$Li_{1+x}CoO_2$ 의 합성조건과 특성에 관한 연구

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Synthesis and characterization of $Li_{1+x}CoO_2$

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Introduction

The layered oxides, $LiMO_2$(M=Co, Ni, Mn, V), have been extensively studied as potential cathode materials of a lithium ion secondary battery with high energy density. Much attention has recently focused on $LiCoO_2$ as the most promising alternative cathode material for the molten carbonate fuel cell. From the hydroxides LiOH and $Co(OH)_2$ as starting material, the precursor of $LiCoO_2$ powders were synthesized at various temperatures by precipitation process and freeze-drying. In this study, the $LiCoO_2$ samples were calcined at 800℃ in a short time(2 hours). Measurements of XRD and SEM were performed to characterize the properties of the prepared materials. The effects of LiOH concentration on the structural change in powder were investigated using the XRD analysis. The morphology and particle size of the powders were examined using SEM. It was found that the obtained powders have large specific surface area and are high temperature-$LiCoO_2$(HT-$LiCoO_2$) and homogeneous with the range of grain size in the order of hundreds of nanometers. Finally, The structure of HT-$LiCoO_2$ was simulated by the commercial software Creius^2(Molecular Simulations, Inc.) from the results of Rietveld analysis.

Experiment and simulation

$LiCoO_2$ precursor was synthesized by sintering (800℃, 2 hours) from starting material consisting of LiOH(Lithium hydroxide) and $Co(OH)_2$(Cobalt hydroxide) powders. The $LiOH \cdot H_2O$(Lithium hydroxide monohydrate, Sigma, 99%) particles were dehydrated by a freeze dryer to get fine LiOH(Lithium hydroxide) particle and the dried particles were grinding by a mortar. We freeze-dried a suspension of $Co(OH)_2$ in aqueous lithium hydroxide solution. A suspension was necessary because all well-known Li salts are soluble in water and can not be precipitated in the same pH range at which $Co(OH)_2$ is insoluble. $Co(OH)_2$ was precipitated by adding a 0.1M solution of $Co(NO_3)_2 \cdot 6H_2O$(Aldrich, 98%) in deionized water to a stirred aqueous solution of $LiOH \cdot H_2O$(Sigma, 99%) in deionized water, continuously monitored and titrated by a solution of $LiOH \cdot H_2O$ to maintain the pH at 11, near the minimum solubility point $Co(OH)_2$. After precipitation the suspension was left at room temperature without stirring for several hours and then settled by centrifugation. A critical step was the removal of nitrate ions from the suspension by a rinsing procedure, which otherwise reform low-melting nitrate compounds upon drying. On subsequent calcining, melting of these salts can cause compositional segregation. The supernatant liquid from the precipitation was first decanted, and the $Co(OH)_2$ ultrasonically dispersed in a buffer solution of $LiOH \cdot H_2O$ in water at pH 11. The precipitate was settled by centrifugation and the supernatant again decanted. For complete rinsing, this cycle of dispersion in buffer solution, settling by centrifugation, and decanting was conducted a total of four times. Finally, to obtain a highly homogeneous $Co(OH)_2$ powders, the rinsed precipitate was freeze-dried by a freeze dryer(EYELA, FD-81). And then, After LiOH powders were completely dissolved in methyl alcohol(assay above 99.5%), $Co(OH)_2$ powders were dispersed in LiOH alcoholic solution. The amount of LiOH and $Co(OH)_2$ was determined by the ratio Li:Co. To obtain a highly homogeneous physical mixture of LiOH and $Co(OH)_2$, then, suspension was dried on hot plate with stirring at 70℃. $LiCoO_2$ was synthesized by calcining the mixture of precursors at 800℃ and for 2 hours.

Results and discussion

Powder X-ray diffraction(XRD, Rigaku, D/MAX-A) using CuKα radiation was used to identify the crystalline phase of the material calcined at various conditions such as described above. Particle morphology of the material were examined by scanning electron microscopy(SEM, Hitachi, S-3500N). Rietveld analysis was then performed on the X-ray diffraction data (from 15° to 140°, 3126 data numbers) to obtain the lattice constants. The structure was investigated by X-ray diffraction data using the RIETAN program. The structure of HT-$LiCoO_2$ was simulated by the commercial software Cerius^2. In the ground equilibrium state, Li-O bonds distance, Co-O bonds distance, O-Co-O bonds angle in the octahedral layer and O^{2-}- O^{2-} distances in the interstitial tetrahedral site in $Li_{1+x}CoO_2$ were investigated using Cerius^2 program package. It have found that these distances and angles which were investigated by Cerius^2 program package had a tendency. XRD patterns of series of the synthesized products, $Li_{1+x}CoO_2$, are shown in Fig. 1. shows the XRD patterns for $Li_{1+x}CoO_2$ calcined at 800℃ for 2 hours with various molar ratio of lithium ions to cobalt ions (x= 0.10, 0.15, 0.18, 0.20, 0.30). In spite of increasing molar ratio of lithium ions to cobalt ions, the crystallinity of materials is not largely changed. The value x in the figure shows nominal(before sintering) ratio. Scanning Electron Microscope(SEM) images(Fig. 2) demonstrate a dramatic variation of grain size. The particle size of powders increases gradually from 0.375㎛ to 2.5㎛.

A comparison was made between $LiCoO_2$ powders prepared by different conditions to know which would be more effective structure. The results in this investigations are summarized in table 1, 2. N. Imanishi et. al. [2] explains the refined lattice parameters decrease monotonously with Li/Co ratio and then the parameter stops decreasing around Li/Co =1.15 [3]. the presence of a discontinuity at Li/Co = 1.15 (nominal ratio) is consistent with the fact that at this composition the lattice constant stops decreasing, and the lattice parameter changes of the oxygen-treated samples. But, S. Levasseur et al. [4] explained the lattice parameters are very similar to each other, so that no correlation with the Li/Co ratio can be established. Our lattice parameters are shown in Table. 1. They are in good agreement with the literature [4]. It is reliable c/a to be almost close to the 4.99.

As shown in Table. 2, The amount of excess can be determined by these tendencies. In these tendencies, these ideal Co-O interlayer distance, Li-O interlayer distance and O-Co-O angles (Table. 2) [3] are nearly similar to over 20% excess (x=0.2) in $Li_{1+x}CoO_2$. In Co-O distance (Table. 2), the length of nominal 10%, 15%, 18% Li excess is smaller than the nominal 20%, 25%, 30% Li excess. It is explained that as the concentration of Li^+ ions is increasing, the electrostatic interactions between tetrahedral lithium ions and neighbouring octahedral cobalt ions would be rather strong('LiO_4' tetrahedra share one face with 'CoO_6'octahedra)[4]. So Li-O distance of second group is smaller than that of first group, Co-O distance of first group is smaller than that of second group. In fact, the O^{2-}-O^{2-} intralayer distance is nearly maintained 2.810Å~2.817Å, and the ideal O^{2-}-O^{2-} interlayer distance is also similar to the over 20% excess (x=0.2) in $Li_{1+x}CoO_2$. However the size of a over 20% excess(x=0.2) is too large in Fig 2. Because the primary particles are connected each other by the excess of LiOH which melted at about 450℃, and then the agglomerated subgrains form large $LiCoO_2$ during calcinations.

Therefore, a modified solid state reaction suggested in this study will be able to consider as a valuable process for manufacturing the $LiCoO_2$ with excellant electrochemical properties.

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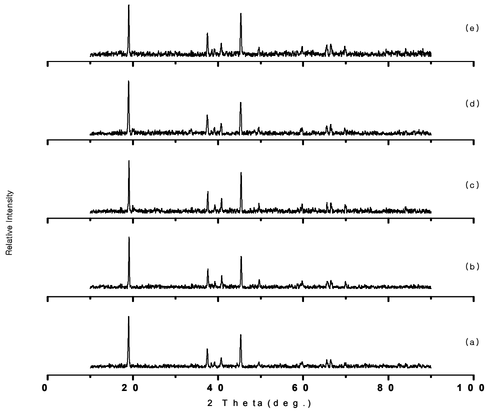
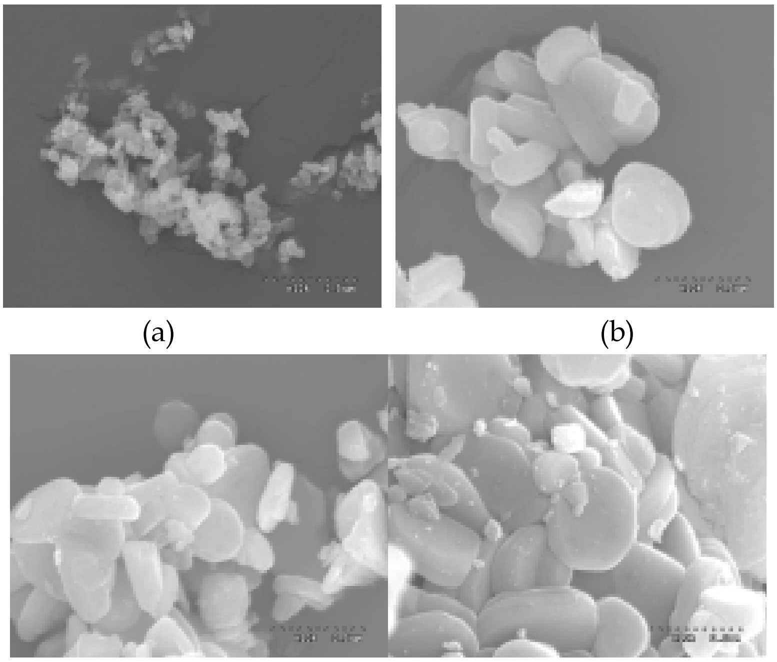


Fig. 1. X-ray diffraction patterns of $Li_{1+x}CoO_2$ powders calcined at 800℃ for 2 hours.

(a) x=0.10

(b) x=0.15 (c) x=0.18

(d) x=0.20 (e) x=0.25



(a) (b)

(c) (d)

Fig. 2. Scanning Electron Microscope of $Li_{1+x}CoO_2$ powders calcined at 800℃ for 2 hours. (a) x=0.10 (b) x=0.18 (c) x=0.20 (f) x=0.25

Excess x		a	b	c	c/a	alpha	beta	gamma
Nominal	ICP-AES							
0.10	0.01	2.81355	2.81355	14.04017	4.9902	90	90	120
0.15	0.03	2.81011	2.81011	14.03424	4.9942			
0.18	0.06	2.81273	2.81273	14.03663	4.9904			
0.20	0.10	2.81641	2.81641	14.05980	4.9921			
0.25	0.12	2.81377	2.81377	14.04503	4.9915			

Table. 1. Lattice parameter is refined by Rietveld analysis / ICP-AES result

Excess x (nominal)	Co-O	Li-O	O-Co-O	Tetrahedral	
				up	down
ideal	1.947	2.064	92.7 or 87.3	2.817	3.019
0.10	1.913	2.099	94.7	2.814	3.114
0.15	1.918	2.089	94.2	2.810	3.093
0.18	1.925	2.083	93.8	2.813	3.074
0.20	1.948	2.064	92.6	2.816	3.018
0.25	1.946	2.062	92.6	2.814	3.015

Table. 2. Several distances and angles is refined by Cerius^2 molecular simulator