The results of an AC impedance response analysis verify that the battery deterioration progresses during the preservation period. In addition, the following knowledge was acquired.

- (1) The amount of a battery’s self-discharge has relational equations with the preservation period for both the AB5 and SL (super lattice) alloy type structures. It was verified that the amount of battery self-discharge for a preservation period of 20 days can be used to estimate the battery self-discharge amount after a two-year period of time.
- (2) The AC impedance response analysis verify that the AB5 alloy type battery’s self-discharge is progressed during the preservation period. The results of the AB5 alloy type battery show that the real impedance of the zero cross point ($Z'' = 0$) increases the battery’s “activation,” “reactivation,” and “(x) days of time” conditions in ascending order.
- (3) The AC impedance response analysis can’t be verified that the SL alloy type battery’s self-discharge is progressed during the preservation

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period. The results of the SL alloy type battery show that the real impedance of the zero cross point ($Z''=0$) maintains its value despite the number of preservation days that have passed.

The study clarified that the AC impedance response analysis methods investigated for penlight sized Ni-MH secondary batteries. The AB5 alloy type are effective and the SL alloy type are not effective for verifying the battery deterioration during the preservation period, and as a future task, to find an effective method applied to the SL alloy type battery will be verified.

6. Acknowledgement

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