

Estimation of Durability of Nickel-Metal Hydride Batteries for Hybrid Electric Vehicles

Tatsuo MINAMI*

ABSTRACT

A method of estimating the durability of the nickel-metal hydride batteries employed in hybrid electric vehicles was studied based on factors contributing to their deterioration. The factors in battery deterioration are battery temperature, current load and state of charge. Based on the expectation that the formulation of a reaction rate equation employing chemical kinetics would enable the durability of the battery to be estimated, the Eyring equation, which enables consideration of temperature and another stress factor was focused on. The number of stress factors in the equation was increased to study the applicability of current load and state of charge.

It was shown that the values of frequency factors which are obtained in durability tests performed under various conditions of battery deterioration factors were the same. These results confirmed that the modified equation enabled multiple factors to be employed in estimations of battery life. The use of this reaction rate equation through quantification of each factor has enabled the estimation of battery life.

1. Introduction

One of the main elements of electric vehicles and hybrid electric vehicles (HEV) is the battery, which needs to have long life. Battery life is greatly affected by deterioration factors such as temperature, current load and state of charge band (SOC band).

For estimation of some type of battery life, it is generally understood that up until now the life of batteries follows the reaction theory Arrhenius equation based on the temperature. In the report of reaction kinetics type estimation for estimating battery life, deterioration reaction rate equation or an approximation equation using the battery temperature as its fundamental factor, were used to estimate battery life^{(2),(3)}. Other deterioration factors have only been added to this equation as singular factor. It is guessed that this is because the equations were developed for commercial batteries where normal use provides a steady current load for which consideration of other factors is not necessary. Recently, with

the increase in HEV sales, a database of market information for battery temperature, current load, SOC band and of how the battery is used, is being developed. Research⁽⁴⁾ has begun on a method that will provide an estimation of battery life using these deterioration factors. However, as in the case of HEV batteries, a reaction rate equation that targets systems (including not only changes in the environment, but also changes in current load, and that includes battery deterioration factors of battery temperature, current load and SOC band) has not yet been reported.

The reaction rate equation that is focused on is the Eyring equation, which includes dependence on both temperature and other types of stress. As an example of the application of the Eyring equation, stress factors other than temperature, such as humidity and current, were used in the evaluation of life expectancy for semiconductor devices and rubber^{(5),(6)}. There is only one stress factor in the Eyring equation; however, in the case of batteries, there are two stress factors other than temperature, current load and SOC band. More

* Tochigi R&D Center

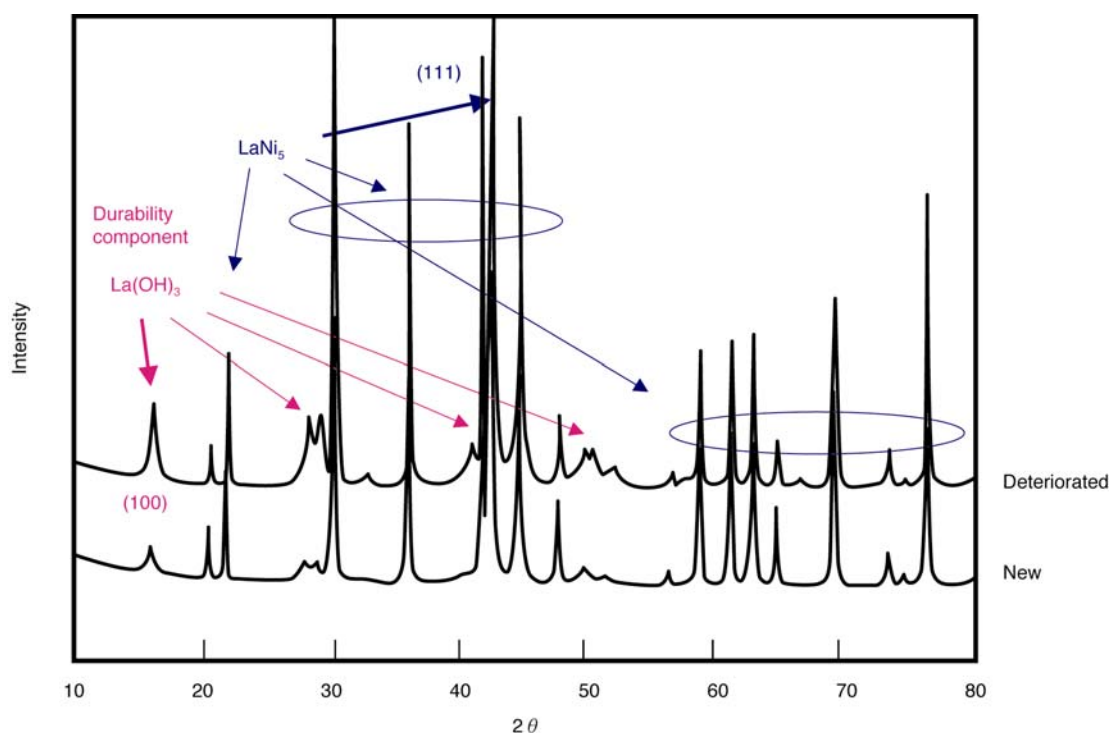


Fig. 1 XRD spectra of new and deteriorated negative

stress factors have therefore been added to the Eyring equation and a battery deterioration reaction rate equation that has more than one stress factor has been developed. Experiments to verify this equation's formation have been performed.

2. Correlation Between Chemical Reaction Induced Electrode Deterioration and the Deterioration of the Battery

The battery that is being primarily used for HEVs is the Nickel Metal Hydride (Ni-MH) battery. The main deterioration mechanisms for the Ni-MH battery are: hydroxidation of the hydrogen-storing alloy active material on the negative electrode, oxidation and change of crystal structure of the oxy nickel hydride active material on the positive electrode, the drying out of the electrolyte in the separator due to swelling of the electrode and elimination of active material on the electrodes. These mechanisms cause a loss of power and capacity. In this manner, the deterioration of Ni-MH batteries are expected to follow reaction kinetics theory, as the main causes of deterioration chemical reaction of the electrodes such as the oxidation and the hydroxidation of the active material. In order to determine if this interpretation is correct, the relationship between battery deterioration and chemical reaction induced electrode deterioration was analyzed.

As high current is required of the battery, internal resistance was chosen as a deterioration dispersion coefficient. Concerning chemical reactions leading to electrode deterioration, the structure of the electrode was analyzed and the behavior of deterioration elements was studied. The differences between the structure of the negative electrode before and after deterioration were analyzed using X-Ray diffraction (XRD). The results of this analysis are shown in Fig. 1. The negative electrode of this battery is a

hydrogen-storing alloy of rare earth metals, primarily made up of lanthanum nickel (LaNi_5). The amount of one of the deterioration elements, lanthanum hydroxide (La(OH)_3), was found, at its peak, to have increased as compared to before deterioration.

Furthermore, the relationship between the increase in elements of deterioration and the increase in internal resistance was considered. The structure of the negative electrodes that had various internal resistances was similarly analyzed using XRD. The amount of the deterioration component La(OH)_3 was shown by dividing its peak intensity by that of LaNi_5 . The peaks used for comparison were the maximum intensity peaks for both La(OH)_3 and LaNi_5 , the peak of La(OH)_3 being the (100) plane and the peak of LaNi_5 being the (111) plane. The index used for the increase in internal resistance is the ratio of increase in internal resistance, defined as the increase in internal resistance after deterioration divided by the original internal resistance. Lastly, the relationship between the amount of the deterioration component La(OH)_3 and the increase in internal resistance was analyzed. The results of this analysis are shown in Fig. 2. This analysis confirmed that there is a

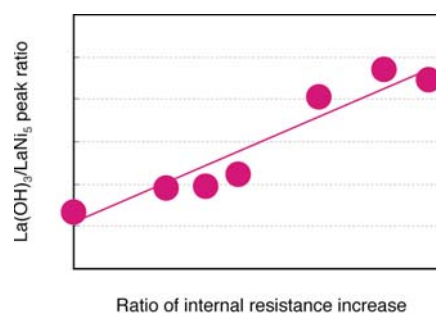


Fig. 2 Relation between $\text{La(OH)}_3 / \text{LaNi}_5$ peak ratio and ratio of internal resistance increase

correlation between the amount of the deterioration component $\text{La}(\text{OH})_3$ and the increase in internal resistance ratio. This correlation shows that the chemical reaction induced electrode deterioration contributes to the battery deterioration mechanism; therefore, it can be treated similar to reaction kinetics. This also leads to the understanding that the amount of chemical reaction induced electrode deterioration is proportionate to the ratio of increase in internal resistance. Therefore it is possible to use the ratio of increase in the internal resistance in place of the battery deterioration reaction rate.

3. Battery Deterioration Reaction Rate Equation

The Eyring equation has been chosen as the reaction rate equation for development of a battery deterioration reaction rate equation. This equation has been generalized through using the original reaction temperature dependence and adding stresses other than temperature as well. Defining the amount of deterioration as x and the rate of reaction as K gives the following equation:

$$dx/dt = K, K = a(kT/h) \cdot \exp(-\Delta E/kT) \cdot S^\alpha \quad (1)$$

- a : Constant
- k : Boltzmann's constant
- h : Planck's constant
- ΔE : Activation energy
- T : Absolute temperature
- S : Stress factors other than temperature
- α : Constant

The following equation can be used for a small range of temperature T .

$$K = \Lambda \cdot \exp(-\Delta E/kT) \cdot S^\alpha \quad (2)$$

- Λ : Constant

On the other hand, using the Arrhenius equation, which only provides dependence on temperature gives the following equation:

$$K = A \cdot \exp(-\Delta E/kT) \quad (3)$$

- A : Constant

Comparing the Eyring equation with the Arrhenius equation, the Eyring equation has had stress factors added. Furthermore, focusing on just the stress factors in Eq. (2) gives the following equation:

$$K = B \cdot S^\alpha \quad (4)$$

- B : Constant

Therefore, Eq. (4) is used when there are stresses other than temperature such as thermal fatigue (hot-cold cycle) deterioration etc. The constants Λ , A , and B are termed frequency factors⁽⁷⁾ in reaction kinetics.

Applying the Eyring equation, Eq. (5) has been developed as an estimate for a reaction rate equation using 2 stress factors other than temperature. These 2 stresses are current load and SOC band.

$$K = \Lambda \cdot \exp(-\Delta E/kT) \cdot S_1^\alpha \cdot S_2^\beta \quad (5)$$

- S_1 : The 1st stress factor
- α : Constant
- S_2 : The 2nd stress factor
- β : Constant

4. Verification and Results

4.1. Verification Method

The constants in Eq. (5) are determined in the following manner. First of all, deterioration reaction rate K is the amount of deterioration, or the amount of increase in internal resistance x divided by the life cycle test time t . Next, the temperature factor constant $-\Delta E/k$ and the other stress factor constants α and β are defined by conducting analysis for each stress factor. Placing each of these deterioration stress factor constants in Eq. (5) completes the deterioration reaction rate equation except for the frequency factor Λ . Finally, through substituting each of the deterioration factor conditions used in testing, it is possible to solve for the unknown frequency stress factor Λ .

In order to establish Eq. (5) as a battery deterioration reaction rate equation, it is necessary for the frequency factor to remain the same through various conditions of temperature, current load, and SOC band. Confirmation is possible through performing life cycle tests while changing conditions of the deterioration factors.

Next a particular method for deriving each of the deterioration factor constants will be shown. The deterioration reaction of the HEV Ni-MH battery is the chemical reaction production of $\text{La}(\text{OH})_3$. The reaction rate increases with temperature because the reaction components collide more frequently at higher temperature. Larger current load and SOC band leads to larger reaction surface area on the electrode, which increases the reaction rate. From this discussion, it can be easily understood that if each single factor is separated, the current load and the SOC band load factors follow Eq. (4) while the temperature follows Eq. (3).

The temperature factor constant $-\Delta E/k$ is found by focusing only on the temperature, allowing use of Eq. (3), the Arrhenius equation. Taking the logarithm of both sides gives the following equation.

$$\ln K = \ln A - \Delta E/kT \quad (6)$$

The deterioration reaction rate K can be shown to be $K = x/t$, therefore Eq. (6) becomes the following when $x = 1$.

$$\ln(1/t) = \ln A - \Delta E/kT \quad (7)$$

This shows both the inverse of temperature and the logarithm of the reaction rate in a first order equation. If it is possible to determine the relationship between the temperature and reaction rate at 2 or more points, it will be possible to find the slope $-\Delta E/k$. In a life cycle test, the temperature is varied while other stresses are held constant.

It is also possible to determine individual influences of the current load constants and the SOC band constants through focusing only on their stress characteristics. Taking the logarithm of both sides of Eq. (4), which focuses only on individual stress factors, gives the following equation.

$$\ln K = \ln B + \alpha \ln S \quad (8)$$

Table 1 Test conditions and test times

No.	Test classification for constant calculation			Test conditions			Test time (hr)
	Battery temperature ($-\Delta E/k$)	Current (α)	SOC band (β)	Battery temperature ($^{\circ}\text{C}$)	Hour rate of charge and discharge current (C)	SOC band (SOC%)	
1	○			35	2	20	2 800
2	○		○	45	2	20	1 800
3	○	○		55	2	20	1 100
4		○		55	3	20	700
5		○		55	5	20	400
6			○	45	2	40	1 500
7			○	45	2	60	1 200

The deterioration reaction rate K can be shown to be $K = x/t$, therefore Eq. (8) becomes the following when $x = 1$.

$$\ln(1/t) = \ln B + \alpha \ln S \quad (9)$$

This shows both the logarithm of the stress factors and the logarithm of the reaction rate in a first order equation. If it is possible to determine the relationship between the stress factors and the reaction rate at 2 or more points, it will be possible to find the slope α . In a life cycle test, one of the stress constants is varied while the other stress constants and temperature are held constant.

4.2. Life Cycle Test

With the battery mounted in a vehicle, in order to make a final, accurate estimate of battery life expectancy, a charge/discharge profile was used from actual driving profile for the life cycle test. And in order for the reaction surface area on the electrode surface to become as large as possible, the profile with a high frequency of switching between current input and current output was chosen. The charge/discharge profile is a control value sent to the charge/discharge battery test equipment and is shown as a current charge/discharge value request per unit time.

The values of each of the deterioration factors are: temperature is the average battery temperature during the tests, the average absolute value of current during the tests for the current load, and the difference between the highest SOC and lowest SOC for the SOC band. The unit used for the average absolute current is C and is the time rated charge/discharge current. It means that 1C is the current value that the battery can be discharged in 1 hour. The unit of SOC is defined to be SOC%. During the driving cycle test the current load of charge/discharge profile was set to 2C and the SOC band set to 20 SOC%. This is called the standard profile.

Also, using this standard profile as a base life cycle test, testing was performed at 2 or more test conditions for each of

the stress factors. During this test, the temperatures that were used were 35 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$, and 55 $^{\circ}\text{C}$. The average current loads that were used are: the standard profile 2C and using the standard profile charge/discharge frequency with the different current load settings of 3C and 5C. The SOC bands that were used are: the standard profile of 20 SOC% and an expanded setting of 40 SOC% and 60 SOC%. These profiles were used repetitively for the life cycle tests. The conditions and test time for each of the deterioration factors is shown in Table 1. For each of the deterioration factors, higher loads lead to a faster rate of increase in internal resistance and shorter test times.

4.3. Deterioration Factor Constants

Using the life cycle test results, each of the deterioration factor constants were derived from the relationship between the reaction rate and the deterioration factors. The reaction rate unit is defined to be (R%/hr). First, the temperature characteristic results are shown in Fig. 3. In order to

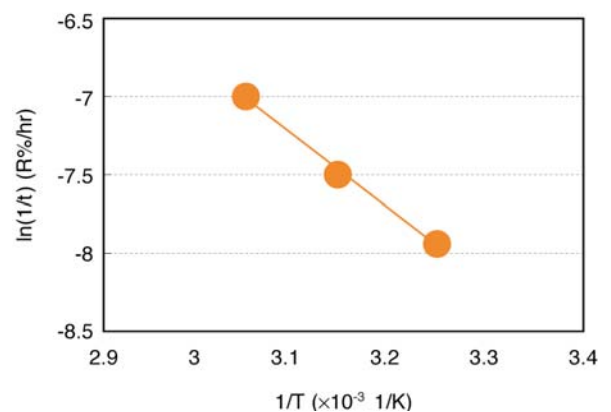


Fig. 3 Relation between inverse of battery temperature and logarithm of reaction rate

determine the values of the constants using Eq. (7), the relationship between the inverse of the absolute temperature for the test and the logarithm of the deterioration reaction rate $\ln(1/t)$ was investigated. For the temperature factor constant $-\Delta E/k$: $-4\ 700(\text{K})$ was obtained from the slope of the first order straight line approximation.

Next, the current load characteristic results are shown in Fig. 4. In order to determine the values of the constants using Eq. (9), the relationship between the logarithm of the current load S_1 and the logarithm of the deterioration reaction rate $\ln(1/t)$ was investigated. For the current load constant α : $1.1(1/\text{C})$ was obtained from the slope of the first order straight line approximation.

Next, the SOC band characteristic results are shown in Fig. 5. In order to determine the values of the constants using Eq. (9), the relationship between the logarithm of the current load S_2 and the logarithm of the deterioration reaction rate $\ln(1/t)$ was investigated. For the SOC band constant β : $0.36(1/\text{SOC}\%)$ was obtained from the slope of the first order straight line approximation.

This shows how the deterioration factor constants were determined from analysis for the constants on the individual deterioration factors.

4.4. Verification of the Battery Deterioration Reaction Rate Equation

Placing the values for the deterioration factor constants obtained in 4.3 in Eq. (5) gives the following equation.

$$K = x/t = \Lambda \cdot \exp(-4\ 700/T) \cdot S_1^{1.1} \cdot S_2^{0.36} \quad (10)$$

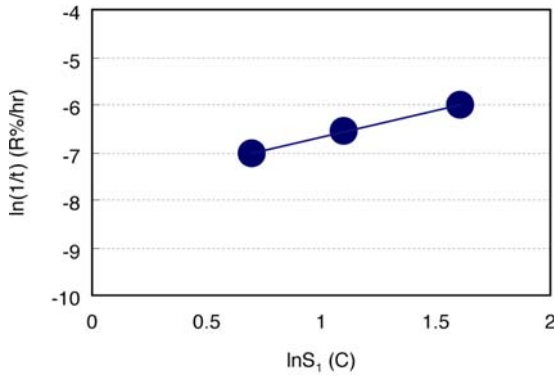


Fig. 4 Relation between logarithm of hour rate of charge and discharge current and logarithm of reaction rate

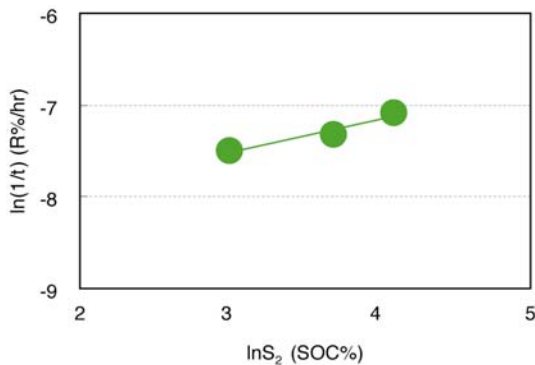


Fig. 5 Relation between logarithm of SOC band and logarithm of reaction rate

Table 2 Test conditions and frequency factors

No.	Test conditions			Frequency factor (R%/hr)
	Battery temperature (°C)	Hour rate of charge and discharge current (C)	SOC band (SOC%)	
1	35	2	20	240
2	45	2	20	230
3	55	2	20	240
4	55	3	20	240
5	55	5	20	240
6	45	2	40	220
7	45	2	60	230

The value of the frequency factor Λ can be found using each of the known life cycle conditions, with $x = 1$. The results are shown in Table 2.

Throughout the tests, the frequency factor Λ remains the same for the most part. The average value was found to be 240 (R%/hr). As the frequency factor was stable throughout tests where the conditions of each of the deterioration factors were changed, the battery deterioration reaction rate equation can be expressed as it is written in Eq. (5), an application of the Eyring equation with stress factors added. The following equation has been defined for the battery used in this life cycle test.

$$K = x/t = 1/t = 240 \cdot \exp(-4\ 700/T) \cdot S_1^{1.1} \cdot S_2^{0.36} \quad (11)$$

The frequency factor is interpreted as the number of collisions that the reaction molecules make in the chemical reaction⁽⁸⁾. The stability of the frequency factor means that the chemical reaction is the same and that the deterioration mechanism does not change. After the life cycle test, the structure of the electrodes was analyzed and the deterioration condition was found to be the same as could be seen in Fig. 1. And, the deterioration effects of the battery deterioration factors are synergism as can be seen in Eq. (11).

Furthermore, if the test time t is solved for, the following equation results from Eq. (11).

$$t = 1/\{240 \cdot \exp(-4\ 700/T) \cdot S_1^{1.1} \cdot S_2^{0.36}\} \quad (12)$$

Therefore, if the vehicle speed during the test mode is known, it is possible to determine the range by multiplying the test time and the vehicle speed. In the application to a vehicle, quantifying values for the average temperature, average absolute current load value and the SOC band for a representative drive cycle mode, makes it possible to estimate the expected time and therefore vehicle range before reaching a specified deterioration amount.

5. Conclusion

Through estimating the life expectancy of HEV batteries, an investigation was performed for the application of the Eyring equation to deterioration reaction rate equation that includes the battery deterioration factors temperature, current load and SOC band. The following were obtained:

- (1) Because the deterioration reaction rate equation frequency factor was stable through changes in each of the deterioration factors, the deterioration reaction rate equation was established as correct.
- (2) The stability of the deterioration reaction rate equation frequency factor through changing conditions of the deterioration factors means that the deterioration mechanism is likewise stable.
- (3) It is possible to estimate the battery life through quantifying each of the deterioration factors and using this deterioration reaction rate equation. It can now be used in the practical application of estimating the battery life for vehicles.

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■ Author ■



Tatsuo MINAMI