films and to understand the ablation process and chemical reactivity of ejected species during the plume expansion and propagation.

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Electrochemical Properties of $Li_xCo_yNi_{1-y}O_2$ Prepared by Citrate Sol-Gel Method

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The electrochemical properties of $Li_xCo_yNi_{1-y}O_2$ compounds (y=0.1, 0.3, 0.5, 0.7, 1.0) prepared by citrate sol-gel method have been investigated. The $Li_xCo_yNi_{1-y}O_2$ compounds were annealed at 850 °C for 20 h after preheating at 650 °C for 6 h, in air. The x-ray diffraction (XRD) patterns for $Li_xCo_yNi_{1-y}O_2$ have shown that these compounds have a well developed layered structure ($R\bar{3}\,m$). From the scanning electron microscopy of $Li_xCo_yNi_{1-y}O_2$, particle size was estimated less than 5 μm. The $Li//Li_xCo_yNi_{1-y}O_2$ electrochemical cell consists of Li metal anode and 1 M $LiClO_4$-propylene carbonate (PC) solution as the electrolyte. The differences in intercalation rate of the $Li_xCo_yNi_{1-y}O_2$ in the first charge/discharge cycle were less than 0.05 e^-. The first discharge capacities of Li_xCoO_2 and $Li_xCo_{0.3}Ni_{0.7}O_2$ were ~130 mAh/g and ~160 mAh/g, respectively.

Introduction

$LiNiO_2$,[1-6] $LiCoO_2$,[7-15] $LiMn_2O_4$,[16-19] and $Li_xCo_yNi_{1-y}O_2$[20-24] have been intensively studied as cathode active materials in lithium secondary batteries. Among them, $LiNiO_2$, $LiCoO_2$, and $Li_xCo_yNi_{1-y}O_2$ are isostructural with α-$NaFeO_2$. In these

phases, alternate layers of Li and Co (and/or Ni) cations occupy the octahedral site of a cubic close packing of oxygen anions. According to previous studies,[4,5,22] $LiNiO_2$ has been nonstoichiometric compound with the formula of $[Li^+_{1-z}Ni^{2+}_z][Ni^{3+}Ni^{2+}_z]O_2$ $(0 \leq z \leq 0.2)$ depending on preparation conditions. A small amount of structural disorder due to the displacement of nickel and lithium ions in $LiNiO_2$ strongly affects the electrochemical properties such as the working voltage and rechargeable capacity. As the deintercalation reaction proceeds below x=0.5 in Li_xNiO_2, some structural irreversible rearrangements occur, leading to irreversible electrochemical reactions.[2] $LiCoO_2$ is easily prepared and gives a high voltage and a good reversibility in $Li/LiMO_2$ cells. Although the $LiCoO_2$ does not have a structural disorder, $LiCoO_2$ is expensive compare with others and has higher voltage (4 V) than $LiNiO_2$ (3.5-4.0 V) so that the electrolyte oxidation can be occurred.

These considerations have led to the electrochemical studies of $Li_xCo_yNi_{1-y}O_2$[20-24] series. In this study, $Li_xCo_yNi_{1-y}O_2$ (y=0.1, 0.3, 0.5, 1.0) system synthesized by citrate sol-gel method has been investigated. The structure and electrochemical properties of the $Li_xCo_yNi_{1-y}O_2$ have been evaluated and compared with those of $Li_xCo_yNi_{1-y}O_2$ prepared by solid state reaction.

Experimental

$Li_xCo_yNi_{1-y}O_2$ (y=0.1, 0.3, 0.5, 1.0) compounds were prepared by citrate sol-gel method ($Li_xCo_yNi_{1-y}O_2$(C)) and conventional solid state reaction ($Li_xCoyNi_{1-y}O_2$(S)). The $Li_xCo_yNi_{1-y}O_2$(C) (y=0.1, 0.3, 0.5, 1.0) were obtained by using citric acid ($C_6H_8O_7$) as follows; Li_2CO_3, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $C_6H_8O_7$ were dissolved with the mole ratio of 1 : y : (1-y) : 3 in distilled water. The solution was adjusted to pH=3-4 with aq. NH_4OH by considering solubility diagram. The solution was evaporated at 80 °C under vacuum and the subsequent organometallic complexes were decomposed into organic compounds and metal oxide precursor at 300 °C. The metal oxide precursor was pre-heated at 600 °C for 6 h and annealed at 850 °C for 20 h, in air to obtain $Li_xCo_yNi_{1-y}O_2$(C) compounds. The synthesis of $Li_xCo_yNi_{1-y}O_2$(S) (y=0.1, 0.3, 0.5, 1.0) with solid state reaction has already been reported.[24] It consists of heating a mixture of Li_2CO_3, $CoCO_3$ and NiO, in appropriate ratio, at 800-1000 °C for 48 h in air after preheating 650 °C for 10 h, in air.

Structural analysis has been performed by x-ray diffractometer (Rigaku RTP 300 RC) with Ni-filtered Cu-Kα radiation (λ=1.5418 Å). Scanning electron microscopy have been recorded by Hitachi S800 microscope in order to investigate the morphology of $Li_xCo_yNi_{1-y}O_2$.

The electrochemical cell was fabricated as follows. A cathode was made 89% (wt.%) $Li_xCo_yNi_{1-y}O_2$, 10% acetylene black, and 1% PTFE binder. The electrolyte used was 1 M $LiClO_4$-propylene carbonate (PC) solution. A lithium metal anode was used in this study. Test cell were assembled in a glove box filled with argon. The cells were cycled in the voltage range 3.0-4.1 V with various current densities using galvanostatic charge/discharge cycler.

Results and Discussion

The x-ray diffraction (XRD) patterns for $Li_xCo_yNi_{1-y}O_2$ obtained by citrate sol-gel method and conventional solid state reaction have been indexed with hexagonal symmetry. Lattice parameters of the $Li_xCo_yNi_{1-y}O_2$(C), which were obtained from least squares method, and c/a ratio are presented in Table 1. The a and c parameters, related to the intralayer metal-metal distance and interslab distance respectively, decrease with increasing cobalt concentration in $Li_xCo_yNi_{1-y}O_2$(C) due to the difference in size between the trivalent cobalt (r(Co^{3+})=0.53 Å, low spin ($t_{2g}^6e_g^0$)) and nickel (r(Ni^{3+})=0.56 Å, low spin ($t_{2g}^6e_g^1$)) ions. The c/a ratio, indicating the structure anisotropy of $Li_xCo_yNi_{1-y}O_2$(C), increases when Co^{3+} is substituted for nickel (c/a=$2\sqrt{6}$ for a cubic lattice). This variation indicates that the 2D character is increased with substituting cobalt for nickel ions. The results of structural analysis for $Li_xCo_yNi_{1-y}O_2$(S) are similar

Table 1. Structural parameters of $Li_xCo_yNi_{1-y}O_2(R\bar{3}\,m)$

y	a (Å)	c (Å)	c/a
0.1	2.877	14.17	4.925
0.3	2.860	14.15	4.948
0.5	2.844	14.11	4.961
0.7	2.833	14.10	4.977
0.9	2.821	14.07	4.987
1	2.814	14.04	4.989

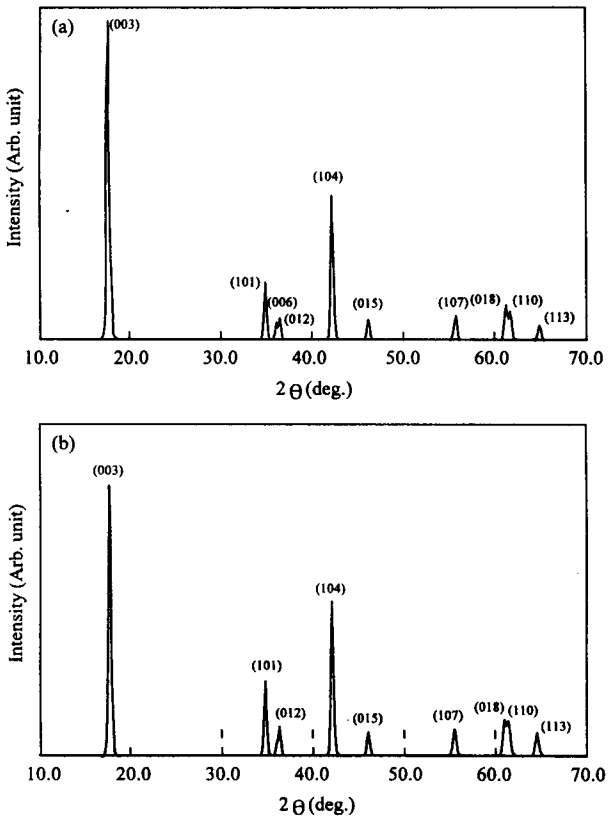

Figure 1. X-ray powder diffraction patterns for (a) $LiCo_{0.3}Ni_{0.7}O_2$(C) and (b) $LiCo_{0.3}Ni_{0.7}O_2$(S).

to those of $Li_xCo_yNi_{1-y}O_2$(C).

The XRD pattern for $Li_xCo_yNi_{1-y}O_2$(C) (y=0.3) shows good splitting of (006) and (012), and (018) and (110) lines (Figure 1(a)). However, $Li_xCo_yNi_{1-y}O_2$(S) (y=0.3) has no (012) line and the split of (108) and (110) lines can be slightly observed (Figure 1(b)). This indicates that the compounds prepared by using citric acid have better crystallinity than those by conventional method. The results of XRD analysis for $Li_xCo_yNi_{1-y}O_2$ (y=0.3) are given in Table 2. As shown in Table 2, the relative intensity of (003) with citrate method was higher than that with solid state one. In the $LiMO_2$ (M=V, Cr, Co, Fe, Ni) phase, alternate layers of Li and M cations occupy the octahedral site of a compact cubic close packing of oxide anions as previously mentioned.[25] When M atoms occupy parts of the octahedral sites of the Li layer, the (003) line intensity decreases. Thus, the strong intensity of (003) line for $Li_xCo_yNi_{1-y}O_2$ indicates that the $Li_xCo_yNi_{1-y}O_2$ have strongly enhanced 2D character. The scanning electron microscopy of $LiCoO_2$(C) exhibits that the compound with citrate method has a well developed layered structure and its particle size is less than 5 μm (Figure 2). The particle size of $LiCoO_2$(C) is smaller than that of $LiCoO_2$(S) ($\leq$10 μm).

The charge/discharge behavior in the first cycle for Li/$Li_xCo_yNi_{1-y}O_2$ cell using the $Li_xCo_yNi_{1-y}O_2$ obtained from citrate organometallic complex and solid state reaction was examined under constant current density (200 μA/cm^2). Figure 3. shows the first cycle of voltage *vs.* *x*. The differences of intercalation rate(x) between charge and discharge for $Li_xCo_yNi_{1-y}O_2$(C) and $Li_xCo_yNi_{1-y}O_2$(S) are ~0.05 e^- and ~0.09 e^-, respectively. This implies that the $Li_xCo_yNi_{1-y}O_2$(C) has smaller irreversible loss and better reversibility of electrochemical reaction compared with $Li_xCo_yNi_{1-y}O_2$(S). The first discharge capacities of Li_xCoO_2 and $Li_xCo_{0.3}Ni_{0.7}O_2$ by citrate method are ~130 mAh/g and ~160 mAh/g, respectively. These values are higher than those by solid state reaction (~120 mAh/g and ~140 mAh/g, respectively). The charge/discharge behavior of $Li_xCo_yNi_{1-y}O_2$(C) shows that the best cycling properties were observed in the Li/$Li_xCo_{0.3}Ni_{0.7}O_2$(C) cell. This behavior means that any structural disorder due to the displacement of nickel (and/or cobalt) and lithium ions in the $Li_xCo_{0.3}Ni_{0.7}O_2$(C) is not appeared.

In order to examine the current dependency of Li/$Li_xCo_{0.3}Ni_{0.7}O_2$(C) cell, the cell has been cycled at various current densities (Figure 4). As the current density increases from 200 μA/cm^2 to 500 μA/cm^2, the changes of capacity and cell polarization were small. The reversibility has been hardly affected even under a high current density. These phenomena proved that the compound obtained by citrate sol-gel method is structurally stable during the electrochemical reaction.

Figure 5 shows the charge and discharge curves of the Li/Li_xCoO_2(C) cell at a current density of 200 μA/cm^2. The current was automatically switched on for 6 h and off for 20 h. The difference of open circuit voltage between decreasing and increasing *x* in the Li_xCoO_2(C), related to cell polarization, is very small. This indicates that the lithium diffusion in the interslab of the Li_xCoO_2(C) is readily occurred due to the small particle size of the compound.

The XRD analysis for the $Li_xCo_{0.3}Ni_{0.7}O_2$(C) with various Li concentration (x=0.6, 0.7, 0.8, 0.9, 1.0) was carried out to investigate the structural change during the electrochemical oxidation (Table 3, Figure 6). The XRD patterns show that crystallinity of $Li_xCo_{0.3}Ni_{0.7}O_2$(C) is well maintained during the electrochemical deintercalation. This implies that 2D structure of the $Li_xCo_yNi_{1-y}O_2$(C) is preserved during the elimination of Li atoms. The decrease in the a

Table 2. Structural analysis of $Li_xCo_yNi_{1-y}O_2$ (y=0.3) (a=2.860 Å, c=14.15 Å in hexagonal cell)

(hkl)	$d^*_{obs.}$	$d_{obs.}$	$d_{cal.}$	$I^*_{obs.}$	$I_{obs.}$	$I_{cal.}$
(003)	4.726	4.726	4.718	100	100	100
(101)	2.441	2.441	2.439	15	28	39
(006)	2.356		2.359	5	0	4
(012)	2.337	2.339	2.337	6	11	12
(104)	2.029	2.030	2.029	37	57	79
(105)	1.865	1.864	1.864	6	9	12
(107)	1.566	1.567	1.566	7	10	14
(018)	1.439	1.439	1.439	10	13	19
(110)	1.430	1.430	1.430	8	13	20
(113)	1.368	1.368	1.368	4	8	13

$d^*_{obs.}$, $I^*_{obs.}$: citrate sol-gel method, $d_{obs.}$, $I_{obs.}$: solid state reaction

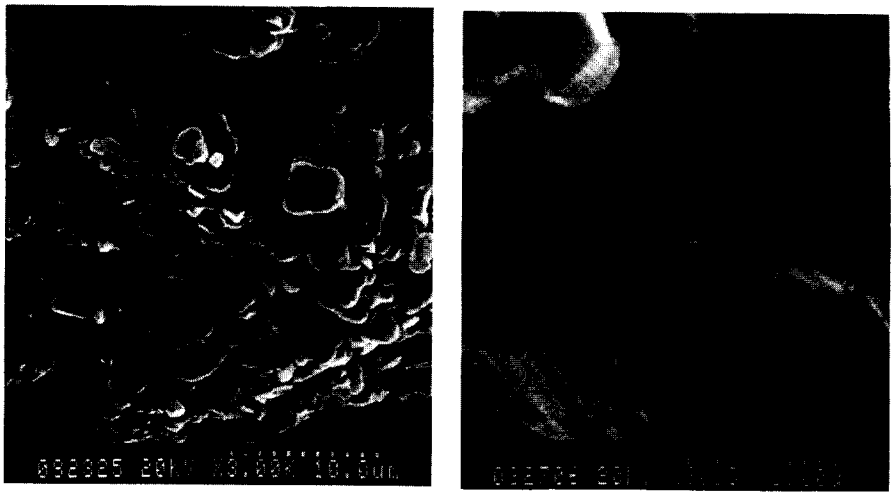

Figure 2. Scanning electron microscopy of $LiCoO_2$(C).

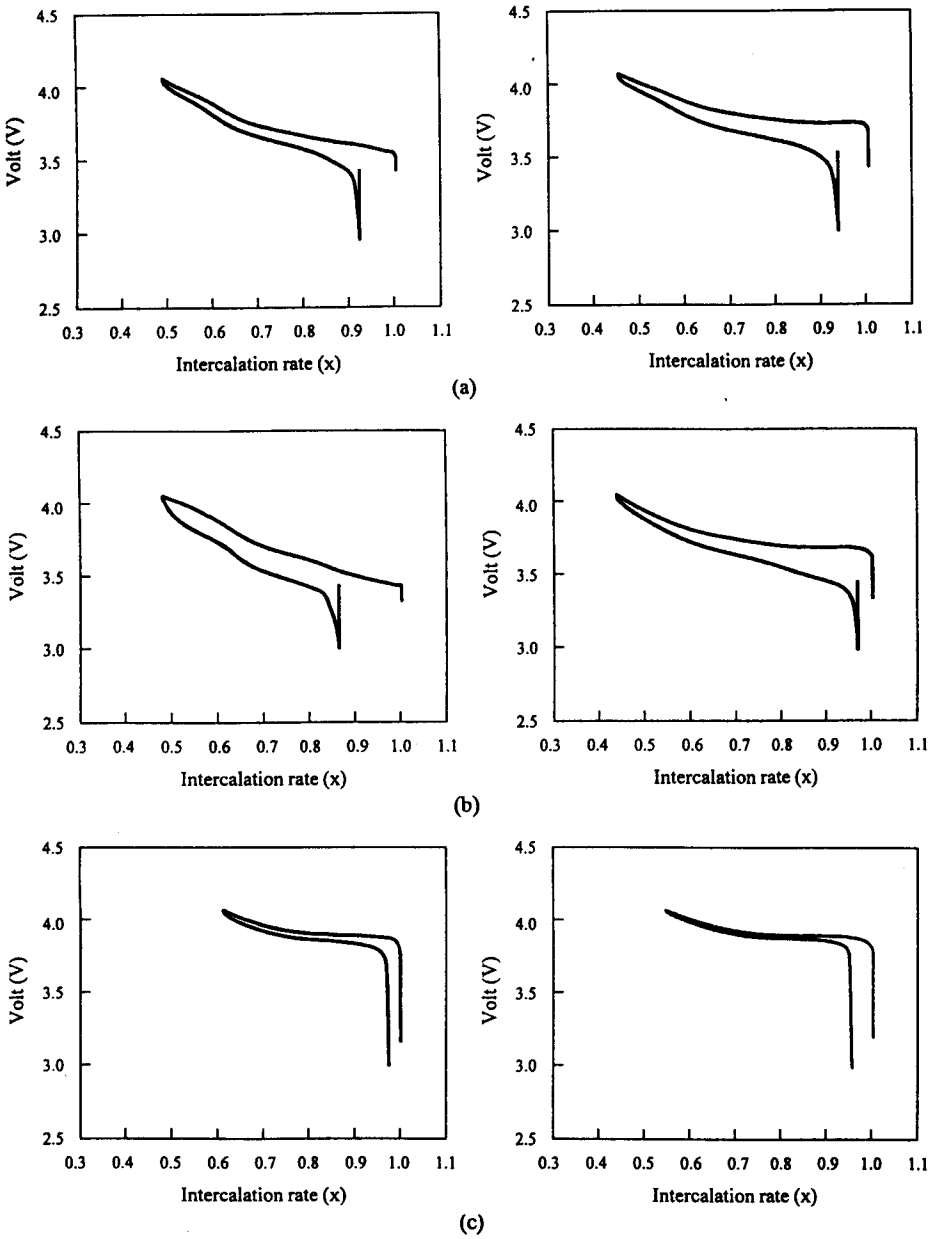

Figure 3. First charge and discharge curves of $Li/Li_xCo_yNi_{1-y}O_2$(C) and $Li/Li_xCo_yNi_{1-y}O_2$(S) with (a) y=0.1, (b) 0.3, and (c) 1.0, respectively at constant current density (200 μA/cm^2).

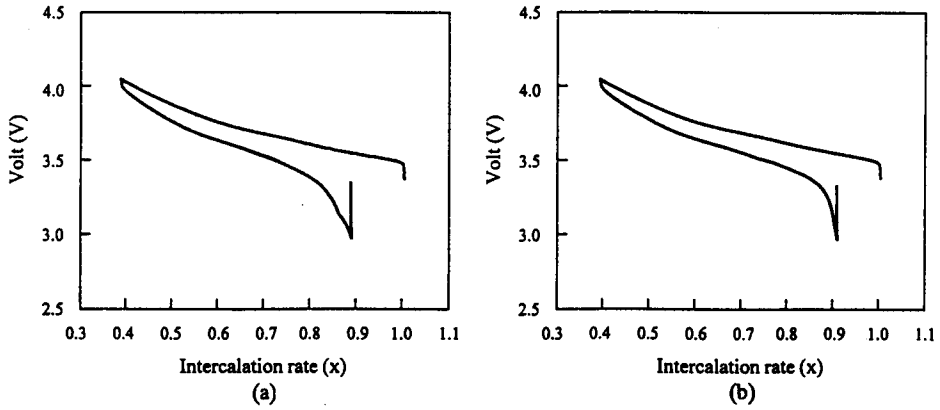

Figure 4. The current dependency of $Li/Li_xCo_{0.3}Ni_{0.7}O_2$(C) cell. (a) 300 μA/cm^2. (b) 500 μA/cm^2.

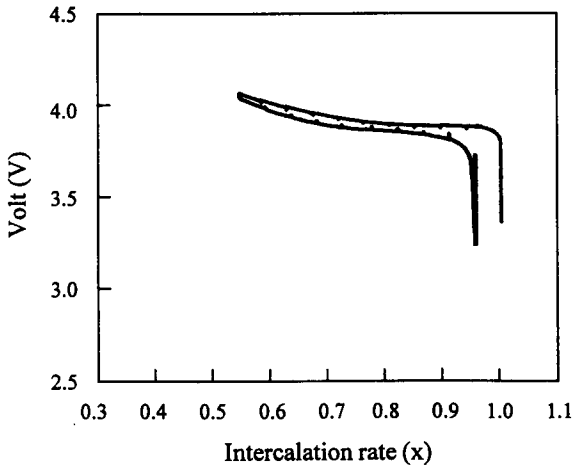

Figure 5. Charge and discharge curves of $Li/Li_xCoO_2(C)$ cell with relaxation (current density=200 $\mu A/cm^2$).

Table 3. Variation of structural parameters for $Li_xCo_yNi_{1-y}O_2$ (y= 0.3) with various Li concentration (x=0.6, 0.7, 0.8, 0.9, 1.0)

x	a	c	c/a
1.0	2.860	14.15	4.948
0.9	2.855	14.18	4.967
0.8	2.847	14.22	4.994
0.7	2.836	14.28	5.035
0.6	2.827	14.32	5.065

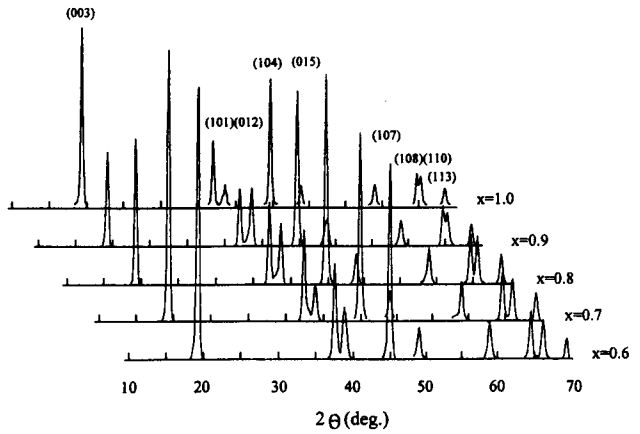

Figure 6. X-ray powder diffraction patterns for $Li_xCo_{0.3}Ni_{0.7}O_2(C)$ with various Li concentration (x=0.6, 0.7, 0.8, 0.9, 1.0).

parameter with decreasing Li^+ ion concentration (x) of $Li_xCo_yNi_{1-y}O_2(C)$ reflects the decrease in Li^+-Li^+ electrostatic repulsion within a basal plane. The c-axis of the $Li_xCo_yNi_{1-y}O_2(C)$ expands rapidly upon delithiation due to the decrease of electrostatic binding energy of the lithium-depleted layers.

Conclusion

$Li_xCo_yNi_{1-y}O_2$ compounds were successfully prepared by citrate sol-gel method. The obtained $Li_xCo_yNi_{1-y}O_2$ exhibit well developed layered structure and were structurally stable during the electrochemical reaction. The $Li_xCo_yNi_{1-y}O_2$ are smaller irreversible loss and better reversibility of electrochemical reaction compared with $Li_xCo_yNi_{1-y}O_2$ prepared by solid state reaction. The first discharge capacities of the $Li_xCo_yNi_{1-y}O_2$ are higher and the changes of capacity and cell polarization are smaller than those by solid state reaction.

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