Electrochemical properties and structural changes of NaCuO$_2$ for Sodium Secondary Batteries

Yoko Ono, Yuhki Yui, Masahiko Hayashi, Katsuya Hayashi, Kaoru Asakura, Ryuichi Kobayashi, Hiroto Kitabayashi

NTT Energy and Environment Labs., Nippon Telegraph and Telephone (NTT) Corporation, Atsugi, Kanagawa 243-0198, JAPAN

Introduction

Sodium secondary batteries are one of the promising alternatives to lithium ion batteries (LIB) due to the abundance of sodium resources. There are many reports for cathode materials containing rare metals such as Na$_x$(Fe$_{1-y}$,Mn$_y$)O$_2$, NaCoO$_2$, and NaCrO$_2$, [1]. NaCuO$_2$ has already been investigated as a cathode material for LIB, and it exhibits a small discharge capacity (70 mAh/g) and low rechargeability [2].

In this study, we focused on NaCuO$_2$ as a rare metal-free cathode for sodium secondary batteries. We investigated electrochemical properties of NaCuO$_2$ and its structural changes during discharge-charge processes.

Experimental

NaCuO$_2$ was synthesized by solid-state calcination. Reagent grade Na$_2$O and CuO were mixed with a Na/Cu ratio of 1 and then heated at 450°C for 10 h in an oxygen gas flow as reported elsewhere [2].

Coin-type cells (CR2032 type) were used to evaluate electrochemical properties of NaCuO$_2$. A cathode mixture was prepared with NaCuO$_2$ (70 wt%), acetylene black (25 wt%), and polytetrafluoroethylene (5 wt%). The cathode mixture was then roll-pressed and cut into pellets. Na metal was used as a negative electrode. As an electrolyte solution, 1 mol/l NaClO$_4$ dissolved in propylene carbonate was used. The cells were assembled in a glove box filled with Ar (H$_2$O < 0.1 ppm).

Electrochemical measurements were carried out at a current density of 0.5 mA/cm$^2$ at 25°C.

Results and discussion

XRD patterns of NaCuO$_2$ powder were mainly indexed to a monoclinic NaCuO$_2$ phase (PDF 01-085-2391) with a small amount of CuO impurity phase and agreed with those reported in the literature [2]. It has been reported that LiCuO$_2$ has the same structure as NaCuO$_2$, and that 1 mol of Li ion could be extracted from LiCuO$_2$ in the first charge process [2][3]. However, according to our preliminary tests, only 0.05 mol of Na ion could be extracted from NaCuO$_2$ in the first charge process, and then low discharge capacity of 70 mAh/g was obtained. Therefore, in this study, the electrochemical evaluation started with the discharge process.

Figure 1 shows the first discharge-charge curves of Na/NaCuO$_2$ cells at a current density of 0.5 mA/cm$^2$ at 25°C.

Figure 2 shows XRD patterns of the cathode pellets at (a) to (f) in Fig. 1. A decrease in crystallinity of NaCuO$_2$ was observed during the first discharge process [Fig. 2(c)] and no NaCuO$_2$ peak was observed at the end of the discharge process [Fig. 2(d)]. Then, NaCuO$_2$ peaks were slightly observed in the charge process [Fig. 2(d),(f)]. These results indicate that NaCuO$_2$ was converted to an amorphous state due to insertion and extraction of Na ion. The degradation of crystallinity is considered to be one of the reason for the decreased capacity.

The above-mentioned behavior might be caused by the instability of the NaCuO$_2$ structure. The electrochemical properties of NaCuO$_2$ would be improved by enhancing of its structural stability by means of partial substitution of Cu site.

References


Fig. 1. First discharge-charge curves of Na/NaCuO$_2$ cells at a current density of 0.5 mA/cm$^2$.

Fig. 2. XRD patterns of electrode pellets during the first discharge and charge processes [see Fig. 1 for (a)-(f)].