Lifetime Extension Technology for Lithium-Ion Secondary Batteries

KAWASAKI Daisuke, ISHIKAWA Hitoshi, SUDO Shinya, UTSUGI Koji

Abstract

NEC Green Innovation Research Laboratories have developed a lifetime extension technology for laminated lithium-ion batteries (LIBs) using manganese positive electrodes featuring safety and high abundance as a resource. This technology uses a NEC-original electrolyte additive and maintains a capacity of 85% even after about 20,000 cycles (1,435 days). Based on the test results, including the above data, a lifetime prediction simulation was performed with an LIB drive pattern assuming the battery-charge from a commercial power supply at nighttime. It was concluded that in the Tokyo area the period until the capacity is halved from the initial capacity is 32 years. This paper introduces the activities summarized above.

Keywords

lithium-ion battery, manganese-laminated battery, electrolyte additive
lifetime extension, lifetime prediction

1. Introduction

The LIB market is expected to grow significantly in the immediate future for use as power supplies for driving EVs and power-assisted bicycles as well as stationary power supplies for system linkage and electricity leveling. This trend is accompanied by an enhanced severity of lifetime requirements for LIBs, with a lifetime of 20 years or more required for system linkage applications (**Fig. 1**). The NEC Group commercialized a manganese LIB that uses lithium manganate - which features a low possibility of thermal runaway thanks to a stable crystalline structure and a low price - as a positive electrode material for the first time in the world. [1] To respond to market expectations, we are currently trying to extend LIB lifetime and also to develop a lifetime prediction technology that can quickly estimate LIB lifetime.

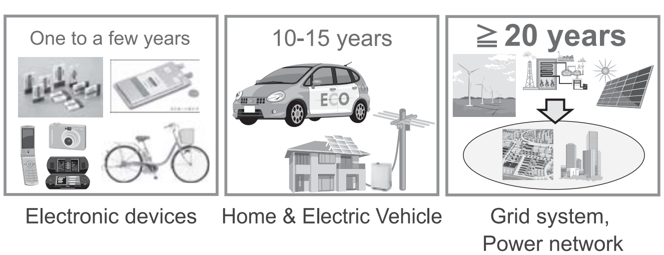


Fig. 1 LIB lifetime requirements for various applications.

2. Key Technologies

It was said in the 1990s that the lifetime of a LIB using lithium manganate - featuring abundant availability as a resource, safety and low cost -as its positive electrode is less than a year. This is because the acid produced in the electrolytic solution dissolved the manganese. The NEC Group developed technologies to alleviate the damage of the acid produced in the electrolytic solution on the positive electrode and succeeded in putting them to practical use. [2)3)] However, these technologies are not sufficient to extend the lifetime to 20 years or more. We therefore focused on the interface between the negative electrode and the electrolytic solution and developed an original electrolyte additive to reduce the electrolyte decomposition reaction on the negative electrode surface. [4]

As shown in **Fig. 2** , the developed additive agent makes it possible to form a stronger protective film on the negative electrode surface and, consequently, to reduce LIB degradation due to the deposition of electrolyte decomposition by-products and the generation of significant decomposition gas. **Table 1** shows the specifications and external view of a test LIB fabricated by applying the above technologies and **Fig. 3** and **Fig. 4** show the results of the cycle test and storage/stand-by test respectively.

The cycle test in a 25 degrees C environment has currently advanced to 23,500 cycles and the tested battery still

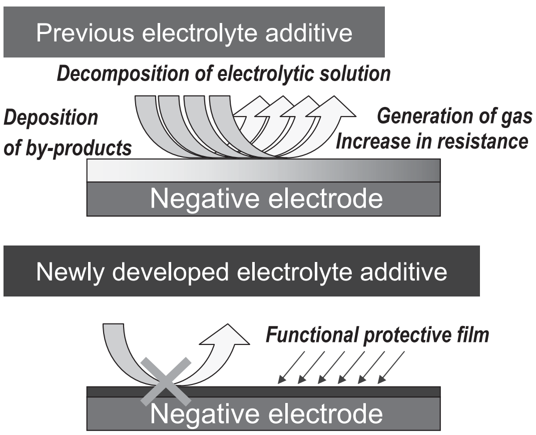


Fig. 2 Role of electrolyte additive.

Table 1 External view (top) and specifications (bottom) of the developed LIB.

Positive electrode	Manganese spinelwith mixed lithium-nickel oxide
Negative electrode	Carbon
Electrolyte	Carbonate type (with additive)
Cell structure	Stacked and laminated type
Capacity	3.7Ah (63Wh/kg)

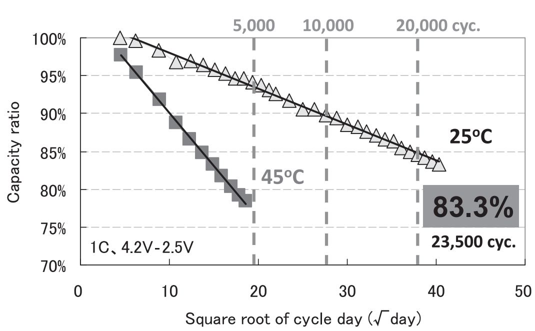


Fig. 3 Results of cycle test.

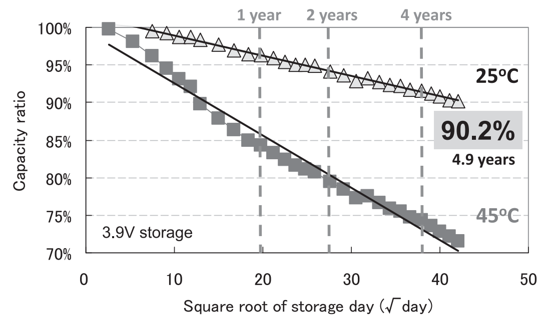


Fig. 4 Results of storage/standby test.

maintains 83.3% of its initial discharge capacity. The storage standby test in a 25 degrees C environment has advanced to 4.9 years and the tested battery maintains 90.2% of its initial capacity. As these graphs adopt straight-line approximations based on what is called the square root rule (= linear relationship with square root of days), their X-axes are plotted with the square roots of the evaluated days.

3. Lifetime Prediction

When the lifetime requirement for an LIB is 20 years or more, lifetime prediction technology based on acceleration testing becomes necessary. This section introduces a lifetime prediction technology proposed by the NEC Group and the results of an actual lifetime prediction test performed based on it.

3.1 Temperature Acceleration Rule

The best-known equation used in temperature acceleration testing is the Arrhenius equation. As our LIB uses organic electrolytic solution, its operation is guaranteed in the range of room temperature ± a few tens of degrees C. In this case, an approximation such as the "double rate per 10 degrees C increase" rule is possible (provided that the activation energy *Ea* is sufficiently larger than the product of the Boltzmann coefficient k and absolute temperature *T*). The "double rate per 10 degrees C increase" rule originally meant that the rate of degradation doubles for every 10 degrees C increase in test temperature in a test conducted for a constant period. With lifetime prediction, the calculations are usually based on the logic that "if the test temperature is increased by 10 degrees C, equivalent degradation occurs in half the original period." In the present testing, we used the following equation, based on the concept that "if the test temperature is increased by α degrees C, equivalent degradation occurs in half the original period":

$$2^{\frac{T_2 - T_1}{\alpha}} = \left(\frac{a_{T_2}}{a_{T_1}} \right)^2$$

α : Temperature acceleration factor (degrees C)
T_2, T_1 : Test temperature (degrees C)
a_{T_2}, a_{T_1} : Degradation inclinations

3.2 Test Environment Temperature

Fig. 5 shows the 10-year average temperatures of the months of the year for the three Japanese cities of Naha, Tokyo and Sapporo. Assuming these temperatures as the environmental temperature, we used a temperature increased by +10 degrees C as the environmental temperature for the cycle test and a temperature increased by +5 degrees C as the environmental temperature for the storage standby test.

3.3 Battery Drive Pattern

LIB degradation accelerates after repeated charge/discharge and long hours of high-voltage operation. For the present testing, we selected a battery drive pattern using nighttime power, as shown in **Fig. 6** , based on the power consumption in a week in October of a 3-member family living in Kasukabe, Saitama Prefecture. [5] With the lifestyle image of this family, power consumption is concentrated in the time ranges of 6:00 to 12:00 and 18:00 to 23:00. This battery drive pattern is used to calculate the daily shares of cycle operation and storage standby operation. According to Fig. 6, the cycle time is 19 hours and the storage standby time is 5 hours. When the square root is calculated, the share of cycle operation is 66.1% and that of storage standby operation is 33.9%.

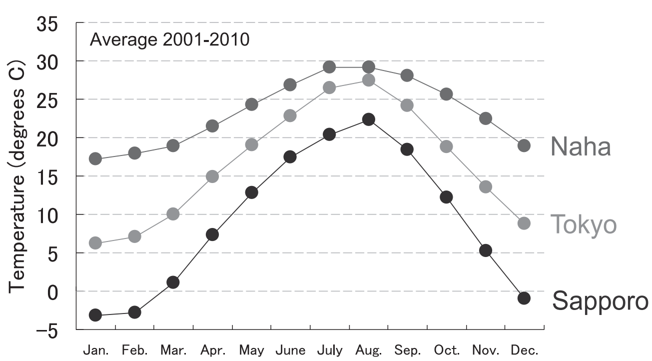


Fig. 5 Monthly average temperatures in three cities in Japan.

3.4 Results of Lifetime Prediction

The shares of cycle and storage standby operations determined from Fig. 6 can be used to obtain the cycle storage integral at 25 degrees C and that at 45 degrees C, and the degradation slopes shown in Fig. 3 and Fig. 4 can be used to calculate the temperature acceleration factor. From these results, it was determined that our developed LIB follows a "double rate per 6.85 degrees C increase" rule, making the lifetime prediction result as shown in **Fig. 7** . It was also calculated that the period until the capacity is halved from initial capacity is 32 years in the Tokyo area. This is about double the lifetime of the previous LIB using an electrolyte additive (developed by NEC Labs). **Table 2** shows the results of lifetime predictions calculated with the test environment temperatures of the three Japanese cities. [6] These results suggest that there

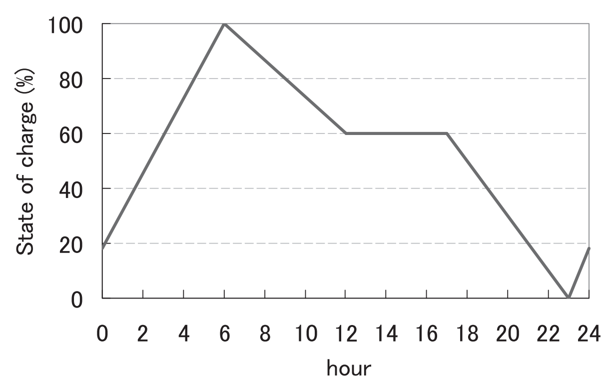


Fig. 6 Drive pattern of a home LIB using nighttime power.

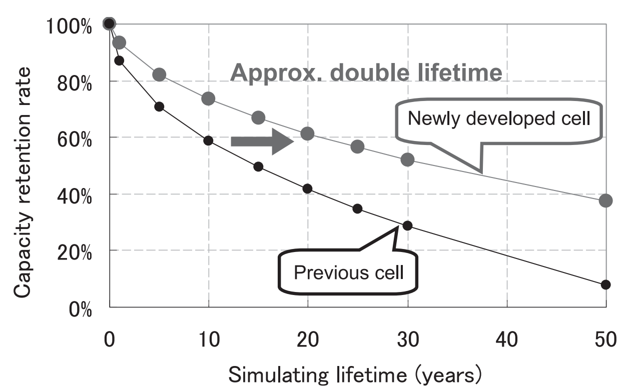


Fig. 7 Results of lifetime prediction considering the average temperature of the Tokyo area.

Table 2 Results of lifetime prediction at three cities in Japan.

Retention rate for the initial capacity	Sapporo	Tokyo	Naha
70%	24.0 years	12.6 years	7.5years
50%	60.7years	32.3years	19.2years

is a greater potential for lifetime extension in low-temperature regions such as Sapporo.

4. Conclusion

At NEC Group, we have recently succeeded in developing a LIB lifetime extension technology using our original electrolyte additive. As a result of LIB lifetime prediction simulations using the developed technology, it has been calculated that the period until battery capacity is halved from the initial capacity is 32 years in the Tokyo area, assuming an LIB drive pattern using nighttime power. We believe that this figure is sufficient to meet the long lifetime requirements for energy storage systems for use in the system linkage applications that are expected to increase in the future. We are determined to continue endeavors for the development of LIBs with high performance, high safety and low price in the future.

Authors' Profiles

KAWASAKI Daisuke
Assistant Manager
Green Innovation Research Laboratories
Central Research Laboratories

ISHIKAWA Hitoshi
Principal Researcher
Green Innovation Research Laboratories
Central Research Laboratories

SUDO Shinya
Assistant Manager
Green Innovation Research Laboratories
Central Research Laboratories

UTSUGI Koji
Senior Manager
Green Innovation Research Laboratories
Central Research Laboratories

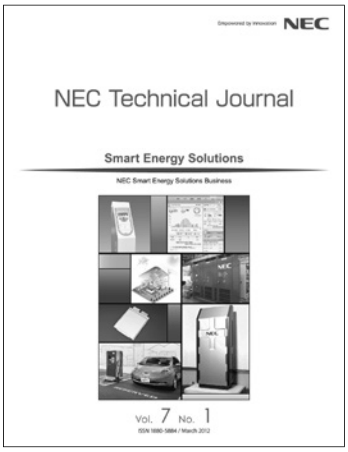
Information about the NEC Technical Journal

Thank you for reading the paper.
If you are interested in the NEC Technical Journal, you can also read other papers on our website.

Link to NEC Technical Journal website

Japanese | English

Vol.7 No.1 Smart Energy Solutions



Vol.7 No.1

March, 2012

Special Issue TOP