Accelerated Test Methods for Life Estimation of High-Power Lithium-Ion Batteries

Yuichi Mita,* Shiro Seki, Nobuyuki Terada, Nobuo Kihira, Katsuhito Takei, and Hajime Miyashiro

Materials Science Research Laboratory, Central Research Institute of Electric Power Industry (2-11-1 Iwado-kita, Komae, Tokyo 201-8511, Japan)

Received November 29, 2009; Accepted January 13, 2010

We proposed accelerated life estimation test methods for high-power lithium-ion batteries used in electrical vehicle. The effects of temperature and state of charge on the degradation of full-scale prototype cells (> 5 Ah) were investigated from the viewpoints of capacity performance and output performance by carrying out storage tests over more than 100 days. The most appropriate charging method during storage was also investigated.

Key Words : Lithium-Ion Secondary Battery, Capacity, Input/Output Property, Accelerated Life Estimation

1 Introduction

To reduce greenhouse gas emissions, next-generation vehicles with lower emissions are expected to become widespread. Recently, high-performance lithium-ion batteries (LIBs) for next-generation vehicles, such as battery electric vehicles (BEVs), plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs), have been researched and developed actively.1,2) For the design of next-generation vehicles, it is very important to evaluate the performance of batteries installed in vehicles, including their life, capacity, power. Regarding the life, highly accurate estimation methods simulating conditions of actual use are required with a shorter test period than that of normal laboratory life tests. To shorten the test period, battery degradation can be accelerated, and it is essential to choose conditions based on the characteristics of batteries to maximize the acceleration factor.

Battery life estimation methods have been proposed on the basis of the extrapolation from test data within a specified period to give experimental formulae assuming linear dependence of degradation on square root of test time,3) linear and geometric dependence of degradation on test time.4) For the simplified simulation of vehicle batteries under conditions of actual usage, life tests were performed by separate storage test and charge-discharge cycle tests. It is assumed that the amount of degradation during both tests are independent and that degradation under conditions of actual usage can be estimated by calculation using the data from both storage and cycle tests.5) The actual operation of a battery depends on the requirements of vehicles. Regarding the state of charge (SOC), batteries are charged and discharged within a wider range in BEVs and PHEVs than in HEVs.6) For BEVs and PHEVs, it is necessary to include test conditions at higher and lower SOC than for HEVs. In general storage life tests, the battery is left in the open-circuit state for a certain period, so that the voltage of the battery decreases; this decrease might affect differences on battery life from actual operation with charging several times a week.

In this study, we investigated accelerated life estimation test methods for LIBs by varying the storage temperature, SOC and charge method during storage using three different types of high-power prototype LIBs.

2 Experimental

The specifications of the prototype cells used for accelerated life evaluation tests are shown in Table 1, which were supplied us by the manufactures in the NEDO Li-EAD project.3) The dependences of performance degradation on the storage temperature (25, 40, 50, 60°C) and SOC (30%, 90%) of the test cells were investigated using Ni-Mn type and hybrid type cells. Cells were charged to a voltage corresponding to the SOC at 25°C by the constant-current and constant-voltage (CCCV) charge, terminated by current reduction to 0.01C-rate or maximum 30 min of CV charge period, and then left in

---

Table 1 Main specifications of the three prototype lithium-ion cells used in this study.

<table>
<thead>
<tr>
<th>Cell type</th>
<th>Ni-Mn type</th>
<th>Hybrid type</th>
<th>Ni type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Capacity / Ah</td>
<td>12.7</td>
<td>6.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Positive Electrode</td>
<td>Ni-Mn based</td>
<td>Ni-Mn-Co based</td>
<td>Ni-Co-Al based</td>
</tr>
<tr>
<td>Negative Electrode</td>
<td>Graphite</td>
<td>Hard carbon</td>
<td>Partially graphitized carbon</td>
</tr>
</tbody>
</table>
constant-temperature reservoirs at each temperature. The dependence of performance degradation on the charging method during storage, “simple storage”, “applied voltage” or “supplied charge”, was investigated using the Ni type cells at 50 °C. Under the simple storage condition, cells were left in the open-circuit state after charging to an SOC of 90%. Under the applied voltage condition, a voltage was continually applied to the cells to retain at SOC of 90%, and under the supplied charge condition, the cells were charged by 1C-rate to given SOC of 90% with 4 h rest after discharged 5% of SOC by 1C-rate. All tests were conducted over more than 100 days. Two test cells were used under all test conditions. Capacity tests were performed under the condition of 1C-rate discharge from an SOC of 100 to 0% at 25 °C. DC-IR were calculated from the slope of -ΔV/ΔI, which was analyzed from the I-V plots of discharge voltages at 10 s by 1, 3, 5 and 10C-rate 10 sec-pulse discharge/charge measurement at an SOC of 30% at 25 °C with sufficient waiting time (10 min) to ensure stabilization.

3 Results and Discussion

Figure 1(a) shows the storage temperature dependence of the relative capacity of Ni-Mn type cells at an SOC of 90%. From the plots, capacity degradation, except the starting point, was proportional to the square root of the number of storage days at all storage temperatures. It was considered that the data at the starting point, defined as the time when we began to measure the cell performance, was affected by the history such as the keeping condition of the cell since it was shipped from the manufacture rather than the test conditions in this study. The gradient, which means the rate of capacity decay, in Fig. 1(a) increased approximately 5-fold with increasing temperature from 25 to 50 °C. The storage SOC dependence of the Ni-Mn type cells was shown in Fig. 1(b). At both temperatures (25 and 50 °C), the gradients increased about 2.8- and 2.3-fold with increasing SOC from 30 to 90%, individually. These results suggest the possibility of accelerated life evaluation test methods for practical-scale cells (>5 Ah) by selecting a suitable temperature and SOC.

Figure 2 shows the storage temperature dependence of the relative DC-IR of the Ni-Mn type cells at an SOC of 90%. Relative DC-IR increased proportionally to the square root of the number of storage days with non-100% intercepts for all storage temperatures, similar to the case of capacity degradation. On the other hand, for

Fig. 1 Relationships between square root of number of storage days and relative capacity for Ni-Mn type cells as a function of storage temperature (a) and SOC (b).

Fig. 2 Relationships between square root of number of storage days and relative DC-IR for Ni-Mn type cells as a function of storage temperature.

Fig. 3 Relationships between square root of number of storage days and relative capacity for hybrid type cells as a function of storage temperature.
a constant SOC (90%), the gradient of the lines in Fig. 2 increased about 1.2-fold with increasing temperature from 25 to 50°C unlike the case of capacity degradation. Therefore, different tendencies were observed for the measurements of capacity and output properties (DC-IR). Thus, it is possible that the relationship between the capacity degradation and the increase in internal resistance is not simple. It is necessary to consider two or more factors as a cause of the capacity decrease, for example, changes in active electrode mass unrelated to the increase in resistance, and the imbalance between cathode and anode capacities. On the other hand, changes in internal resistance (ohmic resistance) might be due to not only the growth of a highly resistive film layer arising from storage at a high temperature and SOC but also the formation of a stable solid electrolyte interface (SEI) layer made from the electrode and the electrolyte. For the requirement to evaluate both the capacity and input/output performances, the necessity of detailed measurements of both capacity and resistance was clarified from the above results.

We also investigated accelerated life evaluation tests using hybrid type cells, the results of which are shown in Fig. 3. The rate of capacity degradation increased about 2-fold with increasing temperature 25 to 50°C, and capacity degradation had a highly linear relationship with the square root of the number of storage days at temperatures between 25 and 50°C. Of course, we should note the range of test storage temperatures with the same type of degradation mechanism, for example, by Arrhenius-type, logarithmic data analysis. From the results for this cell system, it is possible that the degradation mechanism of the cells changes at approximately 50°C.

Finally, the charging method (simple storage, applied voltage, supplied charge) dependences of relative capacity for Ni type cells at 50°C are shown in Fig. 4. Although variations were observed in the first ten days, all results were in close agreement regardless of the test conditions. Therefore, in the case of storage tests on LIBs, the charge method during storage has little effect on battery degradation, unlike storage SOC and temperature. In this paper, we only reported the capacity and DC-IR results for various types of LIBs. However, in the case of accelerated tests on the LIBs, understanding of the main degradation factors is a very important issue. Not only charge/discharge measurements (capacity, DC-IR) but also AC impedance (resistance, capacitance) measurements should be performed. 8,9

4 Conclusion

The effects of temperature, SOC and charging method during storage on the degradation of high-power prototype LIBs were investigated to devise suitable accelerated test methods with a shorter test period. Following the results of tests on two types of LIBs (Ni-Mn type, hybrid type) carried out over more than 100 days, the use of a high temperature and high SOC appears to be promising. Moreover, the charging method during storage (simple storage, applied voltage, supplied charge) appears to have little effect on the test results. In future, we will investigate storage tests for life evaluation under optimized SOC and temperature conditions to reduce the test period as well as consecutive charge/discharge cycle tests simulating battery operation in PHEVs using newly designed high energy density LIBs.

Acknowledgement

This work was carried out as research project as part of the ‘Li-EAD project’, supported by New Energy and Industrial Technology Development Organization (NEDO) of Japan. The authors acknowledge Mr. H. Hanawa, H. Hosoi and N. Kuwabara (Electric Power Engineering Systems Co., Ltd.) for technical support in the experiments.

References

1) S. Yumitori, 14th International Meeting on Lithium Batteries, Tianjin, China, 22-28 June 2008.
2) T. Q. Duong, 14th International Meeting on Lithium Batteries, Tianjin, China, 22-28 June 2008.