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Synthesis of monolayers and bilayers of cobalt oxyhydrates (Na,K)_x(H₂O)_yCoO_{2-δ}

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Potassium sodium cobalt oxyhydrates (Na,K)_x(H₂O)_yCoO_{2-δ} were synthesized from γ -Na_{0.7}CoO₂ by using aqueous KMnO₄ solution in a one-pot process. Chemical and structural analyses revealed that a partial or even almost complete replacement of K⁺ for Na⁺ in the alkaline layers occurs. Direct formation of the $c \approx 13.9$ Å phase is apparently associated with the larger size of K⁺ (~ 1.4 Å) as compared to Na⁺ (~ 1.0 Å). Formation of (Na,K)_x(H₂O)_yCoO_{2-δ} not only involves de-intercalation, oxidation and hydration processes, but also an ion exchange reaction. Based on a systematic study, the phase formation of (Na,K)_x(H₂O)_yCoO_{2-δ} with $c \approx 19.6$ Å is a slow process, particularly when using aqueous KMnO₄ solution with low molar ratio of KMnO₄/Na. When comparing the Co K-edge X-ray absorption spectra of (Na,K)_x(H₂O)_yCoO_{2-δ} with those of Na_x(H₂O)_yCoO₂ obtained from Br₂/CH₃CN solution, the edge energy of the main peak of the bilayered hydrate is found to be 3.5 eV higher than that of the monolayered hydrate for (Na,K)_x(H₂O)_yCoO_{2-δ}. In contrast, the edge energy of the main peak of the bilayered hydrate is 0.4 eV lower than that of the monolayered hydrate for Na_x(H₂O)_yCoO₂. In addition, the hydration behavior of monolayered of (Na,K)_x(H₂O)_yCoO_{2-δ} is different from that of Na_x(H₂O)_yCoO₂. These results seem to suggest that they are two different systems.

Keywords: layered oxides; phase transformation; thermogravimetric analysis; X-ray spectroscopy; XRD

1. Introduction

The discovery by Takada et al. [1] of superconductivity in Na_{0.35}(H₂O)_{1.3}CoO_{2-δ} with $T_c \approx 4$ –5 K was a surprise after several years of studies on the potential thermoelectric material γ -Na_xCoO₂ [2]. The parent material of γ -Na_{0.7}CoO₂ crystallizes in a hexagonal lattice with the space group $P6_3/mmc$ (#194) and belongs to a category of γ -Na_xCo_yO₂ phases with $0.55 \leq x/y \leq 0.74$ (also classified as the P2 phase) [3]. The sodium is considered as a charge reservoir and located between CoO₂ layers

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with prismatic surroundings. There are two different sites for the sodium in the crystallographic positions, which are usually not fully occupied by the sodium and hence have vacancies on them. This situation, however, makes this class of compounds more complicated in structure and rich in properties. The Co ions form a layered triangular sublattice, on which geometric frustration of anti-ferromagnetic arrangement could occur. In the presence of strong correlation of 3d electrons of Co ions, the magnetic geometric frustration is of particular interest and could be associated with the unusual electronic, thermoelectric and magnetic properties [2,4,5].

The superconducting phase of bilayer hydrate $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.3}\text{CoO}_{2-\delta}$ was obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ powders in $\text{Br}_2/\text{CH}_3\text{CN}$ solution followed by filtering and rinsing [1]. Upon intercalation, bilayers of water molecules are intercalated into the host lattice to form the fully hydrated sodium cobalt oxyhydrates $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.3}\text{CoO}_{2-\delta}$ with the c -axis of the parent compound $\gamma\text{-Na}_{0.7}\text{CoO}_2$ expanding from 10.9 Å to 19.6 Å. Since the bilayer hydrate phase preserves the structural integrity of the host lattice, the reaction can be viewed as a topotactic transformation process. Formation of superconducting $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.3}\text{CoO}_{2-\delta}$ is generally considered as an oxidative de-intercalation by removing Na^+ partially from the host lattice, followed by a hydration reaction. It is well known that KMnO_4 is a strong oxidizing agent with a unique affinity for oxidizing organic compounds, which is particularly useful for *in situ* remediation of organic compounds in ground water and subsurface soils when coupled with delivery techniques. We have recently reported that superconducting potassium sodium cobalt oxyhydrates with $c \approx 19.6$ Å can be obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ either in the aqueous KMnO_4 or NaMnO_4 solution without resort to the volatile and flammable $\text{Br}_2/\text{CH}_3\text{CN}$ solution [6,7]. In this work, we show that a new phase of cobalt oxyhydrates $(\text{Na},\text{K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ with $c \approx 13.9$ Å can be directly obtained when the molar ratio of KMnO_4 relative to the Na content in the parent compound is equal to or greater than 4.286 ($\text{KMnO}_4/\text{Na} \geq 4.286$). It should be noted that the $c \approx 13.9$ Å phase with monolayers of water molecules residing within the alkaline metal layers cannot be directly obtained by using aqueous NaMnO_4 solution even at the molar ratio of $\text{NaMnO}_4/\text{Na} = 40$ [7]. It is well known that the superconducting cobalt oxyhydrates are not stable with respect to the ambient conditions, applied pressure or evacuation [8,9]. When subjected to heating, pressure or evacuation, the $c \approx 19.6$ Å phase of the bilayer cobalt oxyhydrates tends to lose water and transforms into the $c \approx 13.9$ Å phase, although preserving the structural integrity with little change of the a -axis. In the course of careful studies, we have found that the de-intercalation of Na^+ first occurs and proceeds relatively rapidly and leads to the non-hydrate phase of $c \approx 11.2$ Å. In contrast to the fast de-intercalation, the subsequent hydration is a slow process and results in the $c \approx 19.6$ Å phase, particularly when using a low molar ratio of KMnO_4/Na . At sufficiently high molar ratio of KMnO_4/Na , partial or almost complete substitution of K^+ for Na^+ via an ion exchange process leads to the $c \approx 13.9$ Å phase due to size effects. Therefore, formation of the mixed alkaline metal cobalt oxyhydrates not only involves the oxidative de-intercalation and hydration reaction but also the ion exchange reaction in one pot using the aqueous KMnO_4 solution route.

2. Experimental

Polycrystalline parent compounds of sodium cobalt oxides $\gamma\text{-Na}_{0.7}\text{CoO}_2$ were prepared using a rapid heat-up procedure in order to avoid the loss of Na in the heating process. High purity powders of Na_2CO_3 (Aldrich) and CoO (SDIC) were thoroughly mixed and ground using a Retch MM2000 laboratory mixer mill, followed by calcination in a preheated box furnace at 800°C for 12 h. The resulting powders (0.5–1 g) were immersed and stirred in 50–680 ml of aqueous KMnO_4 solution with different molar ratios of KMnO_4/Na labeled 0.05X–40X at room temperature for five days. The concentrations of KMnO_4 used to obtain the 0.05X, 0.1X, 0.3X, 1.529X, 2.29X, 4.286X, 10X and 40X samples were 0.00327M, 0.00654M, 0.0196M, 0.2M, 0.3M, 0.28M, 0.192M and 0.1923M, respectively. It should be mentioned that high molar ratio of KMnO_4/Na would need more water to dissolve KMnO_4 due to the limited solubility of KMnO_4 in water. For the 40X sample, it would need 680 ml water to completely dissolve KMnO_4 . The products were filtered and washed by de-ionized water several times with a total volume of 150–200 cm^3 . Note that the contents of potassium and sodium of the products depend slightly on the volume of water in the washing process because they would lose a little in the water as confirmed by ICP analyses. The powders were then stored in a wet chamber with relative humidity of 98% to avoid loss of the water content.

Powder X-ray diffraction (XRD) patterns were obtained using a Shimadzu XRD-6000 diffractometer equipped with Fe K_α radiation. The data were collected over the range $5^\circ \leq 2\theta \leq 90^\circ$ with 0.02° 2θ steps. The unit cell parameters were computed using a Rietveld structure refinement program, Rietica. Elemental compositions of the resulting products were determined by using a Perkin Elmer Optima 3000 DC inductively coupled plasma–atomic emission spectrometer (ICP-AES). Thermogravimetric analysis (TGA) was carried out to determine the water content of resulting products by using a Perkin Elmer Pyris 1 thermogravimetric analyzer at a heating rate of $0.1^\circ\text{C min}^{-1}$ in flowing oxygen. The water content of the samples was determined by a systematic study of combination results of TGA and XRD. After completion of TGA experiments at different temperatures, phase purity of the sample is checked by the XRD experiments. Oxidation number of Co and oxygen content were determined by iodometric titration. X-ray absorption spectra were recorded at wiggler beamline BL17C at the National Synchrotron Radiation Research Center, Taiwan using transmission mode (two ionization chambers) on the powder samples. The X-ray absorption measurements were carried out at Co K-edge using the Si (111) double-crystal monochromator. The energy calibration was made according to the K-edge of the Co foils.

3. Results and discussion

Figures 1 and 2 show the powder X-ray diffraction patterns of cobalt oxyhydrates obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in different molar ratios of KMnO_4/Na . According to XRD patterns, they can be classified into four categories by the molar ratio of KMnO_4/Na , i.e. $\text{KMnO}_4/\text{Na} \leq 0.1$, $0.3 \leq \text{KMnO}_4/\text{Na} \leq 0.4$, $0.5 \leq \text{KMnO}_4/\text{Na} \leq 2.29$ and $4.286 \leq \text{KMnO}_4/\text{Na} \leq 40$. After immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in the KMnO_4 solution for five days, the XRD patterns of the 0.05X and 0.1X show a

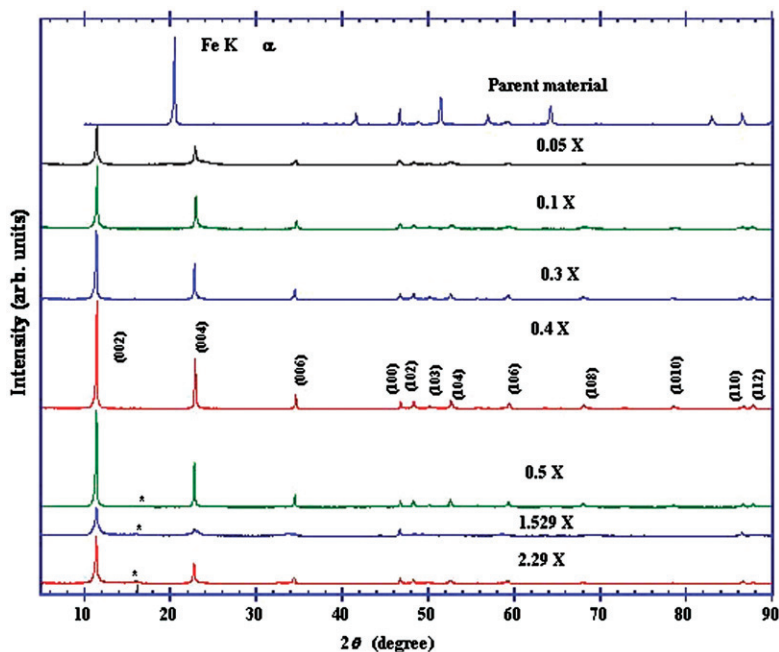


Figure 1. Powder X-ray diffraction patterns of $\gamma\text{-Na}_{0.7}\text{CoO}_2$ and $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in low molar ratio of aqueous KMnO_4 solution with respect to the Na content in the parent compound ($0.05 \leq \text{KMnO}_4/\text{Na} \leq 2.29$). The 0.5X sample is that where the molar ratio of KMnO_4/Na is 0.5. The asterisk (*) indicates the (002) reflection of the $c \approx 13.9 \text{ \AA}$ phase.

mixture of the $c \approx 19.6 \text{ \AA}$ phase and the $c \approx 11.2 \text{ \AA}$ phase; the XRD patterns of the 0.3X and 0.4X samples show a pure $c \approx 19.6 \text{ \AA}$ phase; the XRD patterns of the 0.5X, 1.529X, and 2.29X samples show a mixture of the $c \approx 19.6 \text{ \AA}$ and the $c \approx 13.9 \text{ \AA}$ phase; and the XRD patterns of the 4.286X, 10X, 20X, and 40X samples show a pure $c \approx 13.9 \text{ \AA}$ phase. Moreover, we find that when storing the as-prepared 0.05X and 0.1X samples in a wet chamber with a relative humidity of 98% for a long period of time, the $c \approx 19.6 \text{ \AA}$ phase grows at the expense of the $c \approx 11.2 \text{ \AA}$ phase. These results indicate that intercalation of the water molecules could undergo a gas–solid interaction in addition to that through a liquid–solid reaction.

Ion exchange has been defined as a process in which ions are released from an insoluble permanent material in exchange for other ions in a surrounding solution. Ion exchange involves a reversible reaction with the structural integrity of the host lattice essentially preserved throughout the process. Table 1 summarizes the chemical compositions obtained by the ICP-AES analyses and the lattice parameters of KMnO_4 -prepared $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$. The sum of the sodium and potassium falls in the range of 0.28 and 0.38 in terms of the molar ratio with respect to cobalt. More alkali metal (the sum of K and Na) is de-intercalated from the host lattice when using a higher molar ratio of KMnO_4/Na with respect to $\gamma\text{-Na}_{0.7}\text{CoO}_2$. Based on the structural and chemical analyses, the structural integrity is preserved with slight

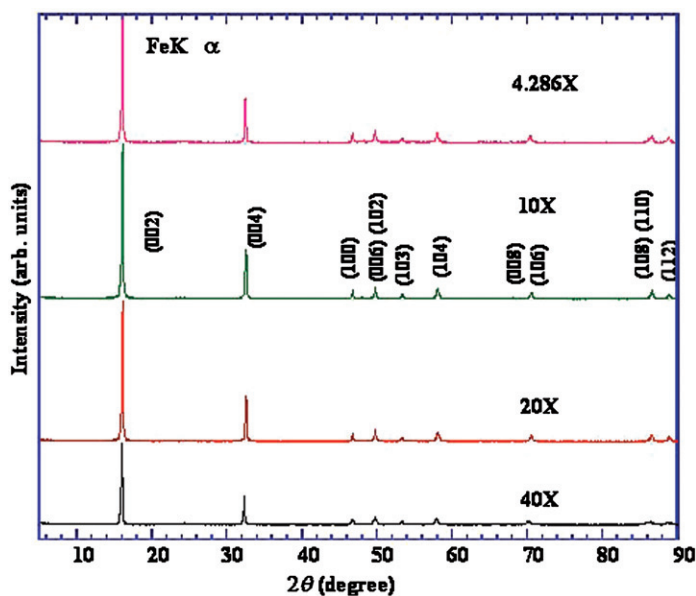


Figure 2. Powder X-ray diffraction patterns of $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in high molar ratio of aqueous KMnO_4 solution with respect to the Na content in the parent compound ($4.286 \leq \text{KMnO}_4/\text{Na} \leq 2.29$).

variation of the lattice constants and the Na^+ is partially replaced by K^+ , indicating the occurrence of the ion exchange between Na^+ and K^+ . It can be seen that the sodium content in $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ decreases significantly at the molar ratio of KMnO_4/Na equal to or greater than 4.286, whereas the potassium content increases with increasing molar ratio of KMnO_4/Na . In case of the 40X sample, $\text{Na}_{0.03}\text{K}_{0.25}(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$, the K^+ almost replaces the Na^+ completely. Therefore, if more K^+ is present in the aqueous solution with respect to the Na^+ in the insoluble $\gamma\text{-Na}_{0.7}\text{CoO}_2$ (a higher molar ratio of KMnO_4/Na), the more ion exchange of K^+ for Na^+ would occur.

As can be seen in Table 1, high X samples ($\geq 4.286\text{X}$) obviously show a shorter c -axis of $\sim 13.9 \text{ \AA}$ as compared to $\sim 19.6 \text{ \AA}$ for the low X samples. In conjunction with the ICP-AES results, apparently the content of K^+ in the sample is associated with the size of the c -axis. This situation is reminiscent of the case in $\text{A}_x(\text{H}_2\text{O})_y\text{MS}_2$ ($\text{A} = \text{Group IA or IIA metal}$, $\text{M} = \text{Ti, Nb or Ta}$). On contact with water vapor or with liquid water, A_xMS_2 undergoes a topotactic process and forms hydrated compounds $\text{A}_x(\text{H}_2\text{O})_y\text{MS}_2$ with water molecules intercalated into the host lattice A_xMS_2 , which results in the c -axis expansion. The size of c -axis expansion is apparently associated with the size of the alkaline metal. It has been found that an alkaline metal with the ionic radius $< 1 \text{ \AA}$ would lead to bilayers of water intercalated between the MS_2 layers and hence a larger c -axis, whereas the alkaline metal with the ionic radius $> 1 \text{ \AA}$ would lead to monolayer of water inserted within the alkaline metal layers and hence a smaller c -axis [10]. The c -axis of $\text{A}_{0.3}(\text{H}_2\text{O})_y\text{TaS}_2$ is 23.63 \AA and 18.18 \AA for $\text{A} = \text{Na}^+$ (ionic radius: $\sim 1 \text{ \AA}$) and K^+ (ionic radius: $\sim 1.4 \text{ \AA}$),

Table 1. Chemical analyses by ICP-AES and lattice constants of $(\text{Na},\text{K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in aqueous KMnO_4 solution for five days. The error in wt % of each element in ICP-AES analysis is $\pm 3\%$, which corresponds to an estimated error of ± 0.02 per formula unit for each element. The lattice constants were obtained using Rietica, a Rietveld structure refinement program, based on a hexagonal structure ($P6_3/mmc$).

Category ^a	Molar ratio of KMnO_4/Na	K	Na	x = Na+K	Co	a (Å)	c (Å)	Oxidation number of Co	Oxygen deficiency δ	Water content y
I	0.05X	0.00	0.38	0.38	1	2.8268(5)	19.626(2)			
I	0.1X	0.01	0.34	0.35	1	2.8261(3)	19.573(1)			
II	0.3X	0.02	0.33	0.35	1	2.8249(1)	19.669(1)	+3.56(1)	0.05(1)	1.33
III	1.529X	0.05	0.31	0.36	1	2.8115(1.5)	19.750(5)			
III	2.29X	0.08	0.28	0.36	1	2.8250(3)	19.735(2)			
IV	4.286X	0.18	0.15	0.33	1	2.8286(1)	13.917(1)			
IV	10X	0.21	0.07	0.28	1	2.8261(2)	13.864(1)			
IV	40X	0.25	0.03	0.28	1	2.8251(2)	13.960(1)			

Notes: ^aCategories I, II, III, and IV refer to $\text{KMnO}_4/\text{Na} \leq 0.1$, $0.3 \leq \text{KMnO}_4/\text{Na} \leq 0.4$, $0.5 \leq \text{KMnO}_4/\text{Na} \leq 2.29$, and $4.286 \leq \text{KMnO}_4/\text{Na} \leq 40$ in terms of the molar ratio of KMnO_4/Na used to treat the parent material. Both categories I and III are mixture phases.

respectively. The interlayer height between MS_2 layers is ca. 5.77 \AA and 3.04 \AA for $\text{A} = \text{Na}^+$ and K^+ , respectively. They correspond well to once and twice the van der Waals diameter of a water molecule of $\sim 2.8 \text{ \AA}$. Similar relationships between the size of the alkaline metal and the c -axis could be found in our KMnO_4 -prepared cobalt oxyhydrates. Based on the XRD and ICP-AES results, the $c \approx 13.9 \text{ \AA}$ phase having more K^+ content has an interlayer expansion of ca. 1.5 \AA , whereas the $c \approx 19.6 \text{ \AA}$ phase having less K^+ content has an interlayer expansion of ca. 4.35 \AA . Further evidence can be seen in the TGA results, shown in Figures 3 and 4. The $c \approx 13.9 \text{ \AA}$ phase has hydration water content of $y \approx 0.63$, whereas the $c \approx 19.6 \text{ \AA}$ phase has $y \approx 1.33$. Note that the water content was found to be $y \approx 0.5\text{--}0.7$ for $\text{A} = \text{K}$ and $y \approx 1.6\text{--}1.8$ for $\text{A} = \text{Na}$ in $\text{A}_x(\text{H}_2\text{O})_y\text{MS}_2$. Therefore, direct formation of $c \approx 13.9 \text{ \AA}$ phase of cobalt oxyhydrate could be attributed to the significant increase of K^+ in the $\geq 4.286\text{X}$ samples. In addition, the KMnO_4 -prepared $c \approx 13.9 \text{ \AA}$ phase of the high X samples cannot be transformed to the $c \approx 19.6 \text{ \AA}$ phase by exposing the sample to a humid environment even for a long period of time. Note that the transformation between the $c \approx 13.9 \text{ \AA}$ phase and the $c \approx 19.6 \text{ \AA}$ phase is reversible for the low X and Br_2 -treated samples. It is noted that using aqueous NaMnO_4 solution to treat $\gamma\text{-Na}_{0.7}\text{CoO}_2$ only leads to the $c \approx 19.6 \text{ \AA}$ phase even with the molar ratio of NaMnO_4/Na as high as 40.

We also find that the transformation from the non-hydrate phase ($c \approx 11.2 \text{ \AA}$) to the bilayer hydrate phase ($c \approx 19.6 \text{ \AA}$) for both of the 0.05X and 0.1X samples is very slow as compared to that for the higher X samples. It is known that the oxidation reaction follows second-order kinetics at low concentration of KMnO_4 solution [11], which means the reaction rate depends on both the concentration of the oxidized compound and the aqueous KMnO_4 solution. At low concentration of KMnO_4

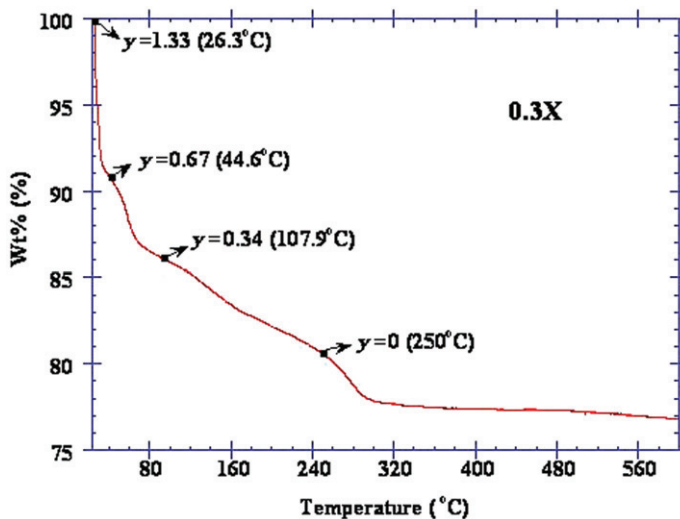


Figure 3. TGA for the 0.3X sample, $\text{Na}_{0.33}\text{K}_{0.02}(\text{H}_2\text{O})_{1.33}\text{CoO}_{1.95}$, obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in the aqueous KMnO_4 solution with the molar ratio of $\text{KMnO}_4/\text{Na} = 0.3$. Above 250°C , the sample begins to show the decomposition product Co_3O_4 .

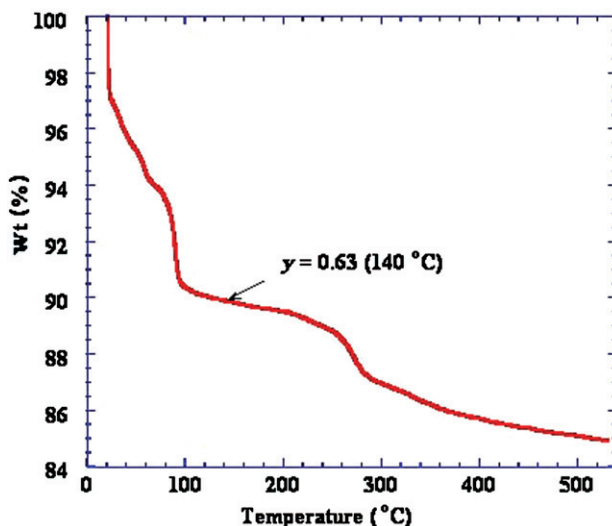


Figure 4. TGA for the 10X sample, $\text{Na}_{0.07}\text{K}_{0.21}(\text{H}_2\text{O})_{0.63}\text{CoO}_{1.81}$, obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in aqueous KMnO_4 solution with the molar ratio of $\text{KMnO}_4/\text{Na} = 10$. The water content is determined by choosing the temperature of 140°C as the complete removal of water from the sample based on a systematic study on the combination results of XRD and TGA. Above 140°C , the sample begins to show the decomposition product Co_3O_4 .

solution, this could make the oxidation process slow, and in turn slow down completely the formation of fully hydrated phase. This is evidenced by the facts in our systematic study by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in different concentrations of aqueous KMnO_4 solution for different periods of time. As shown in Figure 5, the $c \approx 19.6 \text{ \AA}$ phase has already appeared after one-day immersion for the 0.3X (the second category) and 1X sample (the third category). The 0.05X sample (the first category) appears only as the non-hydrate phase ($c \approx 11.2 \text{ \AA}$). Moreover, as shown in Figure 6, the $c \approx 19.6 \text{ \AA}$ phase shows up after two days of immersion for the 0.05X sample. It can be readily seen that the amount of non-hydrate phase existing in the sample is smaller for a larger X sample based on the relative reflection intensity of $I_{\text{max}}(c \approx 19.6 \text{ \AA})/I_{\text{max}}(c \approx 11.2 \text{ \AA})$. In addition, for the 0.05X sample already immersed in the KMnO_4 solution for five days, a small amount of non-hydrate phase still remains after an additional four days of exposure to the water vapor. For a higher X sample ($\geq 0.3\text{X}$), the non-hydrate phase would not be observed after five days of aqueous KMnO_4 treatment. Table 2 summarizes the ICP-AES results for the products with different immersion periods of time. Due to the presence of potassium, the formation of the new phase $(\text{Na},\text{K})_x(\text{H}_2\text{O})_y\text{CoO}_2$ involves an ion exchange reaction in addition to the de-intercalation and hydration process.

One would expect an increase of the oxidation number of Co due to the de-intercalation of Na^+ from the host lattice. An X-ray absorption spectroscopy (XAS) study of Na_xCoO_2 indicates that the oxidation number of Co increases with decreasing x [12]. The oxidation number of cobalt has recently been determined by wet chemical analyses. The oxidation number of cobalt is $+3.26$ and $+3.48$ for $\gamma\text{-Na}_{0.77}\text{CoO}_{2.02}$ and Br_2 -treated bilayer hydrate $\text{Na}_{0.36}(\text{H}_2\text{O})_{1.3}\text{CoO}_{1.92}$,

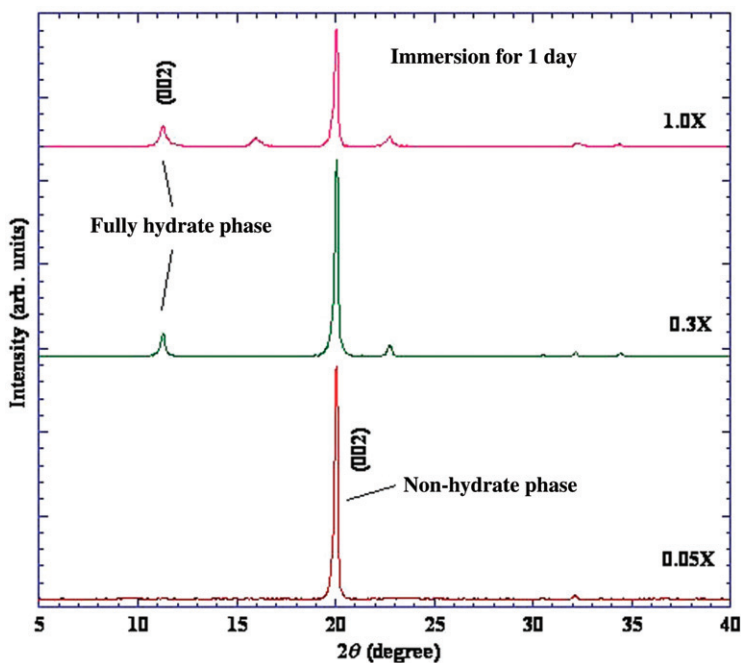


Figure 5. Powder X-ray diffraction patterns of the 0.05X, 0.3X and 1X samples obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in aqueous KMnO_4 solution for one day. The fully hydrate phase ($c \approx 19.6 \text{ \AA}$) is observed both in the 0.3X and 1.0X sample, indicated by the reflection peak at $2\theta \approx 11.3^\circ$, but not for the 0.05X sample. It suggests that formation of the fully hydrate phase is a very slow process when using a low concentration of aqueous KMnO_4 solution.

respectively [13]. The oxidation number of cobalt for bilayer hydrate is lower than that simply calculated from charge balance by neglecting the oxygen deficiency. The lower-than expected oxidation number of Co has been ascribed to the presence of H_3O^+ , which compensates the deviation from the charge neutralization [14]. However, a recent study of Co-K edge spectra of $\text{Na}_{0.3}(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ indicates that there is essentially no change in oxidation number of Co [12,15]. Therefore, an alternative explanation of oxygen deficiency in $\text{Na}_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ for the deviation of the analyzed oxidation number of Co from the calculated value could be considered as follows. First of all, a similar system of $\text{Li}_{1-x}\text{CoO}_{2-\delta}$ could be compared with the present system of $(\text{K},\text{Na})_x\text{CoO}_{2-\delta}$. It has been reported that the oxygen deficiency δ of $\text{Li}_{1-x}\text{CoO}_{2-\delta}$ increases with decreasing Li content and the oxidation number of Co increases with decreasing Li content down to $x=0.5$ and remains almost constant [16]. The oxygen deficiency in $\text{Li}_{1-x}\text{CoO}_{2-\delta}$ could be considered as holes introduced into the $\text{O}^{2-}:2p$ band [17]. The above results for $\text{Li}_{1-x}\text{CoO}_{2-\delta}$ could be explained as follows according to [15]. Due to the overlap of the $\text{Co}^{3+/4+}:t_{2g}$ band with the top of the $\text{O}^{2-}:2p$ band, the oxidation is mainly occurring in the $\text{Co}^{3+/4+}:t_{2g}$ band due to de-intercalation of Li^+ for $x < 0.5$, whereas further de-intercalation of Li^+ would lead to oxidation in the $\text{O}^{2-}:2p$ band for $x > 0.5$ and consequently oxidizing the oxide ions to oxygen and release the oxygen from the lattice.

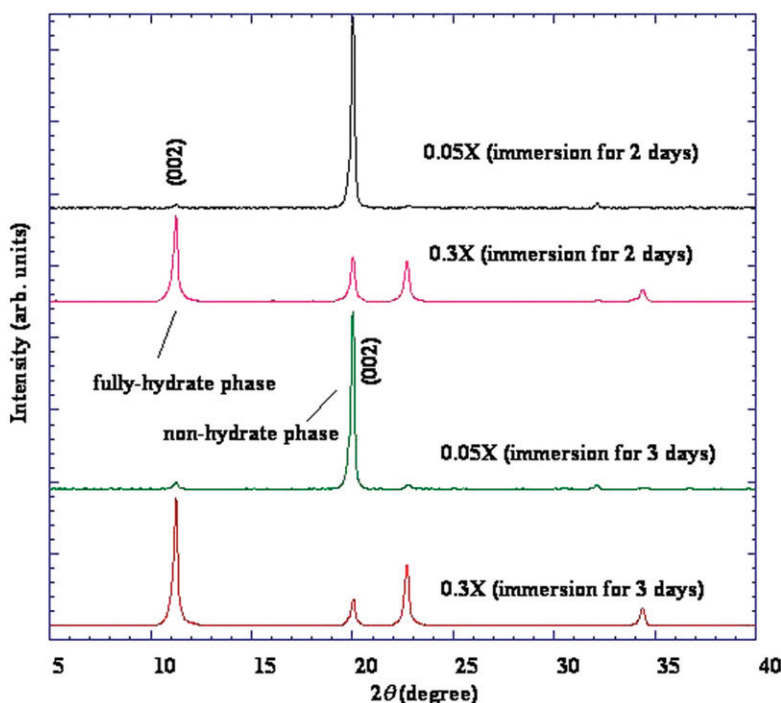


Figure 6. Powder X-ray diffraction patterns of the 0.05X and 0.3X samples, obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in aqueous KMnO_4 solution for two days and three days. The fully hydrate phase ($c \approx 19.6 \text{ \AA}$) appears after two-day immersion in the aqueous KMnO_4 solution for the 0.05X sample. Formation of the $c \approx 19.6 \text{ \AA}$ phase for the 0.05X sample is much slower than that of the 0.3X sample.

Table 2. Chemical analyses by ICP-AES for $(\text{Na},\text{K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in aqueous KMnO_4 solution for various periods of time.

Sample/immersion time	K	Na	Co
0.05X/1 day	0.001	0.42	1
0.05X/3 days	0.002	0.42	1
0.3X/1 day	0.012	0.37	1
0.3X/3 days	0.023	0.36	1

This scenario could well be happening in the system of sodium cobalt oxide system. Oxygen vacancies are constantly observed in $\text{Na}_x\text{CoO}_{2-\delta}$ having low x values [18]. The trigonal crystal field splits the three-fold $\text{Co}^{3+/4+}:t_{2g}$ band into a_{1g} band and two-fold e'_g band [19]. De-intercalation of each Na^+ from the host lattice can be considered as removing an electron from the highest occupied molecular orbital (HOMO) [20], which is associated with the relative energy level of $\text{Co}^{3+/4+}:a_{1g}$ band with respect to the $\text{O}^{2-}:2p$ band. Removing electrons from the $\text{Co}^{3+/4+}:a_{1g}$ band

increases the oxidation number of $\text{Co}^{3+/4+}$, whereas removing electrons from the $\text{O}^{2-}:2p$ band leads to oxidation of the oxide ions and consequently the loss of oxygen from the lattice at further de-intercalation of Na^+ . Since the existence of hydronium ion (H_3O^+) is considered as the origin of the difference between the analyzed oxidation number of Co and that calculated from the x value for $\text{Na}_{0.35}(\text{H}_2\text{O})_y\text{CoO}_2$, we have also prepared samples without potassium of bilayered hydrates of $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.4}\text{CoO}_2$ and monolayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{0.7}\text{CoO}_2$ in order to clarify this issue. The former was obtained by immersing $\gamma\text{-Na}_{0.7}\text{CoO}_2$ in 3M $\text{Br}_2/\text{CH}_3\text{CN}$ solution [1], and the latter was obtained by placing the former in a vacuum chamber of 10^{-9} torr for one week. Figure 7 shows the X-ray absorption near edge structure of Co K-edge spectra for the anhydrous and hydrated samples together with those of reference compounds. Two of the spectra were taken from [12]. An energy calibration of 0.57 eV was applied to both spectra from [12]. This 0.57 eV energy shift was to make coincident the main peaks in the spectra of the Co-K edge of the present CoO sample and that from [12]. The X-ray absorption spectroscopy shows that the edge energy of the main peak of the Co K-edge for bilayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.4}\text{CoO}_2$ is about 0.4 eV lower than that for the monolayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{0.7}\text{CoO}_2$ [21]. These results are in sharp contrast to those found for potassium-including bilayered and monolayered hydrates. A blue chemical shift of 3.5 eV is observed for $\text{Na}_{0.33}\text{K}_{0.02}(\text{H}_2\text{O})_{1.33}\text{CoO}_{2-\delta}$ as compared to $\text{Na}_{0.07}\text{K}_{0.21}(\text{H}_2\text{O})_{0.63}\text{CoO}_{2-\delta}$, which clearly indicates a higher oxidation number of Co in bilayered hydrate of $\text{Na}_{0.33}\text{K}_{0.02}(\text{H}_2\text{O})_{1.33}\text{CoO}_{2-\delta}$ shown in Table 2 of [22]. In contrast, the estimated oxidation number of bilayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{1.4}\text{CoO}_2$ is lower than that of the monolayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{0.7}\text{CoO}_2$. In addition, monolayered hydrate of $\text{Na}_{0.07}\text{K}_{0.21}(\text{H}_2\text{O})_{0.63}\text{CoO}_{2-\delta}$ behaves differently

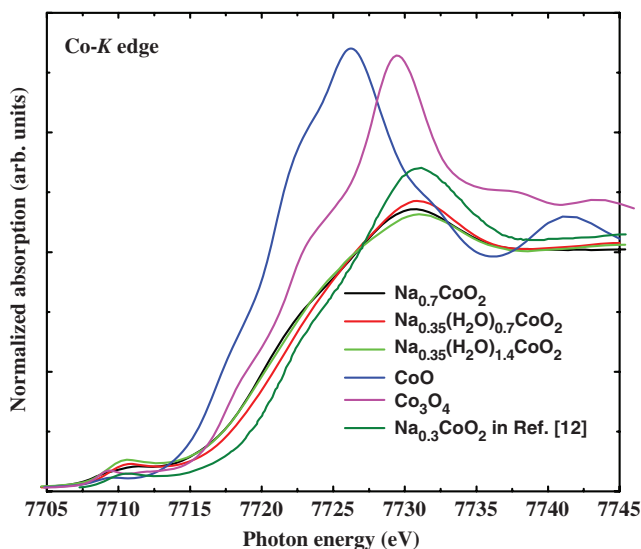


Figure 7. (Color online). X-ray absorption near-edge structure of Co K-edge spectra for the anhydrous and hydrated samples together with those of reference compounds.

from the monolayered hydrate of $\text{Na}_{0.35}(\text{H}_2\text{O})_{0.7}\text{CoO}_2$. The former cannot be transformed into bilayered hydrate, whereas the latter can be transformed into the bilayered hydrate upon hydration or vice versa by dehydration. The iodometric titration method was used to simultaneously determine the oxidation number of Co and the oxygen content. The oxidation number of Co was first determined from the titration data by the iodometric titration method. The oxygen stoichiometry was then calculated based on the charge neutrality in the compound. For our results determined by iodometric titration, the oxidation number of cobalt is $+3.56(1)$ and $+3.32(4)$ for bilayered hydrate of $\text{Na}_{0.33}\text{K}_{0.02}(\text{H}_2\text{O})_{1.33}\text{CoO}_{1.95}$ and monolayered hydrate of $\text{Na}_{0.07}\text{K}_{0.21}(\text{H}_2\text{O})_{0.63}\text{CoO}_{2-\delta}$, respectively. Therefore, it is plausible to consider that the two systems $\text{Na}_x(\text{H}_2\text{O})_y\text{CoO}_2$ and $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ could be different.

4. Conclusions

We have synthesized the potassium sodium cobalt oxyhydrates $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ using aqueous KMnO_4 solution. Formation of the $(\text{Na,K})_x(\text{H}_2\text{O})_y\text{CoO}_{2-\delta}$ involves not only de-intercalation, oxidation and hydration but also an ion exchange reaction. When using high molar ratio of KMnO_4/Na (≥ 4.286) to treat $\gamma\text{-Na}_{0.7}\text{CoO}_2$, it led to significant removal of Na^+ and a pure $c \approx 13.9\text{\AA}$ phase with a monolayer of water locating within the alkaline layer as a result of partial or almost complete substitution of K^+ for Na^+ . The hydration is a very slow process particularly when using aqueous KMnO_4 solution with a low molar ratio of KMnO_4/Na .

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