# *Articles*

## Hydration of Sodium Cobalt Oxide

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It was found that $Na^+$ ions in $Na_xCoO_2$ can be partially substituted by $H_3O^+$ ions while maintaining a constant Co valence simply by immersion in water. The magnetic susceptibility of $Na_x(H_3O)_zCoO_2$ ($x + z = 0.70$) changed drastically from Curie–Weiss type to Pauli paramagnetic type, indicating that the electronic band structure was modified by the isovalent ion substitution of $Na^+/H_3O^+$. Two possible origins of the change in the electronic structure are discussed.

### Introduction

Sodium cobalt oxide, $\gamma$-$Na_xCoO_2$, has been attracting much attention from the perspective of application and fundamental research. The compound has large thermoelectrical performance[1] and is therefore a promising candidate material for the generation of electrical power from heat. On the other hand, it displays a variety of physical properties due to strongly correlated electrons, such as charge ordering,[2] a magnetic transition,[3] and moreover, unconventional superconductivity after hydration.[4] Recently, the solid-solution range with regard to sodium ($0.70 \leq x \leq 0.78$) was elucidated by conventional solid-state reaction, and it was found that the physical properties are quite sensitive to changes in $x$,[5,6] which indicates that precise control of the Na content is indispensable if reliable experimental data of this system are to be obtained.

On the other hand, we have noticed that the magnetic susceptibility changes substantially after long-time exposure to the air. For example, the susceptibility of $Na_{0.78}CoO_2$ showed a broad maximum at 50 K[5] just after it was synthesized, as seen in Figure 1. However, the temperature corresponding to the maximum susceptibility decreased to 40 K after 1 week and completely disappeared after 6 months. One may consider that this phenomenon is caused by the deintercalation of Na atoms, because the temperature corresponding to the maximum susceptibility tends to decrease with decreasing $\nu$.[5] However, it is highly unlikely that Na atoms are spontaneously deintercalated from the sample to form Na metal and increase the Co valence in the Co oxide. Moreover, deterioration of the sample did not occur, even after 4 months, when a sample was stored in a nitrogen atmosphere, which suggests that water vapor in the air could play a role in the deterioration of samples. These observations suggest a certain chemical reaction between water vapor and the Co oxide. The chemical reaction between water and the Co oxide was investigated in order to elucidate a mechanism for the deterioration, and its subsequent effect on the physical properties. It was also expected that this investigation would provide a solution to the problems regarding discrepancies in the physical properties reported for $Na_xCoO_2$,[7] which have been attributed to “sample dependencies”.

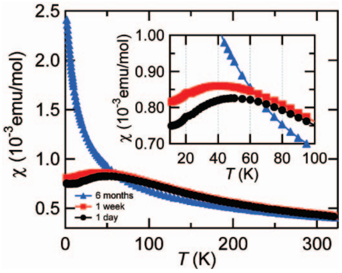

**Figure 1.** Magnetic susceptibility of $Na_{0.78}CoO_2$ samples just after synthesis (black circles), kept in air for 2 week (red squares), and for 6 months with 70% humidity (blue triangles).

### Experimental Section

Precursor $Na_{0.70}CoO_2$ was prepared from a stoichiometric mixture of $Na_2CO_3$ and $Co_3O_4$ by the conventional solid-state reaction

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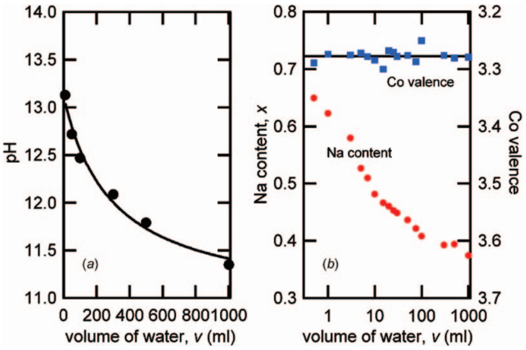

**Figure 2.** (a) pH of solutions in which the samples were immersed, and (b) Na content (red circles) and Co valence (blue squares) of the samples shown in a logarithmic scale of $\nu$.

reported elsewhere.[5] A composition of $x = 0.70$, which is the lowest limit of the solid solution, was selected because the phase with a higher $x$ value of ~0.78 shows a spinodal-like decomposition[5,6] and would cause further complexity. The precursor (1 g) was immersed in a certain volume of water ($\nu$ mL) at 25 °C for 3 days. After immersion, the water becomes alkaline, with the pH depending on the volume of water, as seen in Figure 2a. The sample was then filtrated, washed with acetonitrile, and stored in a nitrogen atmosphere. Washing was performed carefully and thoroughly, in order to remove Na on the surface of the particles, which can cause experimental error in the bulk Na content, $x$. Powder X-ray diffraction (XRD) was measured using Cu Kα radiation on a commercial diffractometer (Rint2200HF, Rigaku) to identify the phase obtained. The Na and Co contents were determined using inductively coupled plasma−atomic emission spectroscopy (ICP−AES). The Co valence was determined by redox titration using the Co content determined from the ICP−AES analysis. Details of the chemical analyses are described elsewhere.[8] Magnetic measurements were performed using a superconducting quantum interference device (MPMS, Quantum Design). There was no significant difference between the data collected under zero-field-cooling and field-cooling conditions.

## Results and Discussion

XRD patterns of the starting precursor ($\nu = 0$ mL) and the samples immersed in $\nu = 25$, 50, and 1000 mL are shown in Figure 3. After immersion in water ($\nu \leq 3$ mL), the sample was identified as single phase, as no substantial changes were seen in the X-ray pattern except for slight peak shifts due to changes in the lattice constants. However, for immersion of samples in $\nu \geq 5$ mL, very small peaks appeared near $2\theta = 36.4$ and 37.7°, as indicated by the arrows in Figure 3; the peak intensities and positions were almost independent of $\nu$. No compound that is expected to give these two peaks has been reported for the Na−H−Co−O system. One may consider that these peaks are related to a distortion of the crystal lattice after reaction with water. However, the *hk0* electron diffraction patterns of the $\nu = 10$ mL sample showed 6-fold symmetry consistent with the space group of the $\gamma$-phase ($P6_3/mmc$), without any satellite spots corresponding to additional XRD peaks. Thus, we considered that the two peaks were attributed to unknown impurity phase(s) formed by some side reaction between the sample and water. For $\nu \geq 20$ mL, another extra peak appeared that changed position according to the value of $\nu$ (see the broken line in Figure 3), and the peak was characteristic of CoOOH (or $(H,Na)_xCoO_2$).[9] Strictly speaking, the presence of impurity phases causes experimental errors in the chemical analyses of the main phase. However, the amount of impurity phases was minimal and their presence had practically no effect on the results of the chemical analyses. Indeed, as shown later, the Co valence does not change across the entire $\nu$ range although CoOOH has trivalent Co ions, and the lattice parameters and the magnetic susceptibility change very systematically to the $x$ value determined by ICP-AES.

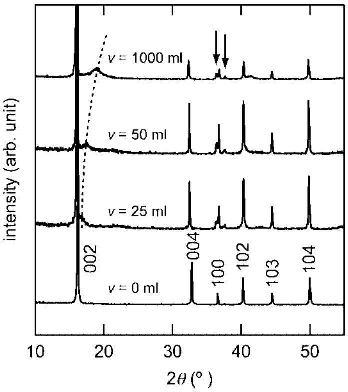

**Figure 3.** X-ray diffraction patterns for the precursor ($\nu = 0$ mL) and the $\nu = 25$, 50, and 1000 mL samples. The arrows indicate the additional peaks, and the broken line indicates the 002 peak of CoOOH or its related compound.

The Na content and the Co valence determined by the chemical analyses are shown in Figure 2b, where the Na content decreases with increasing $\nu$, whereas the Co valence is kept constant. The decrease in the Na content of the oxide is consistent with the increase in pH shown in Figure 2a due to formation of NaOH in the solution. Indeed, the $x$ value was calculated from the pH and volume of water, to agree with that estimated by ICP-AES; the differences between them (= the latter − the former) were −0.075, 0.017, 0.024, 0.087, 0.024, and −0.086 for $\nu = 10$, 50, 100, 300, 500, and 1000 mL, respectively. The Co valence was quite close to the initial value of +3.30 (on the basis of the composition $Na_{0.70}CoO_2$) over the whole range of $\nu$, indicating that any reduction/oxidation did not occur during the immersion in water. These results indicate clearly that deintercalation of $Na^+$ ions was compensated by intercalation of other cations, i.e., an ion-exchange reaction took place as in the case of $NaNi_{1-x}Co_xO_2$ ($x \leq 0.5$).[10] Partial replacement of $Na^+$ ions by oxonium ions has been reported to be accompanied by hydration for the oxyhydrate superconductor.[8] On the other hand, as seen in Figure 4, the lattice parameter of $c$ in the present compound increases with decreasing $x$, which indicates that the substituent ion is larger than the $Na^+$ ion, ruling out protons as possible substituent ions. (CoOOH, a

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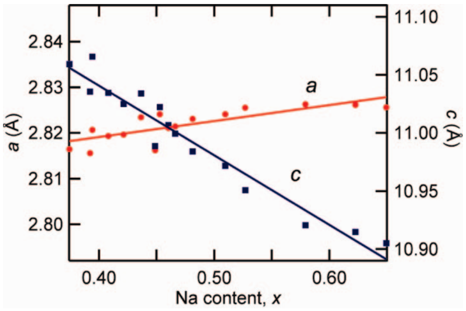

**Figure 4.** Lattice constants *a* (red circles) and *c* (blue squares) of the samples. The solid lines represent $a = 2.81 + 0.0350x$ and $c = 11.28 - 0.5986x$.

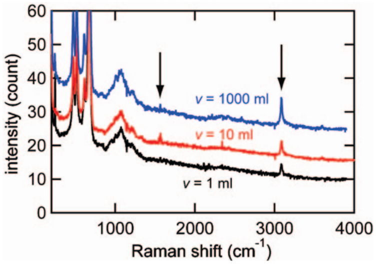

**Figure 5.** Raman spectra of the $\nu = 1$, 10, and 1000 mL samples. The two latter curves have been shifted by 8 and 15 counts, respectively, so as to be easily distinguished from each other. The arrows indicate the peaks at 1570 and 3100 cm$^{-1}$.

proton derivative substitution of $NaCoO_2$, has a much smaller *c* value of 4.7 Å.) These observations imply that the cation in question must be the oxonium ion, $H_3O^+$.

The presence of oxonium ions was confirmed by Raman spectroscopy measurements for the $\nu = 1$, 10, and 1000 samples, as seen in Figure 5. The Raman spectra of these samples exhibited intense modes and broad bands in the wavenumber regions lower than 800 cm$^{-1}$ and higher than 2000 cm$^{-1}$, respectively. The predominant peaks in the 100–800 cm$^{-1}$ region are attributable to vibrations of the host lattices, whereas the latter are molecular vibration characteristic of –OH groups. In addition to these modes, Raman spectra exhibit additional vibrational modes and many weak features in the 900–1200 cm$^{-1}$ region. In $Na_x(H_3O)_zCoO_2$, the complexity of the primitive cell makes it difficult to assign all observed modes from the realistic model. The activation of additional modes is connected to either second-order phonon lines or superlattice modes. In this paper, we discuss several intense modes related to –OH groups. The details of interpretations of the spectra are described in a separate paper.[8,11] The peaks at 1570 and 3100 cm$^{-1}$ correspond to characteristic bands for bending and stretching modes of the oxonium ion.[12] On the other hand, water molecules were not detected, which is distinct from the case of the oxyhydrate superconductor.[8]

Thus, it was concluded that the following reaction occurs between the Co oxide and water.

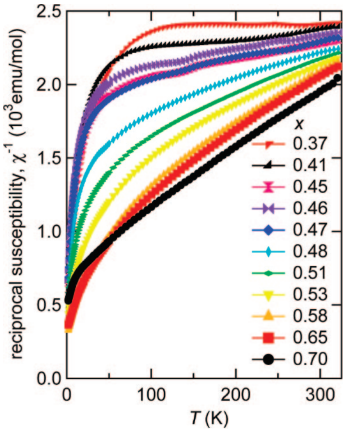

**Figure 6.** Inverse magnetic susceptibility of $Na_x(H_3O)_zCoO_2$ ($x + z = 0.70$).

$$Na_{0.70}CoO_2 + 2zH_2O \rightarrow Na_x(H_3O)_zCoO_2 + zNaOH \quad (x + z = 0.70) \qquad (1)$$

In the case of the formation of the oxyhydrate superconductor, reduction of Co by water takes place in the hydration process as well as in the ion exchange. Although the reduction is promoted in an alkaline environment,[8] the Co valence in the oxyhydrate decreases to only +3.5, even in a 2 M NaOH aqueous solution (pH 14).[13] In the present case, reduction by water does not occur, because the Co valence is much lower than +3.5.

Magnetic susceptibilities of the samples are shown in Figure 6. For the range of $x \geq 0.58$, the Curie constant determined from higher-temperature data is almost independent of *x*, whereas enhancement of the magnetic susceptibility in the low temperature region (below ~20 K for $x = 0.70$) becomes more pronounced with decreasing *x*, as seen in the reciprocal susceptibility. This enhancement is intrinsic, as confirmed by some nuclear magnetic resonance measurements.[14] For the range of $x \leq 0.53$, the temperature dependence of the susceptibility in the higher-temperature region becomes smaller with decreasing *x*. In this range of *x*, substitution of $H_3O^+$ for $Na^+$ seems to cause the change from Curie–Weiss type magnetism to the Pauli paramagnetic type. It is very unlikely that this change is caused by the small amount of secondary phase or by a certain phase decomposition because there is, in general, no compound whose magnetic susceptibility shows so large and divergent a drop with decreasing temperature to compensate the upturn of the Curie–Weiss term; therefore, it reflects the intrinsic nature of the system. Similar change has been observed for the magnetic susceptibility of $Na_xCoO_2$ when *x* decreases, although holes are introduced in this case.[2,15,16] The magnetism is essentially governed by the electronic band structure and carrier content. Because the carrier content (the Co

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valence) was kept constant in the present case, the aforementioned results suggest that the band structure of the compound is adjustable by structural modification induced by the ion exchange.

The change in the band structure caused by isovalent ion exchange has also been observed in the oxyhydrate.[17] It is believed in this case that such a change is caused by the variation in the thickness of the $CoO_2$ layer, because between the two kinds of Fermi surface, one is very sensitive to the thickness.[18] In $Na_{0.7}CoO_2$, only one kind of Fermi surface is expected to exist[19] and it appears to be less sensitive to thickness; thus, the change in the band structure would occur by another mechanism. Two possibilities are considered; (1) the transfer integral between Co and O orbitals may be changed by the ion exchange, as suggested by the change in the lattice constant of $a$ (see Figure 4), or (2) the two-dimensionality of the band structure may be enhanced by the ion exchange, because $Na_{0.7}CoO_2$ has a relatively large interaction along the $c$ axis[20] due to an O−O hopping assisted by the Na $sp^2$ hybridized orbitals.[21] At present, it is not clear whether the intralayer or the interlayer effect is more dominant for the change in the band structure. Quite recently, it was pointed out that the local minimum of the bands at Γ-point can play an important role in the magnetism of $Na_xCoO_2$.[22] The magnetic behavior of the present system may also be influenced by the depth of the minimum, which can be changed by the structural modification.

In many studies, Na contents in $Na_xCoO_2$ were estimated from the $c$-axis length. Such treatment is valid only when the sample does not contain oxonium ions. If oxonium ions are present and substituting $Na^+$ ions, then single parameters such as the $c$-axis length or the Na content are not sufficient to determine the nature of the sample. It was found that ion exchange occurs even when the sample is stored in a desiccator containing silica gel, unless nitrogen gas is substituted for air. Thus, we suspect that contamination with oxonium ions has occurred in many previous studies, and that this has caused the strong sample dependency of the physical properties of $Na_xCoO_2$.[7]

## Conclusion

We found that $Na^+$ ions in $Na_xCoO_2$ can be partially substituted by $H_3O^+$ ions simply by immersion in water. The Na content decreases with increasing volume of water used, and the Co valence is kept constant. The presence of oxonium ions in the compounds is consistent with the change in the lattice constant, $c$, and the Raman spectra of some samples. On the other hand, the magnetic susceptibility is strongly influenced by the substitution, and the temperature dependence of the susceptibility changes from Curie–Weiss type to the Pauli paramagnetic type, which implies that the electronic structure of this system is significantly sensitive to the substitution. We suggested that this unnoticed ion substitution is one of the origins of the noted "sample dependency" of the Co oxide.

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