A comparative analysis on the aging effect of the high power lithium-ion battery using NMC and NCA materials

* Pyeong-Yeon Lee and Chang-O Yoon ¹), Jonghoon Kim²) and Minho Jang³)

¹), ²) Department of Electrical Engineering Chungnam National University, Daejeon 34134, Korea
³) Launcher Electronics Team, Korea Aerospace Research Institute, Daejeon, Republic of Korea

¹) leep9826@naver.com, youn_co@naver.com
²) whdgns0422@cnu.ac.kr
³) minho@kari.re.kr

ABSTRACT

As the number of high power applications increases, the issue of the battery degradation is important. However, some papers have not taken account of the aging factors in the state of charge (SOC) and state of health (SOH) estimation algorithms. In this paper, through the electrochemical analysis and the incremental analysis method, the parameters of aging derived. The accuracy of the algorithms will improve by combining the effects of aging in the cell. This paper performed the cycle life test to determine the effects of aging in the high power lithium ion cell. To confirm the effects of aging, a constant trend was identified through the incremental capacity curve and capacity fade. This results in the aim of improving accuracy and stability by modifying the algorithms of the batteries in the battery’s SOC and SOH algorithms to compensate for the effects of the battery degradation.

1. INTRODUCTION

Nowadays, the increase in greenhouse gases is one of the causes of global warming. Among them, the use of fossil fuels such as coal and oil is a major cause. The importance of renewable energy is emphasized to solve this problem. The renewable energy is used in various industries by utilizing solar, ocean, and wind energy. As the importance of the renewable energy increased, the demand of the storage devices is increasing. The secondary battery, which is one of the storage devices, is used from small applications such as mobile devices to large applications such as electric vehicles.
and satellites (Fig.1). As the secondary battery is applied to a variety of applications, the importance of the BMS (battery management system) is also increasing for the stable and efficient operation of the battery. The BMS monitors the state of charge (SOC) of the battery and SOH, which is an indicator of the battery degradation. The BMS also prevent the overcharge and overdischarge of the battery. The SOH is attracting attention as one of the components of battery management system. It can predict the lifetime as an indicator of the battery degradation, which will increase the stability and efficiency of the application. The secondary battery can be divided into the high energy battery and the high power battery depending on the applications.

Fig. 1 electric vehicle (EV), launch vehicle

In this paper, the two types of the high power 18650 lithium ion batteries with the different cathode material were used. In order to observe the SOH of the two type of the high power lithium-ion cells, the cycle life test and HPPC (hybrid pulse power characterization) test based on charge and discharge processes was performed. The discharged curves of the cells were extracted by the cycle life test. The incremental capacity (IC) was calculated through the discharged curves to confirm the aging effects of the cells. In addition, the internal resistances were extracted every 30 cycles through HPPC test. The two types of the cells were compared through the electrochemical properties and the effect of aging was confirmed.

2. EXPERIMENT METHOD

Fig. 2 (a) cycle life test,(b)HPPC(hybrid pulse power characterization) profile
In this paper, the lithium ion 18650 high power cells with the different cathode materials were experimented at room temperature. The cell specification is shown in Table 1. The experiments were performed with the cycle life test and the HPPC test based on cell specification (Fig.2). The cycle life test considered the CC-CV (constant current constant voltage) method and cycled from the fully charge (SOC 100%) to the fully discharge (SOC 0%). The discharge capacity was extracted by applying a current profile that considers the cut-off voltage and 1C-rate. The HPPC test considered a 10% SOC interval.

Table 1 cell specification

<table>
<thead>
<tr>
<th>Item</th>
<th>IMR HE2</th>
<th>INR 20S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal capacity[Ah]</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Nominal voltage[V]</td>
<td>3.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Max. charge voltage[V]</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Max. discharge voltage[V]</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cathode material</td>
<td>NMC</td>
<td>NCA</td>
</tr>
</tbody>
</table>

3. ANALYSIS METHOD OF UNIT CELL AGING EFFECT

As batteries are used in applications, it is difficult to maintain initial electrochemical properties due to the mechanical damage and the long-term cycle. As the age of the battery progresses, the discharged capacity decreases, the internal resistance of the battery increases, and the SOH (state of health) of the battery decreases. The SOH is defined by Eq. (1) and represents a indicator of the life of the battery. The $C_{aged}$ is a initial discharged capacity of 80%. That is, when the battery becomes aged and the discharged capacity becomes 80% or less, the battery is considered to have ended. The Eq. (1) can be used to determine the remaining capacity of the battery, and it can be operated reliably when applied to the applications.

$$SOH_{capacity} = \frac{C_{current} - C_{aged}}{C_{fresh} - C_{aged}} \quad (1)$$

$$\frac{\Delta Q[Ah]}{\Delta V[V]} = IC \left[ \frac{Ah}{V} \right] \quad (2)$$

Considering the electrochemical aging effects, the effects of the battery aging can be divided into the loss of active material (LAM) and the increase in resistance and loss of lithium inventory (LLI). The LAM can be mainly caused by damage in the electrode and LLI is caused by a side reaction such as SEI film formation. As a result, the capacity of the battery decreases and the internal resistance of the battery increases. Generally, the methods such as the XRD (X-ray diffration) and the SEM (scanning electron micro
scopy) are used to identify the cause of battery degradation. However, these methods require disassembly of the battery. In this paper, the ICA (incremental capacity analysis) was performed to observe the effect of battery aging without disassembling the battery. The ICA is a method applied to remaining capacity estimation, which can indicate gradual changes in the battery during battery degradation process. The IC is calculated by Eq. (2) and can confirm the change of discharged capacity. The electrochemical characteristics of the battery degradation can be diagnosed by changing the peak positions and the IC curve. In other words, the ICA is closely related to aging and it can be useful information for SOH algorithm.

4. RESULT

The discharged curves of the lithium-ion cell from the 1 cycle to the 300 cycle are shown in Fig.3. As the cycle life test progressed, a decrease in discharged capacity due to battery degradation was confirmed. As the cycle test progresses, the discharged capacity results are shown in Fig.4. According to the definition of SOH, the cell of the NMC material reaches the end of its battery life in the 241 cycle, which is 80% of the discharged capacity. In addition, the cell of the NCA material was confirmed to have reached the end of its life in the 601 cycle. As a result, Fig.3 and Fig.4 show that a cell with the NMC material have a larger variation in discharged capacity than a cell with the NCA material. The rated capacity of a cell with the NCA material is relatively small but is expected to have a long lifetime.

Fig. 3 Discharged capacity curve (NCA(a), NMC(b))
The discharged capacity based on the ampere counting method was calculated with the profile of Fig. 2- (a) and the actual discharged capacity was applied to the profile of Fig. 2- (b). The OCV (open circuit voltage) and the charge/ discharge internal resistances based on the HPPC test were calculated at SOC 10% intervals in the profile of Fig. 2- (b). Fig. 5 and Fig. 6 show the discharged resistance and the charged resistance of the cells. As the number of cycles in the cycle life test increases, the charged resistance and discharged resistance of both cells increase. In other words, as the cycle life test of the cell progresses, the increase of the internal resistance of the cell shows that there is a damaged in the cell internally and the degradation progressed. It is confirmed that the internal resistance of both cells is small in the region of SOC 40 ~ 50%. Fig. 5 and Fig. 6 show that the charged resistance and discharged resistance of high power lithium-ion cells are electrochemically different from each other. The internal resistance trends of the two types of high power lithium-ion cells are identified as similar.
Fig. 6 (a) discharged resistance (NCA), (b) charged resistance (NCA)

Fig. 7 shows the IC curve of two types of the cells according to the cycle. The IC curve calculated through the discharged curve and Eq. (2). The area of the IC curve indicates the discharged capacity of the cell. As the cycle progresses, the area of the IC curve was decreased in both cells. That is, the decrease in the area of the IC curve indicates a decrease in the discharge capacity of the cell and means that the degradation of the cell has progressed. In addition, both cells show that the peaks of the IC curve decrease and shift to a lower potential. It means that the LAM and the LLI occur and the internal resistance is increased. However, the IC analysis method can qualitatively analyze the mechanisms of degradation, but it has limitations in quantitative analysis.

4. CONCLUSIONS
In this paper, the high power 18650 lithium ion cells with different materials were used, and the effects of aging were confirmed through the various experiments. Through the cycle life test, the discharged capacity and the internal resistances of two different types of cells were calculated and compared. As the cycle progresses in the two cells,
the internal resistance increases, the area and the peak value of the IC curve decrease and the discharge capacity decreases. Based on these results, it can be applied to the SOH estimation algorithm to improve the accuracy or to use as important information when selecting the battery of the application.

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