Structural Analysis of NaCuO₂ Cathode at Various Charged/Discharged Stages and Its Reaction Mechanism

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ABSTRACT

We investigated NaCuO₂ as a positive electrode material for sodium-ion energy storage batteries. Its charge/discharge properties and cycling-induced new products depended on the voltage range. In the range of 0.75–4.2 V, NaCuO₂ showed a reversible capacity of 190 mAh/g after ten cycles, with an average voltage of 2.5 V versus Na/Na⁺. The results of an ex-situ XRD analysis of NaCuO₂ electrode at various charged/discharged stages revealed that NaCuO₂ was converted to NaCuO after the second cycle, and then, reversible structural changes occur between NaCuO and CuO.

Keywords : Sodium-ion Batteries, Positive Electrode, Metal Oxide, Sodium Copper Oxide

1. Introduction

Lithium-ion secondary batteries (LIBs) are widely used, owing to their high voltages and high energy density. However, alternatives to LIBs are being sought because of the high price of lithium and the scarcity of lithium resources. Sodium-ion secondary batteries (SIBs) have attracted much attention as alternatives to LIBs due to sodium's low price and abundance.

Layered materials can maintain their crystal structure during Sodium-ion insertion and extraction.1-12 For example, Okada et al. reported that charging and discharging of NaFeO₂ as a host material proceeds by reversibly inserting and extracting 1/3 mol of Sodium ions per mol of NaFeO₂. Furthermore, they obtain a reversible capacity on the order of 100 mAh/g by limiting the extracted amount of Sodium ions to 0.4 mol or less per mol of NaFeO₂. However, they also showed that structural changes become irreversible when the extracted amount of Sodium ions increases.

Transition metals such as Cr, Co, Ni, Mn, and V are used in other NaMO₂-type materials (M = metal). While most show a capacity of about 120 mAh/g, NaMnO₂ has 180 mAh/g.1-7 In particular, Komaba et al. reported that Na₂Feₓ/₃Mnₓ/₃O₂, in which Fe and Mn are solid-soluted, has a high capacity of 190 mAh/g, because stable Mn³⁺ and Mn⁴⁺ states are used in the charge-discharge reaction.8 It is also known that NaFeₓ/₃Co₁₋ₓO₂ and NaNiₓ/₃Co₁₋ₓFeₓ/₃O₂ have a capacity 150 mAh/g or more.10,12 However, in order to improve on the performance of current LIBs, it will be necessary to develop materials with even higher capacity. As for Cu-based materials, NaCuO₂ has not yet been reported as a positive electrode material for Sodium ion batteries, and its properties have not been investigated, while Li₂CuO₂, as a positive electrode material for LIB, has been reported to have complicated reaction mechanism.13-16 Here, we focused on NaCuO₂ as a positive electrode material for SIBs.17-20 The crystal structure of NaCuO₂ is shown in Fig. 1. Since NaCuO₂ has a layered structure17 and has an atomic arrangement similar to that of LiCuO₂, we considered that it would be able to insert and extract Sodium ions.

Theoretically, these Sodium-ion insertion and extraction reactions should obey Eqs. (1) to (3):

\[
\begin{align*}
\text{NaCuO}_2 + x\text{Na}^+ + xe^- & \rightarrow \text{Na}_{1+x}\text{CuO}_2 \\
(0 \leq x \leq 1) & \tag{1} \\
\text{NaCuO}_2 & \rightarrow \text{Na}_{1-x}\text{CuO}_2 + x\text{Na}^+ + xe^- \\
(0 \leq x \leq 1) & \tag{2} \\
\text{Na}_{1-x}\text{CuO}_2 + y\text{Na}^+ + ye^- & \rightarrow \text{Na}_{1-x+y}\text{CuO}_2 \\
(0 \leq y \leq 2) & \tag{3}
\end{align*}
\]

Table 1 shows the theoretical capacities of NaCuO₂ in a Na/NaCuO₂ cell, given the expected reactions (1) to (3). Here, using Na metal for the negative electrode, the theoretical capacity when 1 mol of Sodium ions is inserted/extracted per mol of NaCuO₂ is 226 mAh/g. The reaction starting from the insertion of a Sodium ion into NaCuO₂ is represented by Eq. (1) and corresponds to reduction of Cu^{2+} to Cu^{+}. On the other hand, the reaction starting from the extraction of a Sodium ion from NaCuO₂ is represented by Eq. (2) and corresponds to oxidation of Cu^{2+} to Cu^{3+}. Moreover, the reaction starting from the extraction of a Sodium ion from

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Table 1. Theoretical capacities of NaCuO₂ in a Na/NaCuO₂ cell for expected reactions (1)–(3).

<table>
<thead>
<tr>
<th>Expected reaction</th>
<th>Step</th>
<th>Theoretical capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. (1)</td>
<td>Discharge → Charge</td>
<td>226 mAh/g (x = 1)</td>
</tr>
<tr>
<td>Eq. (2)</td>
<td>Charge → Discharge</td>
<td>226 mAh/g (x = 1)</td>
</tr>
<tr>
<td>Eq. (3)</td>
<td>Charge → Discharge</td>
<td>452 mAh/g (x = 1, y = 2)</td>
</tr>
</tbody>
</table>

NaCuO₂ can also be represented by Eq. (3), and it corresponds to oxidation of Cu³⁺ to Cu⁴⁺ and subsequent reduction of Cu⁴⁺ to Cu²⁺. In this case, the theoretical capacity is 452 mAh/g, because 2 moles of Sodium ions are inserted or extracted per mol of NaCuO₂.

2.3 Characterization of NaCuO₂-containing electrode

The crystal structure of the NaCuO₂-containing electrodes before and after charge/discharge processes was analyzed by XRD. Scanning electron microscopy-energy dispersion X-ray spectrometry (SEM-EDS) was used to observe the surface and cross-sectional structure and analyze the composition of the NaCuO₂ electrodes. The measurements were performed with an ULTRASS5 SEM (Cari Zeiss Co.) and QUANTAX400 (Bruker Co.) with an accelerating voltage of 3.0 kV. EDS maps of elemental compositions were obtained from the SEM images. X-ray photoelectron spectrometer (XPS) analysis of the samples was performed with a PHI XPS-5700 system using AlKα radiation (1486.6 eV) to examine the binding energies for Na 1s, Cu 2p and O 1s of the NaCuO₂ electrodes.

Figure 2. Schematic illustration for 2032-type coin cell.
450°C for 10 h in oxygen. The XRD pattern of the sample could be indexed to a NaCuO₂ phase (PDF #22-1369) and was consistent with the pattern reported in the literature. This result indicates NaCuO₂ was obtained as a single phase. The structure of NaCuO₂ has been reported as monoclinic. The SEM image of the obtained NaCuO₂ powder (inset in Fig. 3) reveals rice-grain-like particles with the sizes of 0.5–1.0 µm. The XRD pattern of the as-prepared NaCuO₂-containing electrode was almost exactly the same as that of the NaCuO₂ powder. Figure 4 shows EDS elemental mapping images of the NaCuO₂-containing electrode. The EDS maps were obtained for elementary Na, Cu, O, and C. The EDS measurements indicated that NaCuO₂ particles of about 1 µm in size were dispersed over the electrode surface. There was no segregation of Na, Cu, O, and C, and no impurities, such as Na₂CO₃ and CuO, were observed.

3.2 Charge/discharge curves of Na/NaCuO₂ cells and new products of NaCuO₂-containing electrode

Figure 5 (i)-top shows the discharge-charge curves of the Na/NaCuO₂ cell in the voltage range of 0.75 to 3.0 V. The first discharge capacity was 140 mAh/g (corresponding to 0.6 mol of sodium-ion insertion; Na₁.₆CuO₂), and the average discharge voltage was 1.7 V. As we previously reported, the second discharge capacity drastically decreased to 90 mAh/g. To investigate the reason for this decrease, we performed a structural analysis of NaCuO₂ at the discharged/charged stage.

Figure 5 (ii) shows XRD patterns of NaCuO₂ electrodes before and after the first discharge [Fig. 5 (ii) a and b] and after the subsequent charge processes [Fig. 5 (ii) c]. After the first discharge, the NaCuO₂ peaks almost completely disappeared, and new peaks that could be assigned to CuO and Cu₂O appeared [Fig. 5 (ii) b]. However, the Na₁.₆CuO₂ phase, which is considered to be the discharge product, was not observed. The XRD pattern remained unchanged after the subsequent charge process [Fig. 5 (ii) c]. The results of the XRD analysis during the first cycle suggest the following reaction. Sodium-ion insertion into NaCuO₂ during the first discharge involves irreversible conversion of NaCuO₂ into the amorphous phase, Na₂CuO₂. Then, charge and discharge reactions proceed between the amorphous phases. On the other hand, the discharge product, Na₂CuO₂ (Na₁.₆CuO₂, to be exact) which formed through the reaction, might be unstable and decompose to form copper oxide and sodium oxide:

$$NaCuO_2 + Na^+ + e^- \rightarrow Na_2CuO_2$$

$$Na_2CuO_2 \rightarrow Na_2O + CuO$$

The CuO then reacts with a sodium ion and produces Cu₂O and Na₂O:

$$CuO + Na^+ + e^- \rightarrow 1/2 Cu_2O + 1/2 Na_2O$$

The instability of Na₂CuO₂ might be a reason for the poor cycle performance. However, the XRD analysis of the NaCuO₂ electrode after the first discharge did not detect any Na₂O. Since Na₂O was in...
the amorphous phase, XPS measurements were then carried out on the discharged NaCuO2 electrodes to analyze the chemical states of the Na in the oxide.

Figure 6 shows Na1s XPS spectra of the NaCuO2 electrodes before and after the first discharge to 0.75 V. While the Na1s main peak had a binding energy of 1072.0 eV before the discharge [Fig. 6 (i)], the peak shifted to 1072.3 eV after the discharge [Fig. 6 (ii)]. The peak at 1072.3 eV is considered to be the sum of the Na1s peaks of the discharge products and unreacted NaCuO2. The components of the peak were therefore identified by multi-peak fitting. The observed peak was separated into two peaks, as shown by the dotted line in Fig. 6 (ii). One peak was at a binding energy at 1072.7 eV; it was assigned to Na2O according to a reference.22 The other peak was at 1072.0 eV; it was assigned to NaCuO2. The intensity ratio of the peaks at 1072.7 and 1072.0 eV was 6:4. The ratio is in agreement with the amount of reacted NaCuO2 (0.6 mol) and unreacted NaCuO2 (0.4 mol), as calculated from the first discharge capacity of 140 mAh/g. No clear peak for Cu2p was detected before or after the first discharge because of its low intensity at the surface of the NaCuO2 electrode. Figure 7 shows depth profiles of the intensity of the binding energy for Na1s, Cu2p, and O1s of NaCuO2 electrodes after the first discharge to 0.75 V. At the surface of the NaCuO2 electrode, Na1s and O1s were the dominant components and the binding energy of Cu2p could not be detected. This result indicates that the discharged product, Na2O, might cover the surface of the NaCuO2 electrode. At deeper positions, the intensity of Na1s decreased, while that of Cu2p increased. The cross-section SEM-EDS analysis of the NaCuO2 electrode after the initial discharge confirmed that a few-µm-thick layer mainly composed of Na and O was formed on the surface (Fig. 8). From these results, it is considered that generation of film-like sodium oxide which is inactive with the electrode reaction was a reason for the poor cycle performance.

In summary, it was revealed that insertion of sodium ions into NaCuO2 formed unstable Na0.4CuO2 that decomposed into CuO, which in turn formed Cu2O. Moreover, Na2O was also formed on the surface of the NaCuO2 electrode.

Figure 5 (i)-bottom shows the charge-discharge curves for the voltage range of 1.7 to 4.2 V. The first charge and discharge capacities were, respectively, 134 mAh/g (corresponding to 0.6 mol of sodium-ion extraction; Na0.4CuO2) and 55 mAh/g (corresponding to 0.2 mol of sodium-ion insertion; Na0.6CuO2), and the average discharge voltage was 2.5 V. The curve shapes changed after the first cycle. This behavior was very similar to that of lithium-ion extraction in Li/LiCuO2, Li/Li1.5CuO2, and Li/Li2CuO2 cells.13-16

Figure 5 (ii) show XRD patterns of NaCuO2 electrodes after the first charge [Fig. 5 (ii) d] and discharge [Fig. 5 (ii) e] and after the subsequent charge processes [Fig. 5 (ii) f]. After the first charge, NaCuO2 retained its pattern and a broad peak that could be assigned to CuO appeared [Fig. 5 (ii) d]. The formation of CuO is similar to the behavior that the first charge of LiCuO2 forms CuO2, and that CuO2 changes into CuO. Therefore, although the CuO2 phase should form by extracting sodium ions from NaCuO2 in accordance with the reaction in Eq. (2), it could not be detected because it changed into CuO. After the subsequent discharge, the NaCuO2 peaks almost completely disappeared, the peak attributed to CuO increased in intensity, and new peaks assignable to Cu2O appeared [Fig. 5 (ii) e]. For the LiCuO2 system, Arachi et al. reported that CuO, formed by extracting lithium ions from 1 mol of LiCuO2, reacts with lithium ions to form Li2CuO and Cu.13 Their results suggest a possible reaction between CuO and sodium ions. However, in the NaCuO2 system, the NaCuO2 phase could not be detected after the discharge process because of the low discharge capacity (x = 0.2) or low crystallinity of NaCuO. The NaCuO2 phase appeared again after the second charge [Fig. 5 (ii) f]. However, the NaCuO2 peaks gradually faded during subsequent cycles, and broad CuO peaks predominated after ten cycles.18 These results indicate that the CuO phase is more stable than NaCuO2 at higher voltage (4.2 V). Therefore, NaCuO2 transformed into CuO during the cycles.

Figure 6. XPS spectra of Na1s for NaCuO2 electrodes (i) before and (ii) after the first discharge to 0.75 V. The test of the Na/NaCuO2 cell started with the discharge process. Dotted lines show Lorenz curves obtained by multi peak fitting with IGOR Pro.18

Figure 7. Depth profiles of binding energy intensity for Na1s, Cu2p, and O1s of NaCuO2 electrodes after first discharge to 0.75 V. The depth was calculated from the sputtering rate of 2.7 nm/min.18

Figure 8. SEM images and EDS elemental mapping images of cross section of NaCuO2 electrode after first discharge.
In summary, we found that the decomposition and charge/discharge products of NaCuO2 produced during the charge and discharge reactions differed from those of the LiCuO2 system. While the LiCuO2 irreversibly changed into CuO during the first charge, NaCuO2 reversibly changed into CuO during the first charge/discharge process and in the subsequent second charge. Figure 9(i) shows charge-discharge curves of the Na/NaCuO2 cell in the voltage range of 0.75–4.2 V. The first charge and discharge capacities were, respectively, 170 mAh/g (corresponding to 0.7 mol of sodium-ion extraction; Na2O2/Cu2O2) and 185 mAh/g (corresponding to 0.8 mol of sodium-ion insertion; Na1.1CuO2), and the average discharge voltage was 1.7 V. The amount of extracted/inserted Sodium ions in 1 mol of NaCuO2 obtained from the ICP analysis of the NaCuO2 electrode after charging and the subsequent discharging was determined to be 0.8 mol, which was almost consistent with the Sodium-ion extraction/insertion amount calculated from the discharge/charge capacities. The initial discharge curve in the voltage range of 0.75–4.2 V was observed as the sum of the initial discharge curves at 1.7–4.2 V and at 0.75–3.0 V. The discharge capacity of 185 mAh/g was almost equal to the sum of the discharge capacities of 55 mAh/g at 1.7–4.2 V and 142 mAh/g at 0.75–3.0 V. After ten cycles, a discharge capacity of 190 mAh/g was maintained. However, the shape of the charge/discharge curve changed as the cycle. These results suggest that NaCuO2 changed into a new compound during charging and discharging and that Sodium-ion extraction/insertion occurred in the new compound.

Figure 9(ii) shows XRD patterns of the NaCuO2 electrodes after the first charge [Fig. 9(ii)a] and discharge [Fig. 9(ii)b], the second charge and discharge [Fig. 9(ii)c and d], and the tenth charge and discharge [Fig. 9(ii)e and f]. After the first charge and discharge, the CuO phase was the main phase [Fig. 9(ii)b]. After the subsequent charge, peaks attributed to the NaCuO2 phase were observed [Fig. 9(ii)c]. This suggests that CuO formed through decomposition of an unstable discharge product generated by Sodium-ion insertion during the discharge process. To investigate the voltage range of NaCuO2 generation, structural changes in the second charging process were examined in detail. Figure 10 shows XRD patterns of NaCuO2-containing electrodes at various voltage stages. When the second charge started from the main phase of CuO at 0.7 V, traces of NaCuO2 phase were observed at 2.3 V. The NaCuO2 peak became clear after charging up to 3.6 V. A new NaCuO phase was generated in the second discharge [Fig. 9(ii)d]. The second discharge process had a clear inflection point (which was not clear in the first discharge) around 2.5 V in. This result indicates that different discharge reactions occurred in the first and second cycles and that the second discharge product (NaCuO2) was different from the first one (CuO). After the third cycle, a reversible structural change between the NaCuO phase and the CuO phase took place that could be described by Eq. (7). After the tenth discharge process, the main phase was NaCuO [Fig. 9(ii)f].

\[
\text{NaCuO} \leftrightarrow \text{CuO} + \text{Na}^+ + e^-
\]  

(7)

The above results indicate that, in the voltage range of 0.75–4.2 V, NaCuO2 transformed into NaCuO during the second discharge, after which a reversible reaction between NaCuO2 and CuO occurred at an average voltage of 2.5 V. Although the theoretical change in valence of Cu in the NaCuO2 electrode reaction is from Cu+ to Cu++, and Cu+, the reversible reaction between NaCu+O and Cu2O could be stably repeated.

3.3 Reaction mechanism of NaCuO2 cathode in a Na/NaCuO2 cell

Figure 11(i) shows the reaction pathway and new products during the charge/discharge processes for the NaCuO2 electrode in the Na/NaCuO2 cell. For comparison, the reaction pathway of a LiCuO2 electrode in a Li/LiCuO2 cell is also shown [Fig. 11(ii)].

Figure 10. XRD patterns of NaCuO2-containing electrodes at various voltage stages in the second charge process.
In summary, the NaCuO$_2$ system has different intermediate products and by-products from those of the Li$_x$CuO$_2$ system, but Cu$^{4+}$O$_2$ is unstable in both systems, and compounds of Cu$^{3+}$, Cu$^{2+}$, and Cu$^{1+}$ are observed. Moreover, a reversible reaction proceeds between Cu$^{1+}$ and Cu$^{2+}$ in both systems.

4. Conclusions

We synthesized a new positive electrode material for SIBs, NaCuO$_2$, and examined the formation of new products during charge and discharge reactions in voltage ranges of 0.75 to 3.0 V, 1.7 to 4.2 V, and 0.75 to 4.2 V. We found that discharging (starting from insertion of Sodium ions into NaCuO$_2$) in the range of 0.75–3.0 V formed Na$_2$CuO$_2$ as a discharge product that might have then decomposed into Na$_2$O, CuO, and Cu$_2$O. On the other hand, charging (starting from Sodium ions from NaCuO$_2$) in the range of 1.7–4.2 V irreversibly changed NaCuO$_2$ into CuO. In the range of 0.75–4.2 V, a new product, NaCuO, formed after two cycles, and a reversible charge/discharge reaction proceeded between NaCuO and CuO with good cycle performance. In the charge/discharge reaction using NaCuO$_2$, the redox reaction from Cu$^{3+}$ to Cu$^{4+}$ and Cu$^{2+}$ did not occur because Cu$^{4+}$O$_2$ and NaCu$_{3+}$O$_2$ are unstable. We found that the redox reaction between Cu$^{1+}$ and Cu$^{2+}$ compounds (NaCuO and CuO) is stable.

References