

Development of Calendar Aging Model for Lithium Ion Rechargeable Batteries

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ABSTRACT

A new life prediction model was developed on the basis of lithium ion rechargeable battery analysis results. This makes it possible to predict an accurate battery capacity fading status that is dependent on storage time and to shorten the time for acquisition of experimental data required for prediction. For this model, attention was focused on the fact that the various causes of aging are electrochemical reactions that occur within the battery, and model equations that have terms for temperature and energy were adopted for this model. The variables that are required in the established equations were determined by curve fitting with the results from accelerated calendar aging tests conducted at three temperature conditions and three state of charge conditions, for a total of nine conditions. The variables obtained from the accelerated calendar aging test conducted at 65°C and state of charge of 80% yielded prediction results that matched the experiment values. Since this model can also be applied to predict the charge and discharge curves of a battery that has aged, it is anticipated that the model can be further applied to estimate the state of charge from the battery terminal voltage.

1. Introduction

As lithium ion rechargeable batteries enter widespread use, there are growing needs for prediction of remaining life and for analysis of aging state, regardless of whether it is for aging caused by repeated cycles of charge and discharge (cycle aging) or for aging caused by storage (calendar aging). In some cases, spare batteries used as service parts need to be available for long-term supply, for as many as 10 years or more after production has finished, as long as there is demand for them. This means that life prediction technology is needed for defining the needed conditions for long-term storage. When batteries are used for emergency power supply, their performance in a long-term stand-by state needs to be guaranteed, and life prediction by calendar aging is therefore a crucial technology. At present, life predictions for 10 years or more are being made from limited data for about two years of testing⁽¹⁾⁻⁽⁶⁾ due to the need to shorten development time. In such cases, the method used is to carry out accelerated calendar aging tests at a higher temperature than the temperature during actual use or at a higher state of charge (SOC), and then to predict aging in the envisioned temperature range of use

by means of the Arrhenius equation. Working from the results for capacity fading due to calendar aging, Su et al.⁽⁴⁾ derived an equation that is similar to the Arrhenius equation to express the aging rate as a function of temperature and SOC. However, battery aging is not something that occurs due to just a single factor⁽⁷⁾⁻⁽¹⁰⁾, so issues are likely to remain regarding the accuracy of aging rate values obtained using just a single equation. There is also the work of Ouyang et al.⁽⁵⁾, which divides the cause of cycle aging between the loss of cyclable lithium, in other words the capture of active lithium by solid electrolyte interphase (SEI) between the electrodes so that there is less active lithium flowing between the electrodes, and single-electrode capacity fading. The respective aging rates were expressed using the Arrhenius equation, incorporating elements from empirical equations when representing the C-rate effect. These approaches all include empirical equations that are not based on the aging mechanism^{(4), (5)}, so issues are likely to remain regarding the accuracy of values obtained by long-term life prediction using limited data from short-term testing.

In a previous report⁽⁷⁾, the authors elucidated the mechanism of calendar aging in high-power lithium ion

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rechargeable batteries and clarified that the principal causes are the loss of active lithium and cathode capacity fading. (These two causes will be referred to hereafter as the aging mechanism.) The purpose of the present research, therefore, has been to create a predictive equation that is based on this aging mechanism and that accords with physical law, and in this way to establish a method for predicting the capacity fading of a cell more accurately from data obtained through short-term testing.

2. Creation of the Prediction Model

2.1. Issues in Conventional Model Equations

As stated above, methods of conducting accelerated tests and employing the Arrhenius equation to predict the aging that will occur in the envisioned temperature range of use were widely proposed⁽¹⁾⁻⁽⁶⁾ for the purpose of shortening the storage test period. However, there are two general types of enhancement that would be desirable for these methods. The first is the need to apply equations that divide battery capacity fading between the cathode and the anode, and the second is to apply the relationship between aging and SOC to the prediction equation.

The former, as has already been reported⁽⁷⁾, arises from the fact that battery aging is not caused by a single chemical reaction, and battery capacity fading therefore cannot be accurately expressed in a single equation⁽⁸⁾⁻⁽¹⁰⁾. The latter arises from the fact that the Arrhenius equation does not clearly express the relationship with SOC. Actually, as shown in Figs. 1 and 2, both cathode and anode display aging behavior that is dependent on SOC (potential), but unless the prediction equation is dependent on SOC, tests will need to be conducted under various SOC conditions so as to determine the dependence on SOC. A prediction equation that includes the relationship between aging and SOC will also be needed in order to cut back on test conditions.

2.2. Extending the Arrhenius Equation to Include Dependence on SOC

The battery aging mechanism can be understood as a change in the form of matter that occurs in conjunction with electrochemical reactions. In the batteries described in this paper, the active lithium amount loss was caused by SEI formation while cathode active material capacity fading was caused by a crystalline structure transformation. This kind of change of state can be expressed by the Arrhenius equation, as shown in Fig. 3(a). The chemical reaction rate k in the process of transition from State A to State B (the chemical reaction process) is expressed using the activation energy E_0 and the temperature T during the process of state transition. In order to provide for dependence on the electrode potential, or in other words the SOC, the energy on the State A side is raised by the external potential V , as shown in Fig. 3(b). As a result, the activation energy that was initially E_0 is reduced by the amount αV . Here α

is a transfer coefficient that is assigned a value of about 0.5. As a result, the reaction rate, which is dependent on the external potential V , can be expected to increase. The model equations were formulated according to this conceptual approach. The conceptual approach for this SOC dependence is the same as for the overpotential dependence in the Butler-Volmer equation⁽¹¹⁾, so the Arrhenius equation extended to include SOC is hereafter referred to as the Butler-Volmer equation.

2.3. Derivation of Model Equations for Active Lithium Loss

As reported in the previous paper⁽⁷⁾, SEI is an accumulation on the anode surface of products of the decomposition of the electrolyte components, including

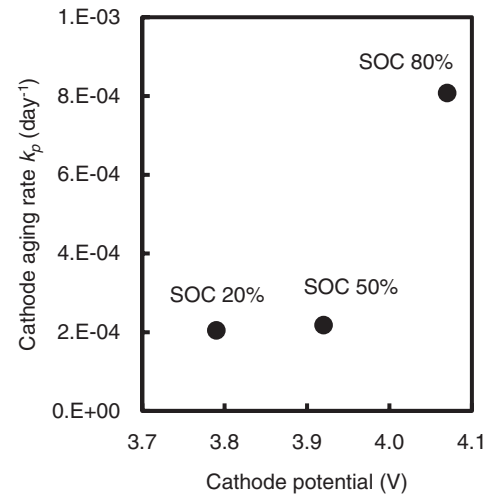


Fig. 1 Cathode aging rate. $Q_{cathode}(t) = (1 - k_p t) Q_{cathode-initial}$ (aging condition: 65°C)

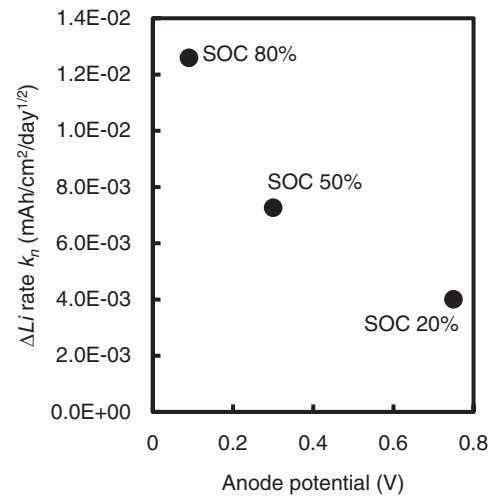


Fig. 2 Anode ΔLi increasing rate. $\Delta Li(t) = k_n \sqrt{t}$, $\Delta Li = Q_{shift} + Q_{cathode}$ (aging condition: 65°C for 100 days)

cyclable lithium, or in other words, active lithium flowing between the electrodes, and this accumulation results in the loss of active lithium. Since this decomposition occurs by an electrochemical reduction reaction^{(7), (12)-(19)}, the Butler-Volmer equation determines the rate of that reaction by the electrode potential at the anode, the reaction temperature, and the concentration of the reactant. The reactant exists in large amounts in the electrolyte, and it is assumed that changes in its concentration over the battery lifetime can be ignored. Therefore the reactant concentration can be treated as a constant. Taking the electrical conductivity of the SEI into consideration, a correction was made to the electrode potential at the anode according to the following rationale.

An ideal SEI is an electrical insulator, and as a solid electrolyte membrane, it can only conduct lithium ions. However, the SEI in an actual battery is said to have slight

electrical conductivity due to the doping effect of electrolyte components⁽¹⁵⁾⁻⁽¹⁷⁾. The gradual SEI growth in lithium ion rechargeable batteries occurs because of this slight electrical conductivity. In such cases, the value of the activation energy of SEI growth will be the difference between the reaction equilibrium potential of the electrolyte components and the electrode potential from which the reduction in potential due to the electroconductive resistance of the SEI is further subtracted. When the term for activation energy in the reaction equilibrium potential is $E_{0,n}$ and the anode overpotential is V_n , the activation energy, as shown in Fig. 3(b), will be reduced by $\alpha_n V_n$ so that it will be $(E_0 - \alpha_n V_n)$. When the SEI thickness is x while the electrical conductivity and electrical resistance of SEI are σ_{SEI} and ρ_{SEI} , respectively, then the term for activation energy will be $\left[E_{0,n} - \alpha_n \left(V_n - \frac{F}{\sigma_{SEI}} x \right) \right]$. Here F is the Faraday constant.

Therefore the SEI growth rate $\frac{dx}{dt}$ can be expressed by Eq. (1) using the Butler-Volmer equation^{(11), (15)}.

$$\nu_{Li} = \frac{dx}{dt} = \frac{N_s - \Delta Li}{N_s} \frac{M_{SEI}}{F \rho_{SEI}} A_n \exp\left(-\frac{E_{0,n}}{RT}\right) \exp\left(\frac{\alpha_n V_n}{RT}\right) \exp\left(-\frac{\alpha_n F}{RT} \frac{1}{\sigma_{SEI}} x\right) \quad (1)$$

Here t is time, N_s is the number of moles of active lithium in the anode, ΔLi is the number of moles of active lithium loss, M_{SEI} is the molecular weight of SEI components, A_n is the frequency factor in the Arrhenius equation, R is the gas constant, T is the absolute temperature, and α_n is the transfer coefficient.

Here k_{s1} and k_{s2} are inserted to form the following:

$$k_{s1} = A_n \exp\left(-\frac{E_{0,n}}{RT}\right) \exp\left(\frac{\alpha_n V_n}{RT}\right) \quad (2)$$

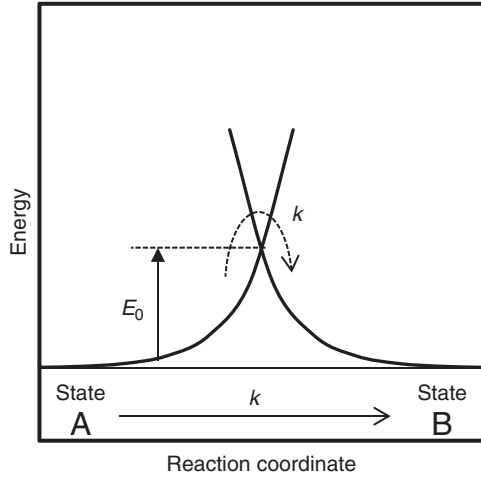
$$k_{s2} = -\frac{\alpha_n F}{R} \frac{1}{\sigma_{SEI}} \quad (3)$$

Equation (1) can therefore be expressed as Eq. (4):

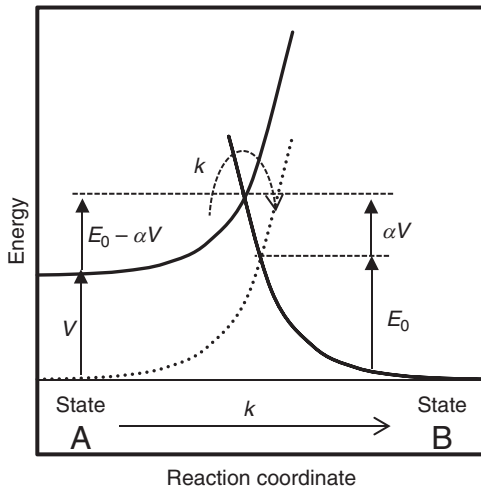
$$\nu_{Li} = \frac{dx}{dt} = \frac{N_s - \Delta Li}{N_s} \frac{M_{SEI}}{F \rho_{SEI}} k_{s1} \exp\left(-\frac{k_{s2}}{T} x\right) \quad (4)$$

The term for k_{s2} expresses the electrical conductivity of SEI, and this is considered to be similar to the mechanism of electrical conductivity in semiconductors⁽¹⁵⁾. In a semiconductor, electrical conductivity occurs due to scattered carriers, and so it is known to be proportional to the temperature raised to the power of 3/2. Therefore k_{s2} can be expressed as shown in Eq. (5), as a function of $T^{3/2}$.

$$k_{s2} = k_{2a} T^{\frac{3}{2}} + k_{2b} \quad (5)$$



(a) Activation energy in transition from State A to State B



(b) Changes in activation energy in case of application of electric potential

Fig. 3 Potential expansion of Arrhenius law in state transition of chemical reaction

In Eqs. (1)-(5) above, V_n , T , and time t are set according to the test conditions, while the variables A_n , $E_{0,n}$, α_n , k_{2a} , and k_{2b} can be determined by fitting the active lithium loss amount derived from electrochemical measurement. Specific usage data groups are given at the beginning of Section 3.1.

2.4. Derivation of Model Equations for Cathode Active Material Capacity Fading

Cathode capacity fading occurs as a result of partial crystalline structure transformation of cathode active material^{(7), (20), (21)}. Its rate v_p is governed by the reaction temperature and cathode potential. As with the anode, v_p can be expressed as Eqs. (6) and (7) using the Butler-Volmer equation⁽¹¹⁾.

$$v_p = k_p \quad (6)$$

$$k_p = A_p \exp\left(-\frac{E_{0,p}}{RT}\right) \exp\left(\frac{\alpha_p V_p}{RT}\right) \quad (7)$$

Here k_p is the rate of crystalline structure transformation of cathode active material determined by testing, A_p is the Arrhenius equation frequency factor, $E_{0,p}$ is the reaction equilibrium potential, α_p is the transfer coefficient, and V_p is the cathode potential. As with the anode, V_p , T , and time t are set according to the test conditions, k_p is determined from testing, and A_p , $E_{0,p}$, and α_p can be derived by curve fitting using Eqs. (6) and (7). Since V_n and V_p are determined by approximation from the battery SOC-Open Circuit Voltage (OCV) curve (Fig. 4), the values defined as test conditions are SOC and retention temperature T .

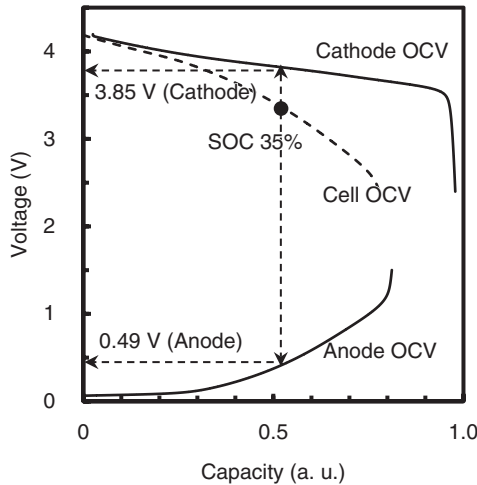


Fig. 4 Calculation of electrode potential from SOC-OCV curve

3. Analysis Results and Discussion

3.1. Computed Prediction of Active Lithium Loss Amount

The results of electrochemical measurement given in the previous report⁽⁷⁾ and Eqs. (8) and (9) were used to calculate the loss amount of active lithium ΔLi . The battery storage periods were defined up to 180 days, and SOC of 80%, 50%, and 20%, together with temperatures of 65°C, 55°C, and 45°C were used for the respective conditions.

$$\Delta Li = Q_{shift} + \Delta Q_{cathode} \quad (8)$$

$$Q_{shift} = Q_{R, cathode} - Q_{R, anode} \quad (9)$$

Here Q_{shift} is the amount of shift, while $Q_{R, cathode}$ and $Q_{R, anode}$ are the remaining discharge capacity of the respective electrodes and $\Delta Q_{cathode}$ is the cathode capacity fading value.

The variables A_n , $E_{0,n}$, α_n , k_{2a} , and k_{2b} were successfully determined from the active lithium loss amount determined by Eq. (8) together with fitting using model equations Eqs. (2)-(5). These values were then plugged back into the model equations again and the active lithium loss amount was predicted (Fig. 5) for validation. The various symbols in the figure represent actual measurements and the lines indicate predicted values. The active lithium loss amount predicted to occur after 180 days or more matched with the actual measurement. This result indicates that the active lithium loss amount can also be predicted over a long term, extending beyond the test period.

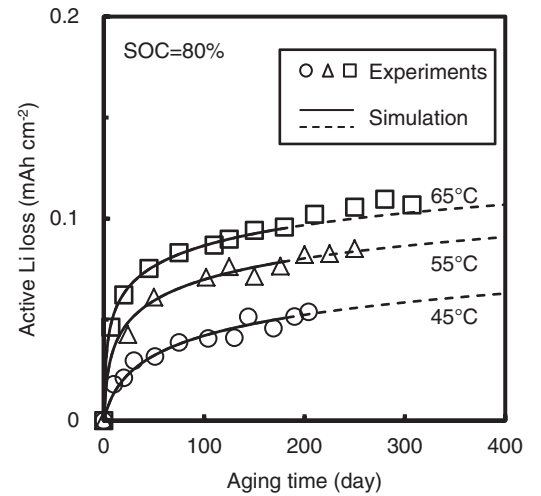


Fig. 5 Parameter fitting for active Li loss by SEI growing

3.2. Computed Prediction of Cathode Active Material Capacity Fading

As reported in the previous paper, the cathode capacity fading value $\Delta Q_{cathode}$ can be measured directly, and its change over time is shown in Fig. 6. These values were used for curve fitting in accordance with Eqs. (6) and (7) to derive the variables A_p , $E_{0,p}$, and α_p .

3.3. Computed Prediction of Battery Capacity Retention

The variables derived in Sections 3.1. and 3.2. were plugged in to the model equations and the results were used to determine the charge and discharge curves for the

electrodes after the passage of a certain amount of time together with the shift amount Q_{shift} . The concept illustrated in Fig. 7 was then followed to rebuild the full cell charge and discharge curves. As a result, it was possible to predict the battery's charging and discharging characteristics and capacity at a certain SOC and a certain temperature and after a certain amount of time. This made it possible to predict battery life below the low limit value set for capacity (Fig. 8). The parameters used were derived from data for up to 180 days at the retention temperature of 65°C shown in Fig. 8, and they matched with test results for up to 610 days, including the distinctive turnoff points in the changes of capacity retention that appear after 180 days (arrowhead

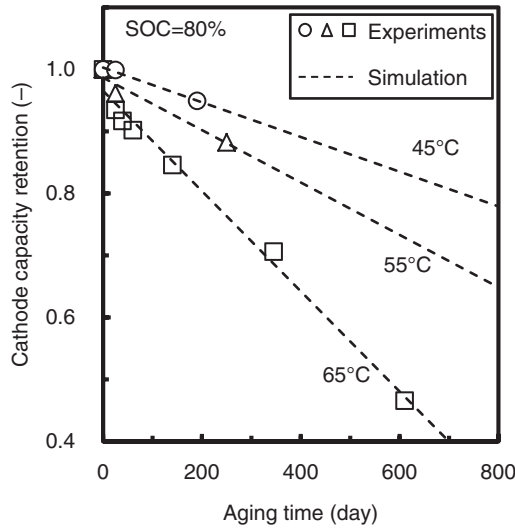


Fig. 6 Parameter fitting for cathode capacity fading

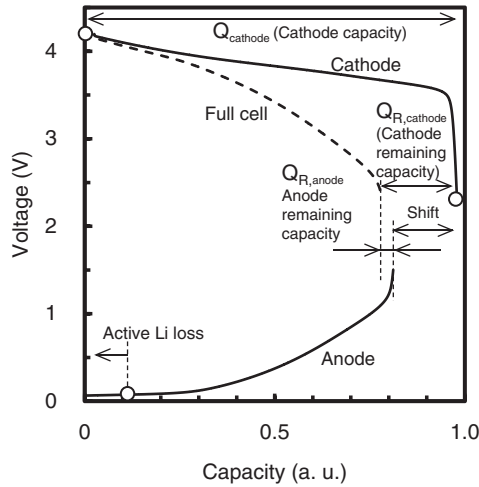
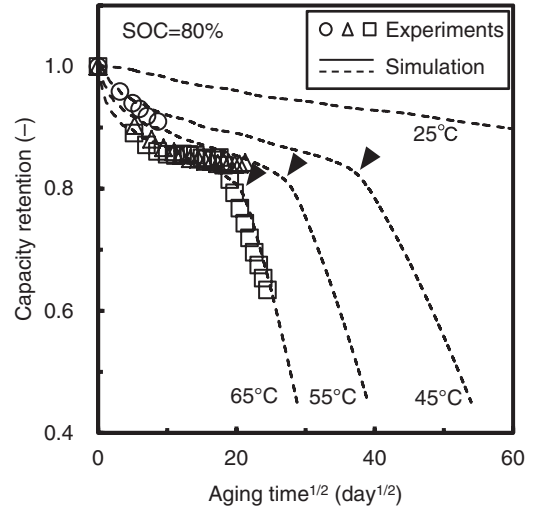
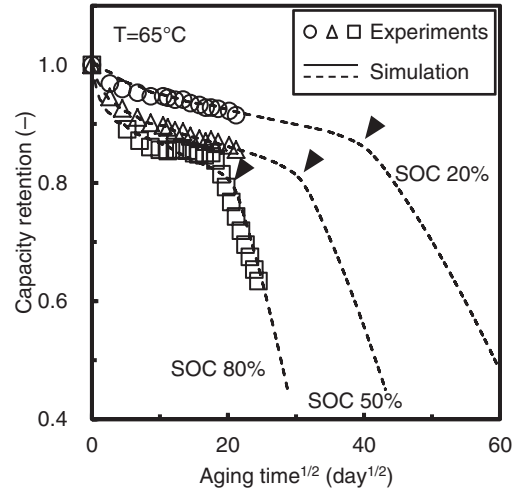


Fig. 7 Schematic drawings about cathode capacity, capacity shift between anode and cathode, and full cell capacity



(a) Temperature variable (aging condition: SOC=80%)



(b) SOC variable (aging condition: T=55°C)

Fig. 8 Results of capacity retention prediction by using the model developed in this work

symbols in Fig. 8), so that prediction was successful. It was apparent from the test results shown in Figs. 5 and 6 that even under conditions of different temperature (55°C and 45°C) and different SOC (50% and 20%), the causes of aging were the same as at 65°C and SOC 80%. Therefore the application of this model is valid. Testing was not carried out to the range where capacity attenuation increases under these conditions, but that timing was successfully predicted [Figs. 8(a) and 8(b)]. As shown by the prediction results at a temperature of 25°C [Fig. 8(a)], it is also possible to predict conditions that have not been tested.

Figure 9(b) shows the discharge curve that was rebuilt at the specific numbers of 453 days and 1220 days at SOC 80% and 55°C. It was predicted that battery aging would be accompanied by changes in the discharge curve. By using this discharge curve and the voltage between the electrodes, it also becomes possible to estimate the SOC so as to be consistent with actual conditions, and the application of this to estimate the remaining capacity in batteries on-board a vehicle can be anticipated.

Since this method can also be used for life prediction over the long term, it also enables the investigation of

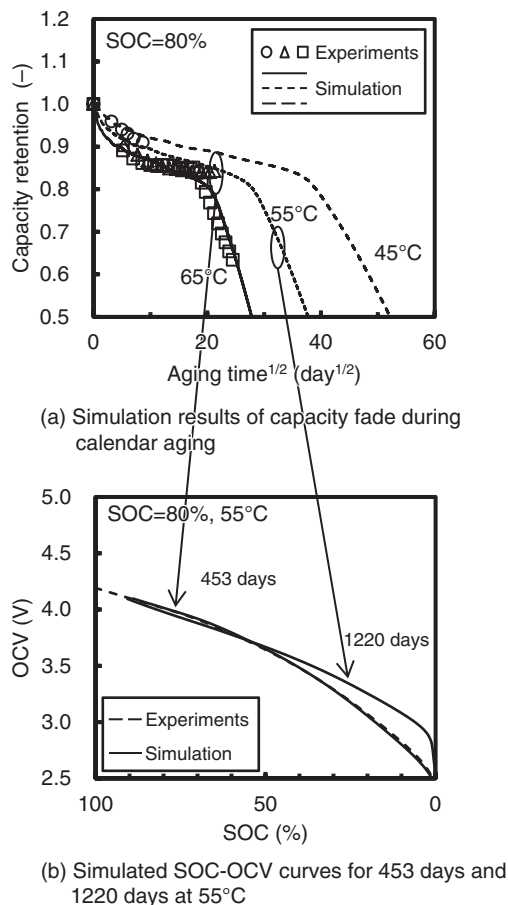
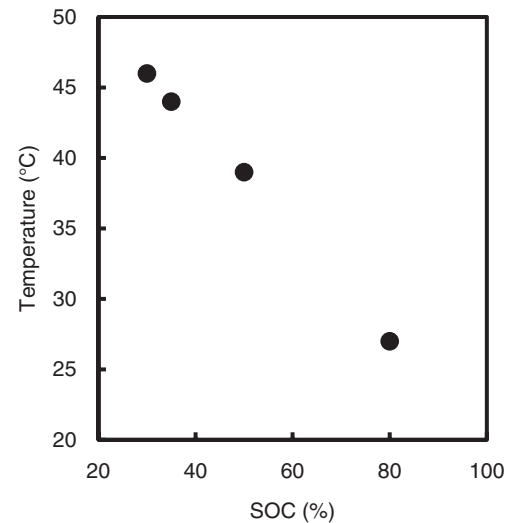


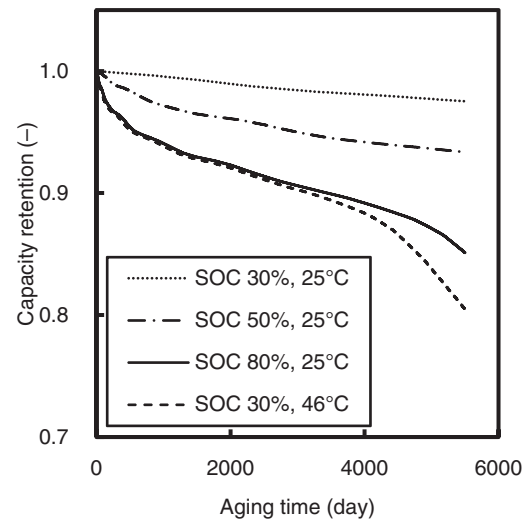
Fig. 9 Simulation results of capacity fade and SOC-OCV curves

constraint conditions on the storage environment for batteries as service parts. For example, the constraining temperature and SOC to realize capacity retention of 80% or more were sought for a storage period of 15 years (5475 days) (Fig. 10). By this approach, it will be possible to determine an appropriate storage SOC even if the storage location is not air conditioned, as long as the temperature at that location can be anticipated.

As this indicates, this model has been created as a physical model. Therefore it can be used for long-term life prediction from a brief storage period of about a half year together with testing at three temperature conditions and



(a) Storage conditions that will result in a capacity retention rate of 80% after 15 years (5475 days)



(b) Simulated calendar aging results near room temperature

Fig. 10 Simulation results of temperature and SOC constraint conditions for long term storage

three SOC conditions, for a total of nine conditions, which takes less time and effort for testing.

3.4. Discussion of Modeling

As indicated up to this point, inserting the temperature and SOC as input to the model equations that were created allows prediction of battery capacity and discharge curve for the desired time. It is possible that this will be able to reduce the number of tests required to create aging maps by one-half or more.

If it is within the scope of applicability of the previously reported⁽⁷⁾ aging mechanism, it will also be possible to apply this approach not only to the high-power batteries already reported on, but also to high-capacity type batteries and cycle aging.

At the same time, this model derives the variables it uses by curve fitting based on test results. This means that measurement errors and individual differences in the batteries used for testing need to be taken into account, and the occurrence of error in the prediction results also needs to be taken into account. Under the accelerated aging conditions of 65°C temperature and 80% SOC, there was also a slight discrepancy between the active lithium loss amount measured in electrochemical testing and the predicted amount. It may be that this is caused by an oxidation reaction that occurs in the electrolyte at the cathode and cancels out the active lithium loss amount^{(8), (22), (23)}. In this model, this oxidation reaction is included in the cathode capacity fading and processed together with it. However, it is conceivable that this oxidation reaction may no longer be negligible in a temperature range and under SOC conditions that produce a faster oxidation reaction rate. As an issue for the future, a term for the oxidation reaction will probably need to be inserted into the model equation in order to further enhance prediction accuracy.

4. Conclusion

A new life prediction model was created on the basis of the battery aging mechanism elucidated by analysis results. The focus of this paper was on the fact that the aging mechanism arises from electrochemical reactions. Taking the Arrhenius equation as the point of departure, a prediction model that takes in SOC (potential) was newly created. The model's variables were derived by curve fitting based on test results. The charge and discharge curves of a battery after aging were successfully predicted from the variables that were obtained. Battery capacity was calculated from those charge and discharge curves, and the time taken to reach the previously decided lower limit for capacity, or in other words the battery life, was successfully predicted. Since this model was created to be a physical model, the short period of about one-half year that is the period of the accelerated calendar aging test, together with the limited test results, consisting of the three lowest conditions of temperature and the three lowest conditions

of SOC, for a total of nine conditions, were used to derive variables by which long-term life prediction has been made possible. As a result, it became possible to use this model to predict capacity retention behavior where the slope of the curve changes, which conventional methods are unable to predict. It is anticipated that this approach will be applied in defining the constraint conditions for the environment in which batteries are stored as service parts and other such matters. The use of predicted charge and discharge curves and the voltage between the electrodes will make it possible to estimate the SOC so as to be consistent with actual conditions. It is also anticipated that this approach will be applied to estimate the remaining capacity in batteries on-board a vehicle.

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