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Study of life evaluation methods for Li-ion batteries for backup applications

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Abstract

The backup characteristics of lithium-ion batteries were investigated using commercial prismatic lithium-ion cells with a $LiCoO_2$/graphite cell system. An accelerated method of estimating the lifetime of lithium-ion batteries was developed. It was found that higher temperatures and voltages accelerate the degradation of the cells: a 15 °C increase in temperature cuts the cell life in half, and about 0.1 V increase in charging voltage also cut the cell life in half.

Keywords: Lithium-ion batteries; Calendar life; Backup use; Accelerated test; Impedance; Capacity fade

1. Introduction

Many stationary backup batteries are needed to supply power to telecommunications equipment during a power outage. In addition, telecommunications networks are now being converted to broadband systems, like Fiber to the Home (FTTH); and there is an explosive increase in traffic. So, the amount of power used is also increasing dramatically. This has led to a search for backup batteries with a higher energy density that can provide the full backup time and occupy only a limited space. The high energy density of lithium-ion batteries makes them a very attractive replacement for current ones, which are mainly valve regulated lead acid (VRLA) batteries.

One of the requirements for backup batteries is a very long life, typically 15 years or more. Time compression of testing duration is an indispensable means of evaluating life of developed batteries for a given periods. However, there have been some studies on the accelerated cycle and storage life tests of lithium-ion batteries [1–3], the accelerated calendar life in continuous float charging have not been proposed yet.

In this study, we aimed to develop an accelerated method of estimating the calendar life of backup batteries. We investigated the two accelerated life tests with the stress factors, temperature and state of charge.

2. Experimental

2.1. Backup characteristics

Cells for backup use are subjected to a peculiar pattern of usage in that they are infrequently charged or discharged, and remain in a fully or partially charged state for most of their operational life.

The special methods illustrated in Fig. 1 were used to examine the backup characteristics. In the continuous float charging test, the cells were charged at a constant voltage from 4.0 to 4.3 V and a rate of 1 CmA, and the voltage was maintained continuously. The cells in each test were discharged every month at the rate of 1 CmA to 2.75 V and then recharged to 4.1 V and discharged to check their capacity. The cells were kept continuously at constant temperatures from 25 to 55 °C.

All tests were conducted on commercialized prismatic lithium-ion cells of 900 mAh capacity (type LP10) from Japan Storage Battery (GS).

2.2. Electrochemical impedance analyses

Electrochemical impedance spectroscopy (EIS) was carried out on charged cells in the frequency range of 10 kHz to 0.05 Hz using a low ac voltage of 10 mV to minimize perturbations to the system. The experiments were carried out at various temperatures with a Solatron 1286 electrochemical interface and a 1255 frequency-response analyzer.

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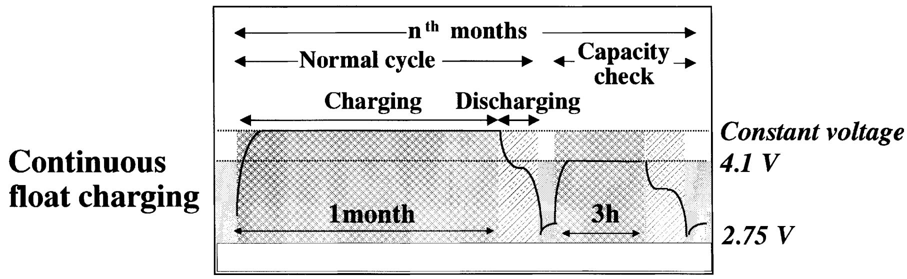

Fig. 1. Conceptual test conditions.

3. Results and discussion

3.1. Dependence of cell capacity on temperature

Fig. 2 shows the results of continuous charging at 4.1 V at various temperatures, with periodic discharging to check the capacity. The capacity retention decreased gradually with an increase in the charging duration and the operating temperature. When the end of life was defined to be a decrease in capacity to 70%, the lifetime of the test cells was estimated to be 2 years or more at 25 °C.

We examined the influence of the temperature on lifetime of the cells. Fig. 3 shows Arrhenius behavior and the activation energy (E_a) was 34.9 kJ/mol. For VRLA batteries, temperature strongly affects lifetime, and it is known that their E_a is about 60 kJ/mol and a 10 °C increase in temperature cuts the lifetime in half [4]. But for lithium-ion batteries, we confirmed that an elevated temperature accelerates degradation and the slope of the Arrhenius plots shows that it takes a 15 °C increase to cut the lifetime in half.

3.2. Dependence of cell capacity on charging voltage

The effect of charging voltage on the backup characteristics was also examined. Fig. 4(a) shows the results of

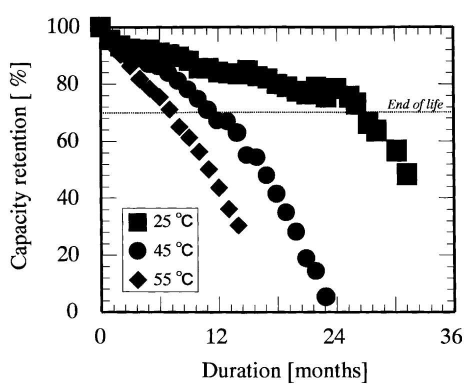

Fig. 2. Capacity retentions during continuous float charging.

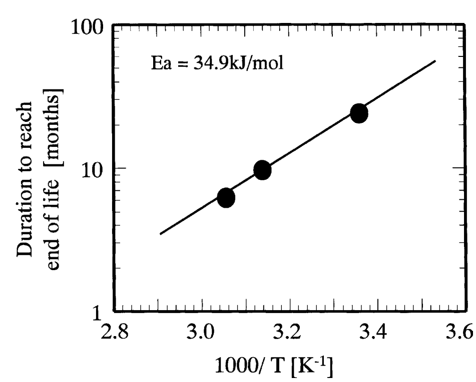

Fig. 3. Temperature dependences on lifetime in continuous float charging tests.

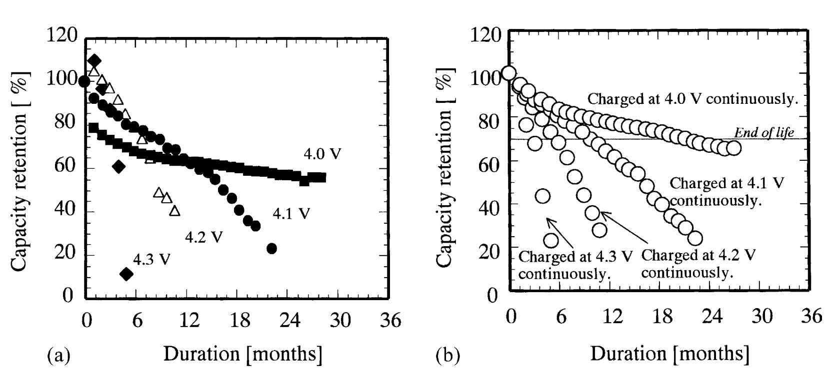

Fig. 4. Capacity retentions in continuous float charging characteristics with various charging voltages at 45 °C. (a) Normal continuous float charging test and capacity check (recharged at floating voltage), (b) capacity check (recharging at 4.1 V).

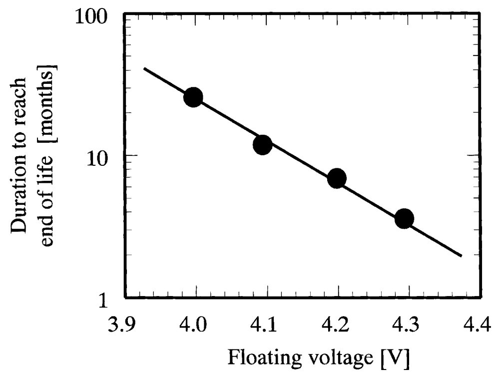

Fig. 5. Dependences of states of charge on lifetime in continuous float charging tests at 45 °C.

continuous charging, with periodic discharging to check the capacity; the parameter is charging voltage. In Fig. 4, 100% capacity is the initial cell capacity on the same condition of the capacity check in Fig. 1 before they were float charged continuously. When the cell was charged at higher voltage, the cell showed large capacity at the beginning of the tests. However they degraded rapidly as the charging duration increased.

Each of the cells was also recharged at 4.1 V and discharged to check the capacity. Fig. 4(b) shows that cell degradation is accelerated at higher charging voltages; and Fig. 5 shows that cell life drops exponentially as the charging voltage increases. We also confirmed about 0.1 V increase in charging voltage cut the cell life in half.

3.3. Electrochemical impedance analyses

Fig. 6 is a typical change in Nyquist plots of batteries in continuous float charging tests. The plots contain two semicircles. An equivalent circuit model similar to that reported by Monma et al. [5] was devised. Simulations performed with the Solatron impedance software ZView 2[TM] (Scribner Associates, Inc.) on the equivalent impedance model produced results that agree quite well with the experimental data.

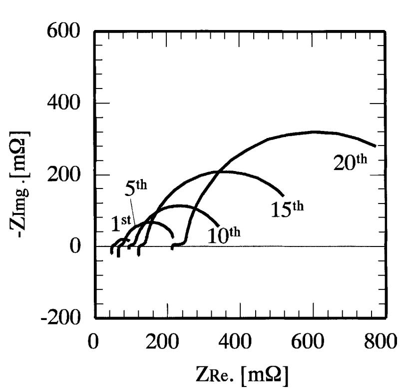

Fig. 6. Nyquist plots of the batteries in continuous float charging test at 45 °C.

An analysis was made of how the impedance parameters change during continuous float charging at various temperatures. We investigated that elevated temperatures and higher charging voltages were found to enhance the increase in the electrolyte impedance and the two charge-transfer impedances. Some possible reasons: (i) electrolyte decompositions on the anode/cathode electrodes and (ii) cathode degradation, are generally suggested for larger increase in the impedance.

In Fig. 6, the electrolyte impedance increased markedly as the charging duration increased. An increase in the thickness and a slight weight loss of the cells was also observed. These phenomena are probably due to the generation of gas, which is attributable to decomposition of the electrolyte on the surface of the electrodes.

In addition, the lower frequency semicircle becomes markedly larger, and the higher frequency one becomes a little larger. It has been reported that the higher frequency semicircle corresponds in large part to the anode reaction, while the lower frequency one mainly corresponds to the cathode reaction [6]. Aurbach et al. reported that the surface firms formed on not only anode but also cathode along with electrolyte decompositions [7]. During backup use, cell degradation may also involve decomposition of the electrolyte and formation of the surface film on the electrodes, thus increasing their cell polarization impedance and charge-transfer impedances.

Other degradation factors must also be considered, such as dissolution of the cathode and the disordering of the crystal structure. It has been reported that $LiCoO_2$ dissolves slightly during aging tests [8]. Table 1 shows the amount of Co dissolution in the electrolyte after 1 month continuous float charging at 55 °C. As shown in Table 1, the test for only 1 month caused the slight Co dissolution from the $LiCoO_2$ cathode. During long charging duration, these Co dissolution phenomena might also increase the charge-transfer impedance of the cathode. On the other hand, there may be little disordering of the crystal structure during backup use because the infrequency of charging and discharging should result in little damage to the crystal structure.

From these data, elevated temperature and higher charging voltage accelerated the cell degradation and these stress factors were appropriate to accelerate the calendar life experimentally. However, further work needs to choose of the degradation mechanism(s) which influence on the

Table 1
The amount of Co dissolution after continuous float charging at 55 °C

Duration	Co dissolution (wt.%)	R[a] (mΩ)	Capacity retention (%)
Initial	0.008	11.4	100
1 month	0.078	33.3	94.5

[a] The charge-transfer impedance related to the lower semi-circle (R).

decrease in the cell capacity, in order to establish universal methods for accelerated life evaluation with all types of cells.

4. Conclusions

We investigated the basic backup characteristics of lithium-ion batteries and two accelerated evaluation methods were experimentally adopted to quickly predict the lifetime of a cell. The cell degradation is accelerated at elevated temperatures and at higher charging voltages. A 15 °C increase in temperature cuts the cell life in half, and about 0.1 V increase in charging voltage also cut the cell life in half.

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