Preparation of Nanoparticles of $LiCoO_2$ Using Laser Ablation in Liquids

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In order to prepare nanoparticles of $LiCoO_2$, laser ablation of $LiCoO_2$ in liquids (water, methanol, and cyclohexane) was carried out at 355 nm. Spherical particles of 10–200 nm in diameters were prepared, while Co_3O_4 were also produced due to liberation of Li. It was found that liberation of Li decreased in methanol and cyclohexane as compared to that in water.

$LiCoO_2$ is an important material for lithium secondary batteries. In order to increase capacity of a $LiCoO_2$ electrode, it is necessary to reduce particle size because the surface/volume ratio increases.[1] So far, nanoparticles of $LiCoO_2$ have been synthesized by using chemical methods such as the hydrothermal method.[2,3] Recently, laser ablation in liquids receives much attention as a new technique to prepare nanoparticles.[4–10] An advantage of the laser ablation method over conventional chemical synthesis methods is simplicity of procedure. Thus, in principle, this method can be applicable to various species of materials, although most of previous works of laser ablation in liquids have focused on simple metals.

Recently, Sugiyama et al. prepared nanoparticles of TiO_2 by using laser ablation in water.[11] Ankin et al. prepared nanoparticles of ZnSe and CdS by using laser ablation in various solvents (isobutanol, diethyleneglycole, ethanol, water, and dimethylsulphoxide).[12] These studies demonstrated that laser ablation in liquids is applicable on compound materials. Thus, in this study we have carried out laser ablation of $LiCoO_2$ in liquids to prepare its nanoparticles. On the other hand, as shown by laser ablation studies in the gas phase,[13] changes in compositions of products, such as atomic composition and crystalline structure, from those of their source materials are an essential issue of laser ablation of compound materials. It has been revealed that composition changes also occur in laser ablation in liquids.[14–16] Thus, proper conditions of laser ablation for $LiCoO_2$ must be investigated to obtain its stoichiometric nanoparticles.

The laser ablation of $LiCoO_2$ was carried out by ablating 20 mg of $LiCoO_2$ powder (average diameter: 3 µm) suspended in 5 mL of water, methanol, or cyclohexane with the third harmonic output (355 nm) of a Nd:YAG laser (Spectra Physics GCR-200). The pulse width and the repetition rate of the laser were 6 ns and 10 Hz, respectively. Laser light was focused in the suspension. Ablation was carried out at 30 mJ/pulse for 60 min. Ablated suspensions were analyzed by means of a transmission electron microscope (TEM) (JEM-2000FX) operated at 200 kV, a Raman spectrometer (JASCO NRS-2100), and an atomic absorption spectrometer (Hitach Z-5310). An X-ray diffraction (XRD) spectrometer (Rigaku RINT2100HLR) was used analyze composition of source $LiCoO_2$ powder and Co_3O_4 powder.

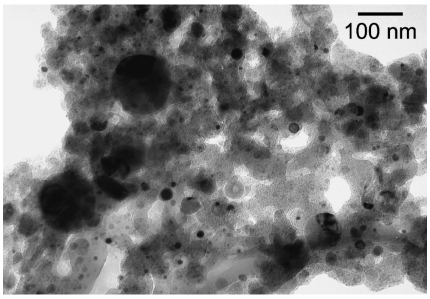

Figure 1. TEM image of nanoparticles produced by using laser ablation of $LiCoO_2$ in water. (×100000)

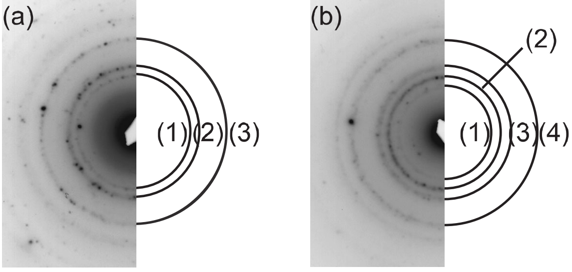

Figure 2. ED patterns of (a) discrete spherical particles and (b) cloudy background observed in Figure 1. *d*-Spacings of prominent rings (numbered) are shown in Table 1.

Table 1. *d*-Spacings (units of Å) of prominent ED rings shown in Figure 2

(a)	$LiCoO_2$[a]	(b)	Co_3O_4[a]
		(1) 2.87	2.86
(1) 2.39	2.40	(2) 2.39	2.44
(2) 2.01	2.00	(3) 2.01	2.02
(3) 1.43	1.42	(4) 1.43	1.43

[a]Estimated from XRD spectra.

First, we have carried out laser ablation in water. After laser ablation, particles larger than 1 µm precipitated and nano-sized particles were dispersed in the supernatant. In this study, we concentrate our attention on the nano-sized particles. The formation efficiency of nanoparticles was about 5 wt % of source powder. Figure 1 shows a typical TEM image of nanoparticles produced in water. Two distinct components were observed. One is spherical particles of 10–200 nm with discrete morphology, and the other is cloudy background which is composed of non-spherical particles of <10 nm. Figures 2(a) and 2(b) show selected area electron diffraction (SAED) patterns of an area in which the spherical particles are mainly contained, and an area in which only the cloudy background is contained, respectively. *d*-Spacings of prominent rings are summarized in Table 1 along with those of the source $LiCoO_2$ powder and Co_3O_4 powder obtained by using XRD spectrometry. It is clear that positions and relative intensities of the prominent rings in the SAED patterns of these components are different from each other. The SAED pattern of the spherical particles is very similar to that of $LiCoO_2$, while the SAED pattern of the cloudy background is very similar to that of Co_3O_4.

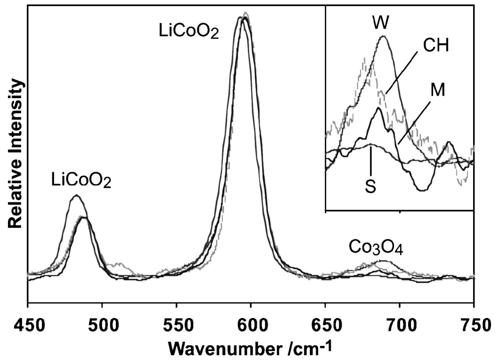

Figure 3. Raman spectra of source $LiCoO_2$ powder and nanoparticles prepared by using laser ablation of various liquids. Inset shows extended view of the Co_3O_4 band. S: source $LiCoO_2$ powder, nanoparticles produced in W: water, M: methanol, and CH: cyclohexane.

Above experimental results shows that laser ablation of $LiCoO_2$ in water produces nanoparticles of both $LiCoO_2$ and Co_3O_4. Morphologies of nanoparticles of $LiCoO_2$ and Co_3O_4 are different from each other. Thus, it is suggested that these nanoparticles are produced by different mechanisms. Upon laser ablation, two types of ablated matters are ejected from source $LiCoO_2$. One is plasma gas containing decomposed species of $LiCoO_2$ and H_2O, and the other is liquid droplets of $LiCoO_2$.[10] In the plasma ejection process, it is reported that light elements such as Li and O atoms are likely to be lost because they are difficult to be deposited to recompose source materials.[1] In the liquid system, reaction between decomposed species and solvent in plasma must be also important. Free Li can react with H_2O to form LiOH due to their high reactivity. Free Co must be oxidized by H_2O to form Co_3O_4 due to high temperature of plasma.[16] Thus, in the plasma ejection process in water, recomposition of $LiCoO_2$ must be difficult, while Co_3O_4 particles must be produced. Non-discrete morphology of Co_3O_4 particles must be due to such a gaseous phase reaction. On the other hand, in the droplets-ejection process, such reactions must be suppressed because free elements are not formed. Thus, $LiCoO_2$ nanoparticles must be produced from droplets. The discrete morphology of $LiCoO_2$ particles is consistent with such formation mechanism. It must be noted that, however, Li will be released from surface of nanoparticles and source powder of $LiCoO_2$ due to continuous irradiation of laser light and such a release must increase with decrease in particle size because of increase in the surface area. An atomic absorption spectrometry showed that amount of total liberated Li was estimated to be about 3% of Li contained in source $LiCoO_2$ powder.

It is necessary to prevent Li from liberating to solvent in order to obtain more purified $LiCoO_2$ nanoparticles. Thus, we have carried out laser ablation in organic solvents such as methanol and cyclohexane, whose reactivity with Li is lower than that of water. Upon laser ablation, colloidal particles similar to those obtained in water were produced in both solvents. Both distinct spherical particles of 10–200 nm, and the cloudy background were observed. In order to compare amount of Co_3O_4 produced in different solvents, Raman spectra of the nanoparticles were measured (Figure 3). The Raman bands at 485 and 595 cm^{-1} was due to $LiCoO_2$, while the band at 695 cm^{-1} was due to Co_3O_4.[17] The relative intensity of the 695 cm^{-1} band indicated that lesser amounts of Co_3O_4 nanoparticles are produced in methanol and cyclohexane than that in water. Further investigation of liberation mechanism is necessary to make complete suppression of liberation.

In summary, laser ablation of $LiCoO_2$ was carried out in liquids to prepare its nanoparticles. It was found that spherical particles of $LiCoO_2$ with 10–200 nm in diameters were prepared, while smaller particles of Co_3O_4 were also produced. The formation of Co_3O_4 decreased in methanol and cyclohexane as compared with that in water. Further experimental studies such as the dependence of size on the laser wavelength, and electrochemical properties of produced nanoparticles are in progress.

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