

Electrochemical properties and structural changes of NaCuO₂ for Sodium Secondary Batteries

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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)O₂, NaCoO₂, and NaCrO₂ [1]. NaCuO₂ 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 NaCuO₂ as a rare metal-free cathode for sodium secondary batteries. We investigated electrochemical properties of NaCuO₂ and its structural changes during discharge-charge processes.

Experimental

NaCuO₂ was synthesized by solid-state calcination. Reagent grade Na₂O₂ 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 NaCuO₂. A cathode mixture was prepared with NaCuO₂ (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 NaClO₄ dissolved in propylene carbonate was used. The cells were assembled in a globe box filled with Ar (H₂O < 0.1 ppm). Electrochemical measurements were carried out at a current density of 0.5 mA/cm² at 25°C.

Results and discussion

XRD patterns of NaCuO₂ powder were mainly indexed to a monoclinic NaCuO₂ 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 LiCuO₂ has the same structure as NaCuO₂, and that 1 mol of Li ion could be extracted from LiCuO₂ in the first charge process [2][3]. However, according to our preliminary tests, only 0.05 mol of Na ion could be extracted from NaCuO₂ 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/NaCuO₂ cells at voltages from 0.7 to 2.7 V. The first discharge and charge capacities were 150 and 139 mAh/g, respectively. Apparent formulas at the end of discharge and charge processes were calculated to be Na_{1.7}CuO₂ and Na_{1.1}CuO₂, respectively. These Na amount are almost in agreement with the analytical values obtained by ICP analysis of charged and discharged pellets. In the second cycle, the discharge capacity decreased to 105 mAh/g. To investigate the reason for this decay of capacity, we examined structural changes of NaCuO₂.

Figure 2 shows XRD patterns of the cathode

electrode pellets at (a) to (f) in Fig. 1. A decrease in crystallinity of NaCuO₂ was observed during the first discharge process [Fig. 2 (c)] and no NaCuO₂ peak was observed at the end of the discharge process [Fig. 2 (d)]. Then, NaCuO₂ peaks were slightly observed in the charge process [Fig. 2 (d),(f)]. These results indicate that NaCuO₂ 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 NaCuO₂ structure. The electrochemical properties of NaCuO₂ would be improved by enhancing of its structural stability by means of partial substitution of Cu site.

References

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- [2] H. Arai et al., *Solid State Ionics*, 106 (1998) 45.
- [3] Y. Arachi et al., *The 53rd Battery Symposium in Japan*, Abst. No. 4B09, p. 166 (2012).

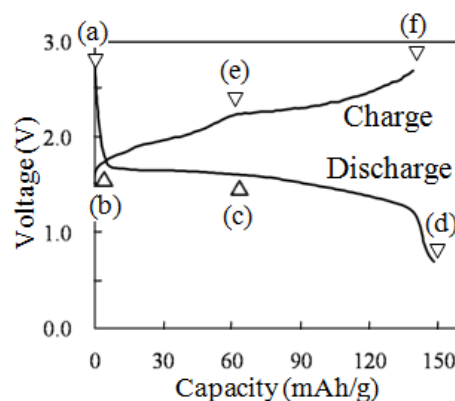


Fig. 1. First discharge-charge curves of Na/NaCuO₂ cells at a current density of 0.5 mA/cm².

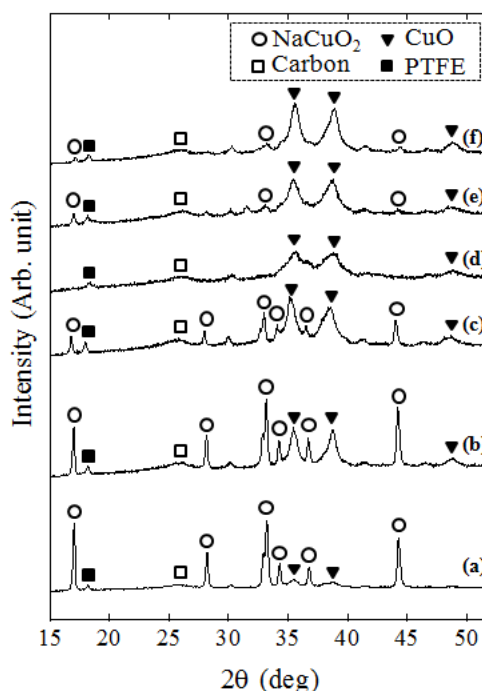


Fig. 2. XRD patterns of electrode pellets during the first discharge and charge processes [see Fig. 1 for (a)-(f)].