

Storage performances of Sodium ion batteries
consisting of layered oxide cathode /
hard carbon anode.

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Introduction

Recently, the demand for large storage battery for electricity supply is remarkably increasing. Although lithium ion batteries (LIB) are the candidates in terms of energy density, there remain some problems such as cost and safety. Therefore, we have been developing the sodium ion batteries (SIB) which consist of NaMO₂ (M is transition metal elements) type layered oxide cathode, hard carbon anode, and carbonate based electrolyte [1]. This type of SIB can work in ambient temperature and has large capacity without rare elements [2,3]. In addition, thermal analysis shows this type of SIB is safer than LIB consist of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) cathode, graphite anode, and carbonate electrolyte [4].

In this study, we demonstrate the storage performance of SIB, which is one of the demanded characteristics for large storage battery, and attempt to suppress the degradation.

Experimental

The electrochemical performances of SIB were evaluated by 2032 coin-type cells. NaFe_{0.4}Ni_{0.3}Mn_{0.3}O₂, acetylene black (AB) and polyvinylidene difluoride (PVdF) were mixed to use as cathode. Hard carbon, carboxymethylcellulose (CMC) and styrene-butadiene rubber (SBR) were mixed to use as anode. 1 mol dm⁻³ NaPF₆ dissolved into propylene carbonate (PC) was used as electrolyte. Galvanostatic charge and discharge tests were carried out between 2.0 V and 4.0 V. In storage performance tests, fully charged SIBs were kept under 25 and 60 °C for 5days, and preserved capacity and recovered capacity were investigated. Electrochemical impedance spectroscopy (EIS) measurements were performed at 4.0 V charged state before and after storage tests respectively.

Results and Discussion

Table 1 summarizes the preserved and recovered capacity of SIB after being kept under 25 and 60 °C for 5days. These capacities are normalized by initial capacity. As shown in Table 1, preserved capacities decreased after 5days, especially being kept under 60 °C. This means self discharge reactions occurred during storage, and were accelerated in higher temperature. As shown in Figure 1, although the self discharge occurred, the recovered discharge curve was almost the same as the initial one.

Figure 2 shows the Nyquist plots of SIB before and after storage tests. Two semicircles were observed, high frequency region (R1) is attributed to anode, and low frequency region (R2) is attributed to cathode. In case of being kept under 25 °C, R1 and R2 remained about the same compared to the initial. In contrast, these two semicircles became enlarged in case of 60 °C.

The result that the discharge curve is almost unchanged even after being kept under 60 °C for 5 days suggests that bulk structures of cathode and anode materials are relatively stable. We suppose that self

discharge reactions could results from the surface degradation of active materials or so-called Solid electrolyte interface (SEI)-like film formation. We will discuss it in detail in our presentation.

Table 1. Results of 5 days storage tests.

Storage temp.(°C)	Preserved cap. (%)	Recovered cap. (%)
25	97.6	103
60	87.6	101

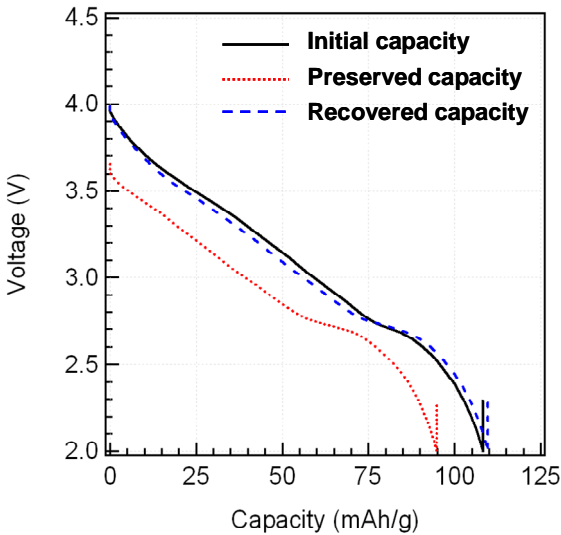


Figure 1. Discharge curves of SIB at 25 °C before and after 60 °C storage tests.

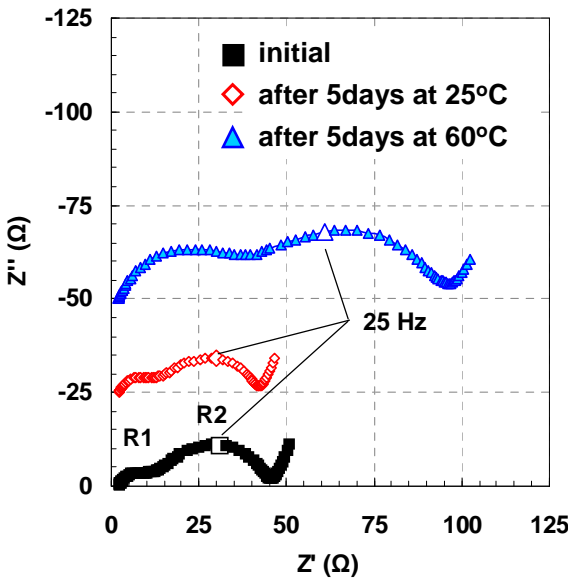


Figure 2. Nyquist plots of SIB at 25 °C before and after storage tests.

References

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