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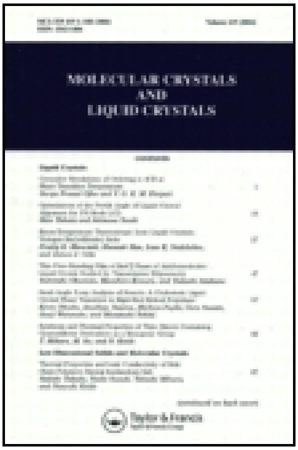

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A Novel Synthetic Route of A_xCoO_2 (A = Li or Na) Through the Ion-Exchange Reaction of CoOOH by the Hydrothermal Method

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A Novel Synthetic Route of A_xCoO_2 (A = Li or Na) Through the Ion-Exchange Reaction of CoOOH by the Hydrothermal Method

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(In final form August 5, 1999)

$LiCoO_2$ and Na_xCoO_2 were synthesized through the ion-exchange reaction of CoOOH using the hydrothermal method. The $LiCoO_2$ single phase was obtained at 170°C for 12h in LiOH solutions (≥ 0.1mol/*l*). The precipitated $LiCoO_2$ had trigonal symmetry ($R\bar{3}m$) corresponding to the high temperature phase of $LiCoO_2$. The precipitate had a hexagonal plate-like shape and the size was between 100nm and 1.5μm Synthesis of Na_xCoO_2 single phase using the hydrothermal method was rather difficult, and Na_xCoO_2 was usually accompanied with secondary phase of Co_3O_4.

Keywords: hydrothermal method; $LiCoO_2$; $NaCoO_2$; intercalation; TEM

Introduction

Recently much attention has been paid to the layered compounds from various points of view. In particular, $LiCoO_2$ is expected as the excellent cathode material for the lithium ion secondary batteries[1]-[3]. Na_xCoO_2, while, is studied as one of the candidates for the oxide thermoelectric converter[4].

These compounds are conventionally synthesized using the calcination method[1], [5]. However, this synthesis method requires high reaction temperature. Moreover, it has difficulties to obtain homogeneous composition and desirable morphology of a material, which are strongly related to material properties. It is, therefore, worthwhile to develop a novel synthetic route which can be carried out at lower temperature and will extract preferable properties for above technical applications. From these standpoints of view, we here attempted to establish a novel preparation method of $LiCoO_2$ and Na_xCoO_2 through the ion-exchange reaction of CoOOH using the hydrothermal method.

Experimental

Both teflon-coated autoclave and high-pressure test tube were used as reactors. The starting material of CoOOH particles, which was directly synthesized at room temperature through the oxidation of $Co(OH)_2$, was dipped into a LiOH or NaOH aqueous solution of pre-determined concentration stored in a reactor. Then the reactor was heated and kept at the desired temperature and reaction time. The reaction temperature was from room temperature up to 600°C. The reaction time was from 12h to 96h. The resultant precipitates were filtered from the alkaline solution and characterized using XRD, SEM and TEM. The chemical compositions of the precipitates were determined using atomic absorption spectrometry.

Results and Discussion

$LiCoO_2$

The $LiCoO_2$ single phase was obtained under the following conditions. The concentration of LiOH aqueous solution was between 0.1mol/*l* and saturated. The reaction temperature was above 170°C. The reaction time was required longer than 12h at 170°C. In Fig.1 (a) and (b), the XRD patterns of CoOOH (starting material) and $LiCoO_2$ precipitated at 170°C for 48h in 0.1mol/*l* LiOH solution are given, respectively. The diffraction peaks of the precipitated $LiCoO_2$ were indexed with a trigonal cell ($R\bar{3}m$), which corresponded to the high temperature phase of $LiCoO_2$.

Figure 2 (a) and (b) present the SEM photographs of the starting material of CoOOH and the precipitated $LiCoO_2$ shown in Fig.1 (b). The CoOOH and $LiCoO_2$ particles had a hexagonal plate-like shape. The average sizes of the particles were ~100nm and a little bigger than ~100nm, respectively. The SEM photograph of the $LiCoO_2$ particles after the hydrothermal re-treatment at 600°C for 96h is shown in Fig.2 (c). The particle size grew up to around 1.5μm. Li concentration of $LiCoO_2$ did not change before and after the hydrothermal re-treatment.

The electron diffraction patterns of the $LiCoO_2$ particle is given in Fig.3. The Laue pattern shows a particle is a single crystal, and the hexagonal surface perpendicular to the incident beam coincides with the crystallographic c-plane. The space group of $LiCoO_2$ determined from the

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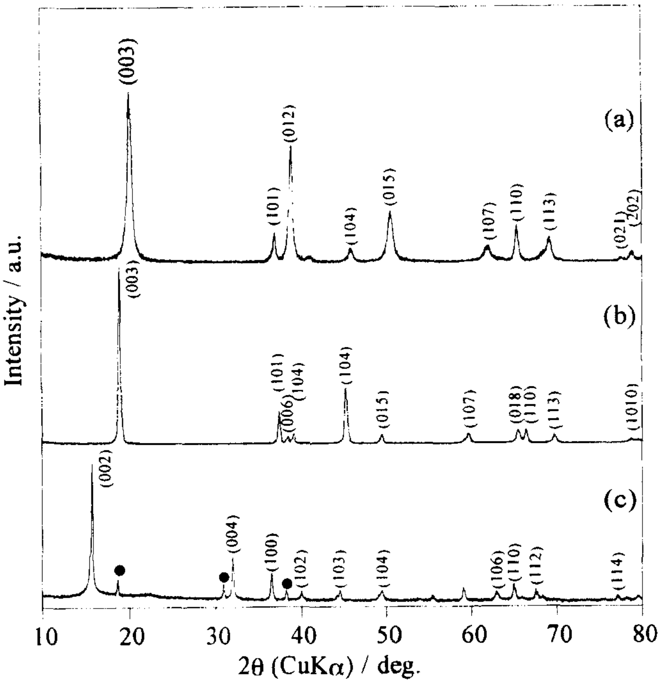

Fig.1 XRD patterns of (a) CoOOH (starting material), (b) $LiCoO_2$ precipitated at 170°C for 48h in 0.1mol/*l* LiOH solution and (c) Na_xCoO_2 precipitated at 250°C for 48h in 8.0mol/*l* NaOH solution. Co_3O_4 is denoted as the solid dots.

Laue spot affirms that the particle has the same crystallographic structure as that of the high temperature phase of $LiCoO_2$.

Na_xCoO_2

The formation of Na_xCoO_2 single phase using the hydrothermal method is rather difficult comparing to that of $LiCoO_2$. The XRD pattern of Na_xCoO_2 precipitated at 250°C for 48h in 8.0mol/*l* NaOH solution is shown in Fig.1 (c). In our experiments, Na_xCoO_2 always accompanied with secondary phase of Co_3O_4. It may suggest that the two different kinds of reactions, one is the ion-exchange of Na ion into CoOOH host lattice and the other is the decomposition of CoOOH, compete with each other. Comparing the ion-exchange reactions of Li and Na as guest ions, the difference of the ion radius

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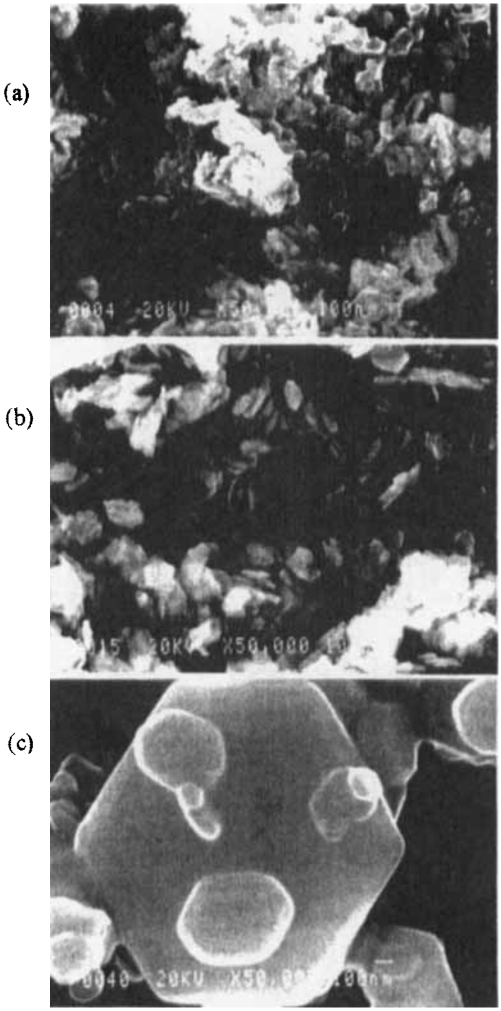

Fig.2 SEM photographs of (a) CoOOH particles and (b) $LiCoO_2$ particles by the hydrothermal method at 170°C for 48h and (c) as-precipitated $LiCoO_2$ particles after the hydrothermal re-treatment at 600°C for 96h.

of Li and Na may determine feasibility of the guest ion diffusion in the host lattice of CoOOH. Co-existence of oxidation reagent, which suppresses the reduction of Co^{3+} to Co^{2+} ion and thus prevents the secondary reaction of Co_3O_4 formation, may enable to obtain the Na_xCoO_2 single phase from CoOOH through ion exchange reaction.

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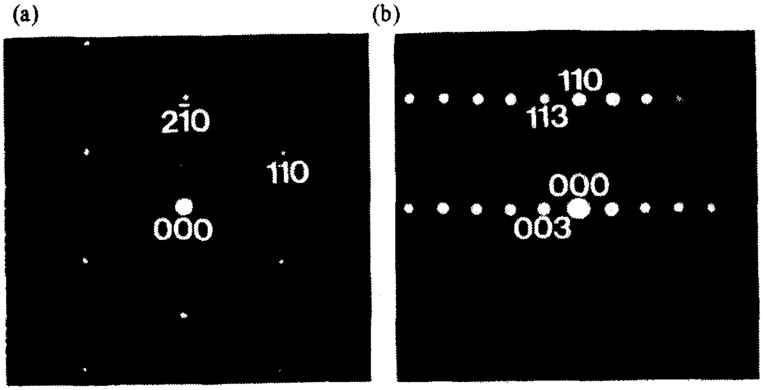

Fig.3 Electron diffraction patterns along (a) <001> direction and (b) that of <100> direction in $LiCoO_2$ prepared using the hydrothermal method.

The stability conditions of Na_xCoO_2 was examined by using calcined Na_xCoO_2 (x=0.75)[5] as starting material, instead of CoOOH. In higher concentration of NaOH aqueous solution than 8.0mol/*l*, Na_xCoO_2 was stable regardless of the reaction temperature used. However, Na concentration of Na_xCoO_2 after the hydrothermal treatment was less than that of Na_xCoO_2 starting material. This indicates Na ions deintercaleted from the host lattice of Na_xCoO_2.

The SEM photograph and the electron diffraction patterns of the Na_xCoO_2 particle after the hydrothermal treatment at 250°C for 48h in 8.0mol/*l* NaOH aqueous solution are given in Fig.4. These figures affirm that Na_xCoO_2 phase can exist as a stable phase under this hydrothermal condition. The Laue pattern shows a particle is a single crystal, and the hexagonal surface perpendicular to the incident beam coincides with the crystallographic c-plane.

Conclusion

The $LiCoO_2$ single phase was synthesized using the hydrothermal method. The precipitated $LiCoO_2$ had the same crystallographic structure as that of the high temperature phase of $LiCoO_2$.

The formation of Na_xCoO_2 single phase was rather difficult than $LiCoO_2$, and Na_xCoO_2 was accompanied with secondary phase of Co_3O_4.

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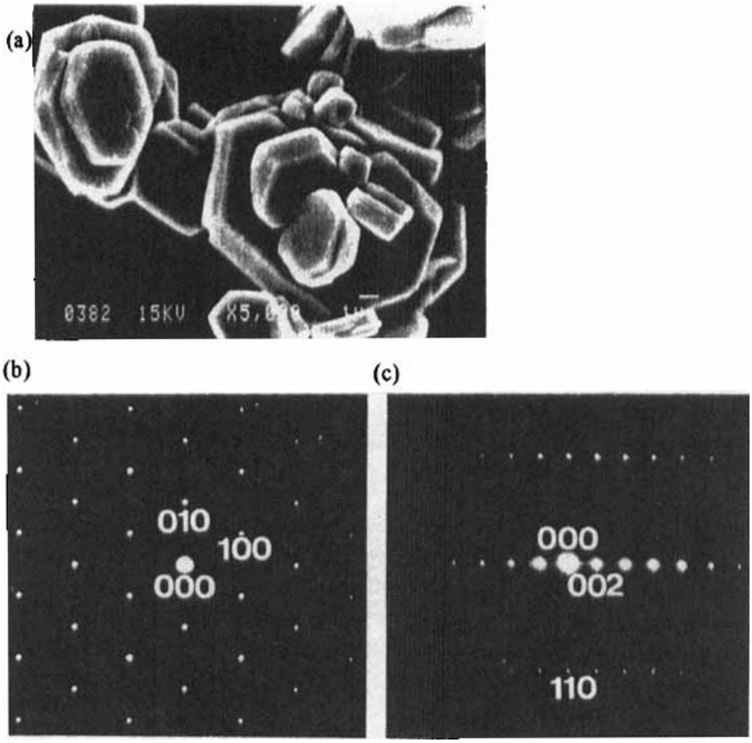

Fig.4 (a) SEM photograph of the Na_xCoO_2 precipitated particles after the hydrothermal treatment of calcined Na_xCoO_2, (b) electron diffraction pattern along <001> direction and (c) that of <100> direction.

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