Prediction of Li-ion Battery Module Performance under Running Condition Based on "Multifactorial Degradation Model"

Yoichi Takagishi 1) Tatsuya Yamaue 1)
1) Kobelco Research Institute Inc
1-5-5 Takastukadai, Nishi-ku, Kobe,651-2271, Japan
(E-mail: takagishi.yoichi@kki.kobelco.com)

Received on May 23, 2017

ABSTRACT: The degradation-thermal coupled simulations of Li-ion battery module have been performed assuming running condition of automotive vehicle. Discharge/charge simulation was based on Single Particle model (SP model), which consists of electrochemical, mass transfer and heat transfer equations. In this study, “Multifactorial degradation model” that we have recently developed was adopted in order to estimate resistance increase and capacity fade with cycle. The model includes side reactions such as growth of passive SEI (Solid Electrolyte Interface), structure transition of positive electrode and detachment between active particles. Each parameter to perform calculation was determined for test battery, composed of typical NCM (LiNi0.5Mn0.4Co0.4O2)-graphite system. As a result, SEI thickness of each battery cell grew with current cycle and the variance increased under typical US-06 mode.

KEY WORDS: EV and HV Systems, Li-ion battery, simulation, battery degradation [A3]

1. Introduction

Simulation technologies for Li-ion batteries have been receiving increasing attention since they have been extensively used in EV (Electric Vehicles), HEV (Hybrid Electric Vehicle) and PHEV (Plug-in Hybrid Electric Vehicle). In particular, prediction of battery degradation under running condition of automotive vehicle is of great importance, in view of battery selection, determination of use condition and heat management etc.

Until now, some simple approaches have been adopted widely, which assume battery resistance as an equivalent circuit composed of resistance R and capacitance C. In most case, their degradation is predicted by using empirical law respectively (1-2). In addition, electrochemistry-based degradation model has been developed. This model calculates SEI growth on graphite (or carbon) surface, and both resistance increase and capacity fade of battery are proportion to the SEI thickness (3-4).

On the other hand, many reports (5-7) of observation and analysis results of aged electrode show there exist various degradation mechanism in both positive and negative electrodes. For example, SEI consists of several compositions grows on graphite. The phase transition might occur on the surface of NCM (LiNi0.5Mn0.4Co0.4O2) active particles, which is a typical positive electrode material. In several cases, cracks might proceed between active particles with charge/discharge cycle.

Recently, we have developed “multifactorial degradation model” (8) of capacity fade and resistance increase, including various degradation mechanisms for battery cell. The model is based on Single Particle (SP) model (9) and added side reactions such as growth of passive SEI, structure transition of positive electrode and detachment between active particles. However, degradation behavior of battery module composed of dozens of battery cell, is still unclear. In particular, the effect of strong coupling between temperature and proceeding of degradation is open to question.

In this study, we have applied “multifactorial degradation mode” to the test battery in order to evaluate various factor of battery degradation and extended it to calculate behavior of battery module. In addition, the degradation-thermal coupled simulations were carried out under running condition of automotive vehicle.

2. Parameter determination of initial performance

2.1. Single Particle (SP) model

Charge/discharge process in Li-ion battery, Lithium ions are transported from positive/negative electrode to the opposite electrode through interfacial reaction on active materials and diffusion and migration in electrolyte. On the interface of typical active material NCM of positive electrode and graphite of negative electrode, the following reactions occur
In SP model, these processes are formulated as diffusion equation, electrochemical equation. In active material particles of positive and negative electrodes, Fick’s law is assumed:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (-D_i \nabla c_i)$$

where $c_i$ and $D_i$ means Li concentration and diffusion coefficient, respectively. Suffix $i$ indicates positive or negative electrode. The Butler-Volmer equation is assumed on the interface between active particle and electrolyte,

$$i_j = i_0 \exp \left( \frac{\alpha_F (RT)}{F} \eta_j \right) - \exp \left( -\frac{\alpha_F (RT)}{F} \eta_j \right)$$

where $F$, $R$, $\alpha$ indicates Faraday constant, Gas constant, and transfer coefficient, respectively. $\eta$ denotes overpotential between active material and electrolyte and $i_0$ indicates exchange current density,

$$i_k = F k_c c_i \exp \left( \frac{\alpha F}{RT} \right) (c_{i,\text{max}} - c_i)^{0.5}$$

where $k_c$, $c_i$, $c_{i,\text{max}}$ indicates rate consta, Li ion concentration, and maximum concentration of active material. In this study, linear potential profile between positive and negative electrode is assumed. Figure 1 shows schematic image of SP model.

Figure 1: Schematic image of single particle model.

2.2. Parameter determination of initial performance

Initial discharge parameters of SP model $D_{si}$, $k_j$ are fitted for discharge curves at 25 [°C] of a test battery composed of typical NCM-graphite by means of the least square method. The test battery specification is listed in Table 1.

The determined parameter values of SP model are shown in Table 2. The value of reaction rate coefficient of positive and negative electrode $k_p$ and $k_n$ is $5.0 \times 10^{-10}$ and $7.5 \times 10^{-11}$ [m²/mol·s¹], respectively. Diffusion coefficient of each electrode is $1.0 \times 10^{-13}$, and $5.0 \times 10^{-14}$ [m²/s], respectively. These values are similar order of previous reports.

Table 2 Determined parameters for initial performance parameter...

3. Modeling of cycle degradation

3.1. Multifactorial degradation model

Recently, we have developed “Multifactorial degradation model”, which is a cycle performance model of Li-ion battery in consideration of various degradation mechanism. The model is based on SP model and added side reactions such as growth of passive SEI, structure transition of positive electrode and detachment between active particles. A brief review on the model are made in this section.

3.1.1. SEI growth in negative electrode

Passive SEI film growth on active particles of negative electrode is formulated assuming of the uniform film growth model, which is a cycle performance model of Li-ion battery in consideration of various degradation mechanism. The model is based on SP model and added side reactions such as growth of passive SEI, structure transition of positive electrode and detachment between active particles. A brief review on the model are made in this section.

$$S + 2Li^+ + 2e^- \rightarrow P$$

where S and P means solvent and product, respectively.

On the interface between active material and electrolyte, current density $J$, of side reaction of SEI growth are assumed as;

Fig. 2 shows the comparison discharge curve of 1C and AC impedance (Bode plot) in SOC 100% between experiment of the test battery and simulation with determined parameters. Both simulation curves with the determined parameters are close to the experimental ones.

Fig. 2: Discharge curve (upper) and Bode plot in SOC 100% (lower) of initial condition of experiment and simulation.

Table 2: Determined parameters for initial performance parameter, $k_p$ (m²/mol·s¹) $D_{si}$ (m²/s) $D_{ni}$ (m²/s) $D_{ei}$ (m²/s)
$$J_s = i_{0s} a 0.5F \eta_s / RT$$

where $i_{0s}$, $\eta_s$, and $a$ indicates exchange current density, overpotential and transfer number, respectively.

Fig.3 shows schematic illustration uniform SEI growth model in negative electrode.

![Graphite](image1)

**Fig.3 Schematic image of degradation model of negative electrode.**

Here, growth rate of uniform SEI thickness $\delta$ is proportional to the current density of side reaction $J_s$.

$$\delta_{sei} = \frac{M}{F \rho} J_s$$

where $M$, and $\rho$ is molar mass, and density of uniform SEI film, respectively. Overpotential of side reaction $\eta_s$ decreases with SEI thickness,

$$\eta_s = \eta_{s,0} - \frac{\delta_{sei}}{\kappa_{sei}} J_s$$

where $\eta_{s,0}$, $\kappa_{sei}$ means the initial overpotential of side reaction, and electric conductivity of uniform SEI film.

Capacity loss $Q_{sei}$ of an active material due to SEI growth is calculated using radius of active material particle of negative electrode $r_n$,

$$Q_{sei} = 4\pi a^2 \frac{F \rho}{M} \delta_{sei}$$

Parameters of uniform SEI growth model are listed in Table 3. In this study, electric conductivity $\kappa_{sei}$ and exchange current density of side reaction $i_{0s}$ are fitting parameters. In general, it is difficult to estimate the properties of SEI such as overpotential of side reaction $\eta_s$, molar weight of SEI M and density of SEI $\rho$ directly. In this study, these values are assumed in reference to previous papers (10-11).

| Parameters | Values |
|------------|--------|
| Overpotential of side reaction, $\eta_{s,0}$ [V] | 0.3* |
| Molar weight of SEI, M [kg/mol] | 1.0×10⁻³* |
| Density of SEI, $\rho$ [kg/m³] | 1000* |
| Electric conductivity of uniform SEI, $\kappa_{sei}$ [S/m] | fitting parameter |
| Exchange current density of side reaction, $i_{0s}$ [A/m²] | fitting parameter |

3.1.2 Phase transition in positive electrode

Near surface region of active materials of NCM, which is typical positive electrode, phases transition of crystal structure from hexagonal to cubic structure has been observed (6, 12).

Schematic illustration of degradation model of positive electrode is shown in Fig.4. In this study, such a cubic phase on active material particles was assumed of a constant resistance layer, and that its rate of coverage is proportional to non-covarage ratio,

$$\theta_p = k(1 - \theta_p), \quad R_p = R_{cubic} \theta_p$$

where $\theta_p$, $k$, $R_{cubic}$ means coverage, cover rate, resistance increase on interface reaction of positive electrode, and resistance of cubic phase. Although $R_{cubic}$ is generally unknown parameter, we assumed that it is two times larger than initial discharge resistance of positive electrode, which is determined in Sec.2.2. Moreover, it is assumed that the phase transition proceeds without capacity loss only with resistance increase. In this model, $k$, is only fitting parameter.

![NCM](image2)

**Fig.4 Schematic illustration of degradation model of positive electrode.**

3.1.3 Crack propagating model

It has been reported that cracks propagate between active material particles, or active material particle and electric collector with charge/discharge cycle proceeds. This might cause exponential increase of contact resistance between them, in particular, after long cycle. In the case of simple 1-dimensional model, contact resistance $R_c$ is described using initial contact resistance $R_{c,0}$, contact length $a_0$ and crack length $a$.

$$R_c = R_{c,0} \frac{a_0}{a_0 - a}$$

In this study, linear propagation of crack with cycle proceeds is assumed,

$$a = C \cdot Q_{total}$$

where $C$ is a constant and $Q_{total}$ means total transported electric charge amount in cycle process. In this model, fitting parameters are $R_c$ and $C$.

3.2 Parameter estimation of multifactorial degradation model

Electric conductivity of uniform SEI $\kappa_{sei}$ exchange current density of side reaction $i_{0s}$, coefficient of cover rate $k$, initial contact resistance $R_0$ and constant $C$ are estimated to follow the exponential increase of resistance and capacity fade at 25 (°C) and 70 (°C), respectively. Evaluation functions below are adopted with L1 norm;

$$\phi_k = \sum [(R_{exp} - R_{calc}(x_1)]^1 + \lambda \| x_1 \|$$

(12)

$$\phi_0 = \sum [(Q_{exp} - Q_{calc}(x_2)]^1 + \lambda \| x_2 \|$$

(13)

where $R_{exp}$ and $R_{calc}$ are experimental and simulation values. $x_1$ and $x_2$ are unknown degradation parameter vectors.
In this study, Parameter $\lambda$ was assumed 0.01.

Determined parameters by using above method at 25 and 70 ($^\circ$C) are listed in Table 4, and comparison of relative resistance and relative capacity between experiments and simulations are shown in Fig. 5. It can be seen that exchange current density of side reaction $i_{0,s}$ of SEI growth on the negative electrode and coefficient of cover rate $k$ on the positive electrode increases with temperature. Therefore, we assumed Arrhenius equation for both parameters,

$$i_{0,s} = 3.99 \times 10^4 \exp \left( -\frac{3.25 \times 10^5}{T} \right)$$  \hspace{1cm} (15)

$$k = 1.76 \times 10^{10} \exp \left( \frac{4.15 \times 10^4}{T} \right).$$  \hspace{1cm} (16)

where $T$ indicates cell temperature. Note that phase transition in the positive electrode is negligible in room temperature, although it has an influence comparable to SEI growth in the negative electrode.

### Table 4 Parameters for degradation model

| Parameters                          | Values                          |
|-------------------------------------|---------------------------------|
| Conductivity of SEI, $\kappa_{sei}$ | 3.41 [S/m] (25 $^\circ$C)       |
|                                     | 5.57 $\times 10^{-1}$ (70 $^\circ$C) |
| Exchange current density of side reaction $i_{0,s}$ | 5.00 [A/m$^2$] (25 $^\circ$C) |
|                                     | 140 [A/m$^2$] (70 $^\circ$C)     |
| Coefficient of coverage rate $k$    | 1.0$\times 10^{-3}$ [1/s] (25 $^\circ$C) |
|                                     | 1.0$\times 10^{-5}$ [1/s] (70 $^\circ$C) |
| Initial contact resistance $R_0$    | 1.0$\times 10^{-6}$ ($\Omega$) (25 $^\circ$C) |
|                                     | 1.0$\times 10^{-7}$ ($\Omega$) (70 $^\circ$C) |
| Constant $C$                        | 7.60$\times 10^{-5}$ [1/s] (25 $^\circ$C) |
|                                     | 1.0$\times 10^{-6}$ [1/s] (70 $^\circ$C) |

4. Degradation-thermal coupled simulation of battery module

4.1. Thermal model of battery module

In battery module, dozens of battery cells connected in parallel and serial. Therefore degradation of each battery cell proceeds differently due to non-uniform temperature distribution. In this study, 2-dimensional thermal-degradation coupled simulation in the battery module was carried using a current pattern. As a battery module, it was assumed that a typical 10 series connections and 3 parallel connection configuration shown in Fig. 6. Temperature distribution in each cell was neglected and representative temperature $T_i$ was introduced for this calculation.

Heat generation $Q_{ht}$ during charge/discharge was calculated by using over potential $\eta$ and current $I$,

$$Q_{ht} = \eta I$$  \hspace{1cm} (17)

It was assumed that energy balance was established between representative temperature $T_i$ of each cell in a battery module and difference of heat generation $Q_{ht}$ and heat extraction $Q_{dis}$ to environment Air,

$$\rho C_p \frac{dT_i}{dt} = Q_{ht} - Q_{dis}$$  \hspace{1cm} (18)

where $a$ and $T_{sur}$ indicates surface to volume ration and environmental temperature, respectively. Heat transfer coefficient of windward edge, indicated by $h_1$ in Fig. 6, has a different value from other edges ($h_2$) reflected by air flow in battery module. We used $h_1=7.0$, $h_2=5.0$ [W/(m$^2$K)], respectively, estimated from 3-dimensional thermal calculation of battery module (13). Moreover, heat transfer coefficient between battery cells ($h_3$) was chosen as 1.0 [W/(m$^2$K)].

In order to simulate battery cell degradation under running condition of automotive vehicle, we adopted typical current pattern of PHEV US06 mode (14). It was assumed that one cycle is composed of the current pattern and subsequent CC-CV charge, shown in Fig. 7.
4.2. Cell temperature and degradation through one cycle

Fig. 8 shows representative temperature $T_i$ of each battery cell in battery module at 0, 2000, 4000, 6000, 8000 and 10000 [s]. Whole $T_i$ raised when current pattern and CC charge had been applied, and decreased gradually in CV period. At the end of 1 current cycle at 10000 [s], $T_i$ of each battery cell was cooled down near environment temperature due to heat dissipation. Note that $T_i$ of a cell located near the center of the module (cell A), are higher than that of outside cells (cell B). Variation of representative temperature of both cells is shown in Fig. 9 (a). Difference of $T_i$ between cell A and B increased with time during current pattern and CC charge applied was applied, and maximum difference of $T_i$ reached about 3.5 [degC] at the end of the current pattern.

Such a nonuniform temperature in the battery module gives rise to a nonuniform degradation. Fig. 9 (b) shows the variation of SEI thickness in cell A and B. Though SEIs grew with time during applying current pattern and CC charge in both cells, growth rate of SEI in Cell A was larger than that in Cell B. At the end of 1 cycle, difference of SEI thickness between both cells raised up to about $8.8 \times 10^{-10}$ [m] (12%). These results indicate that the cells located near the center of the module tend to become higher temperature, accelerating their degradation including SEI growth. In this condition of simulation, the effect of phase transition in positive electrode and crack propagation was extremely small.

In order to evaluate battery degradation with hundreds of current pattern and CC-CV charge cycling, further degradation-thermal coupled simulation was carried out for longer term. The Representative temperature $T_i$ of cell A and B with time were shown in Fig. 10 (a). $T_i$ of cell A was rising and falling from 26 to 30 [degC], although $T_i$ of cell B fluctuated around 25.5 [degC]. Fig. 10 (b) indicates number of cells v.s SEI thickness after the 1st and after 20th cycle. After the 1st cycle, dispersion of SEI thickness in the cells is small, meaning that all cells in the module have been thorough almost the same degradation. On the other hand, their dispersion increased clearly in comparison to the 1st cycle, showing bimodal distribution. This result indicates that bipolarization of the degradation in the battery module could proceed with cycle, and their dispersion could increase.

5. Conclusion

The degradation-thermal coupled simulations of Li-ion battery have been performed and fitted the parameters of charge/discharge and its degradation. As a result, voltage, resistance and capacity change of the simulation model were good agreement with the experimental data. The effect of phase transition in the positive electrode is negligible in room temperature, while it has an influence comparable to SEI growth in the negative electrode.

In addition, the battery module simulation assuming running condition of automotive vehicle has been carried out. These results indicate that the cells located near the center of the module tend to become higher temperature, accelerating their degradation including SEI growth. Furthermore, it suggests that bipolarization of SEI thickness in the battery module could proceed with cycle, and their dispersion could increase.
This paper is written based on a proceeding presented at the JSAE Annual Congress on May 25, 2016.

References

(1) G. Ning et al., Capacity fade study of lithium-ion batteries cycled at high discharge rates, Journal of Power Sources 117 pp.160-169 (2003).
(2) J. Marcicki, Modeling, Parametrization, and Diagnostics for Lithium-Ion Batteries with Automotive Applications, Ph.D thesis, Ohio State University (2012).
(3) P. Ramadass et al., Mathematical modeling of the capacity fade of Li-ion cells, Journal of Power Source 123 pp.230-240 (2003).
(4) G. Ning, et al., Cycle Life Modeling of Lithium-Ion Batteries, Journal of Electrochemical Society, Vol.151, A1584-A1591 (2004).
(5) M. B. Pinson et al., Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction, Journal of Electrochemical Society, Vol.160, A243-A250 (2013).
(6) T. Segi et al., Evaluation of the Transport Properties of a Degenerated Li(Ni1/3Mn1/3Co1/3)O2 Positive Electrode Using Density Functional Theory, Proceedings of Computational Science Workshop Vol.5, 011014 (2014).
(7) F. Shi et al., Failure mechanisms of single-crystal silicon electrodes in lithium-ion batteries, Nature communication, 7, pp.11886 (2016).
(8) Y. Takagishi et al., Mathematical Modeling of aging of Li-ion battery with consideration of long charge/discharge cycle, Proceedings of 55th Battery Symposium 3F18 pp.490 (2014) in Japanese.
(9) S. Santhanagopalan et al., Review of Models for Predicting the Cycling Performance of Lithium Ion Batteries, Journal of Power Sources 156 pp.620-628 (2006).
(10) P. Ramadass, et al., Development of First Principles Capacity Fade Model for Li-Ion Cells, Journal of Electrochemical Society, Vol.151, A196-A203 (2004).
(11) G. Ning, et al., A generalized cycle life model of rechargeable Li-ion batteries, Electrochimica Acta, Vol.51, pp.2012-2022 (2006).
(12) T. Tsubota et al., Experimental Production, Evaluation and Analysis Technologies for Li-ion Secondary Batteries, KOBELCO TECHNOLOGY REVIEW No. 34 pp.65-71 (2016).
(13) T. Yamaue and Y. Takagishi, Modeling Li Transportation and Degradation Phenomena of Li-ion Secondary Batteries, KOBE STEEL ENGINEERING REPORTS 64 No. 2 pp.99-104 (Oct. 2014) in Japanese.
(14) Vincenzo Marano et al., Lithium-ion Batteries Life Estimation for Plug-in Hybrid Electric Vehicles, Proceedings of 2009 IEEE Vehicle Power and Propulsion Conference, pp.536-543 (2009).