

Synthesis of LiCoO_2 nano powders using recycled cobalt precursors from waste WC-Co hard metal

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LiCoO_2 , a cathode material for lithium rechargeable batteries, was prepared using recycled Co_3O_4 . First, cobalt powders were separated from waste WC-Co hard metal with an acid-base chemical treatment. Subsequently, Co_3O_4 powders were prepared by thermal treatment of the resulting $\text{Co}(\text{OH})_2$. By adding a predetermined amount of $\text{LiOH} \cdot \text{H}_2\text{O}$, LiCoO_2 was obtained by sintering for 10 h in air at 800 °C. Nano-sized LiCoO_2 was obtained by thermal treatment of the LiOH -coated Co_3O_4 particles at 500 °C for 3 h. LiOH was coated onto the Co_3O_4 particles by a sonochemical method. The synthesized micro- and nano- LiCoO_2 particles using recycled Co precursors were characterized by X-ray diffraction (XRD) and a scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis.

Key words: WC-Co composite powder; Recycle; Cobalt oxide; Lithium cobalt oxide.

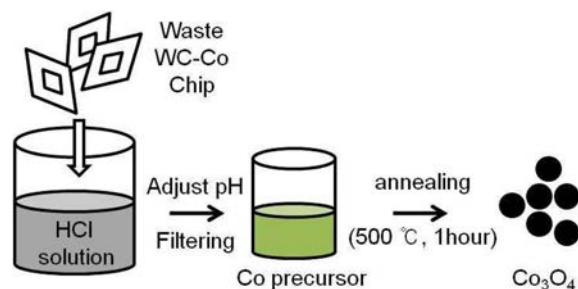
Introduction

WC-Co cermets are widely used in cutting tools, metallic molds and highly wear-resistant tools due to their excellent mechanical properties such as high hardness and high transverse rupture strength [1]. The development of an efficient recycling procedure for WC-Co cermets is important for resource recovery and reducing material costs. Various recycling processes of WC-Co cermets, including chemical modification, thermal modification and zinc melt methods, have been investigated and some have been employed in industry [2-3]. Recently, our group described the decomposition mechanism and promoting factors of waste hard metal for a zinc decomposition process to obtain WC [4]. After WC separation, recycled cobalt can be used for functional materials such as CoFe_2O_4 and LiCoO_2 .

LiCoO_2 is an attractive material due to its high performance in terms of energy density and cycling life in lithium rechargeable cells [5-6]. LiCoO_2 particles are typically prepared by solid state and hydrothermal reactions with various cobalt precursors such as $\text{Co}(\text{OH})_2$, CoCl_2 , and $\text{Co}(\text{OAc})_2$ [7-9]. The synthesis of LiCoO_2 particles by a sol-gel process and sono-chemical method has also been studied [10-11]. In particular, the sonochemical method is relatively suitable for the synthesis of multi-component materials, because it provides an easy surface coating of materials. The sonochemical method has been used to produce metal-

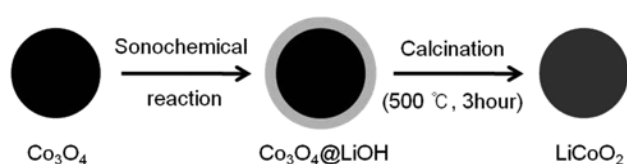
coated materials such as Au coated SiO_2 and Ni coated Al_2O_3 [12-13]. Jugović et al. described an olivine structured LiFePO_4/C composite obtained by the sonochemical method [14].

In this study, we report a method to prepare LiCoO_2 using recycled cobalt precursors extracted from a waste cobalt acid solution by pH control after the recycling of WC-Co cermets. Cobalt precursors were oxidized to Co_3O_4 nanoparticles through an annealing process via dehydration reaction in high temperature (Scheme 1). When the recycled Co precursors are used, process costs could be down and effective synthetic process for Co composite material. Two types of LiCoO_2 powders were prepared by different synthetic methods, a solid state reaction at 800 °C for micro-sized LiCoO_2 . Also, a sonochemical method using $\text{LiOH} \cdot \text{H}_2\text{O}$ coating on a Co_3O_4 surface through low temperature annealing at 500 °C for nano sized LiCoO_2 (Scheme 2) using recycled Co precursors. Synthesized LiCoO_2 particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses.



Scheme 1. Procedure of Co_3O_4 synthesis using extracted Co precursor from waste hard metal.

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Scheme 2. Two step synthesis method for LiCoO_2 through LiOH coating.

Experimental

Synthesis of Co_3O_4 nanoparticles and LiCoO_2 micro-particle

Co precursors were extracted from waste hard materials (WC-Co) by acid treatment and subsequently used to synthesize Co_3O_4 [1-2]. The extracted Co precursors were annealed at 500°C for 1 h in air. During the annealing, Co precursors were oxidized to Co_3O_4 by the heat treatment at a low temperature of 500°C in air. The extracted Co phase existed as CoOOH or $\text{Co}(\text{OH})_2$. These materials are easily oxidized to Co_3O_4 at a low temperature in a NH_3 or NaOH condition [15]. First, micro-sized LiCoO_2 particles were synthesized via a double sintering method using recycled Co_3O_4 . The Co_3O_4 nanoparticles were mixed with a pre-determined amount of different Li precursors such as $\text{LiOH} \cdot \text{H}_2\text{O}$ (molar ratio of $\text{Li}/\text{Co} = 1.00, 1.05$) by grinding for 1h. The mixed powders were formed into disks at a pressure of 50 MPa for 2 minute, and were sintered at 700°C for 5 h. Sintered disks were ground again, formed into disks under the same conditions, and sintered at 800°C for 10 h. The LiCoO_2 powders prepared were characterized by X-ray diffraction (XRD, D/max 2500 v/pc, Rigaku, Japan) measurement using $\text{Cu K}\alpha$ radiation, and scanning electron microscopy (SEM, JSM-6390, JEOL, Japan).

Synthesis of LiOH -coated Co_3O_4 and LiCoO_2 nanoparticles

The recycled Co_3O_4 nanoparticles were mixed with a predetermined amount of LiOH with different molar ratios (molar ratio of $\text{Li}/\text{Co} = 1.00\text{--}10.00$) to form the

coating layer for LiCoO_2 nanoparticles. Scheme 2 shows the synthetic process to obtain LiCoO_2 nanoparticles. The mixed precursors were dispersed in 20 ml of methanol, which was followed by sonochemical reaction at 20 kHz and 220 W for 20 min. They were finally washed several times to remove the byproducts such as unreacted LiOH and the dissolved Co phase during the sonochemical reaction. The color of the LiOH -coated Co_3O_4 nanoparticles was dark gray in a molar ratio of Li/Co above 5.00. LiOH coated Co_3O_4 nanoparticles were sintered at 500°C for 3 h to form nano-sized LiCoO_2 powders.

Results and Discussion

Preparation of Co_3O_4 powders

The zinc melt extraction process of the Co binder phase from WC-Co chips was investigated in order to establish a novel recycled waste WC-Co hard metal [4]. After the zinc melting process, the cobalt binder phase in an acid solution could be extracted to CoOOH or $\text{Co}(\text{OH})_2$, which were used for the synthesis of cobalt-component materials as precursors. Recycled Co precursors were extracted from the waste hard metal acid solutions. It is well known that $\text{Co}(\text{OH})_2$ with some impurities can be oxidized to Co_3O_4 at a higher temperature. While hydrolysis and oxidation are facilitated by increasing the pH, dehydration is more pronounced at higher temperatures and oxidation appears to be mostly affected by the applied oxygen partial pressure [15]. Fig. 1 shows a scanning electron microscope image and the XRD pattern of Co_3O_4 nanoparticles synthesized from Co precursors extracted from waste WC-Co chips by annealing at 500°C for 1 h. Fig. 1(a) shows that all XRD peak positions and relative intensities of synthesized Co_3O_4 particles matched well with Co_3O_4 materials without impurities such as CoO or Co_2O_3 . Fig. 1(b) shows a FE-SEM image of the as-prepared Co_3O_4 nanoparticles. The size of the bare Co_3O_4 nanoparticles was roughly 30 to 40 nm in the FE-SEM image.

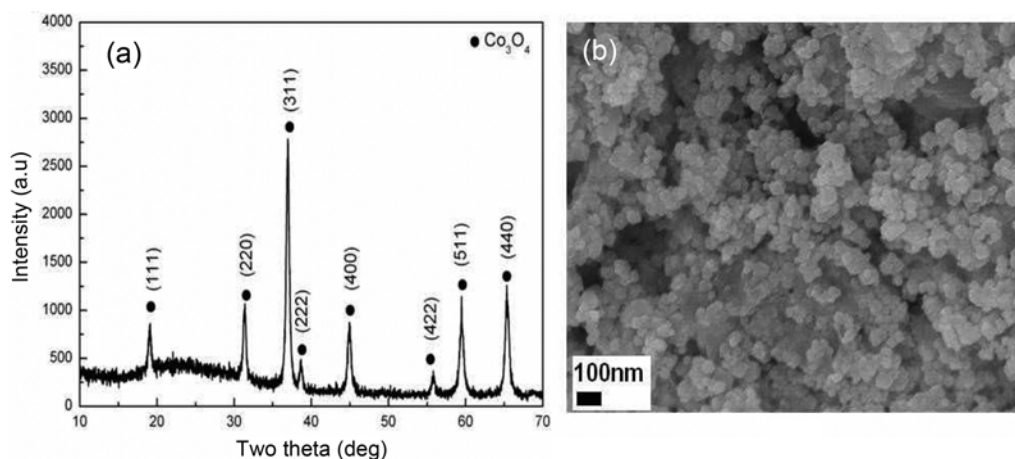


Fig. 1. (a) X-ray diffraction patterns of Co_3O_4 nanoparticles. (b) SEM image of Co_3O_4 nanoparticles.

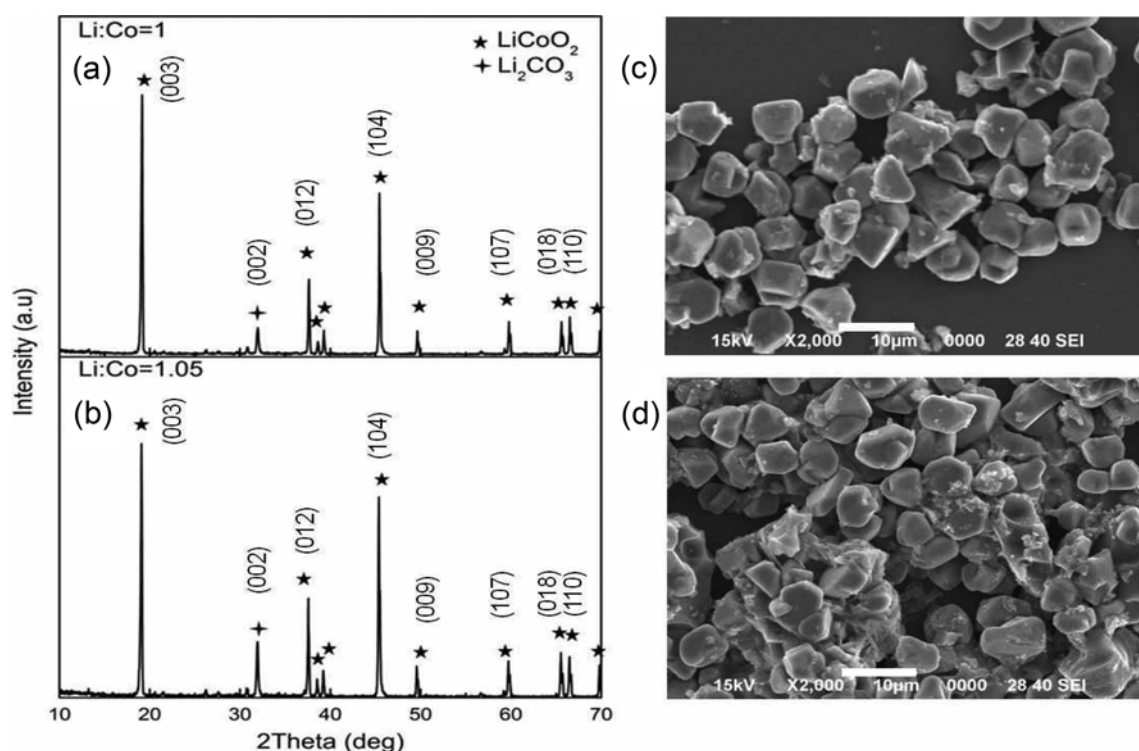


Fig. 2. X-ray diffraction patterns and SEM images of LiCoO_2 using $\text{LiOH} \cdot \text{H}_2\text{O}$ as the precursor prepared at 800°C for 10 h. (a, c) $\text{Li}/\text{Co} = 1.00$, (b, d) $\text{Li}/\text{Co} = 1.05$.

Synthesis of micro sized LiCoO_2 particles

The Co_3O_4 nanoparticles prepared were used for the synthesis of LiCoO_2 particles. $\text{LiOH} \cdot \text{H}_2\text{O}$ was chosen as the Li precursor. The Li/Co molar ratio was controlled by applying different concentrations of $\text{LiOH} \cdot \text{H}_2\text{O}$ and Co_3O_4 ($\text{Li}/\text{Co} = 1.00$ – 1.05). LiCoO_2 micro-particles were synthesized by a two-step sintering process. During sintering, nucleation and growth of LiCoO_2 occurred by a thermal reaction between Co_3O_4 nanoparticles and LiOH . The nucleation and growth reaction of the LiCoO_2 powder can increase the size uniformity and density of the LiCoO_2 micro-particles [16–17]. Fig. 2(a) and (b) shows the XRD pattern of the LiCoO_2 powders prepared. The crystallinity of the LiCoO_2 increased as more Li ions reacted with Co_3O_4 by diffusion. The presence of Li_2CO_3 phase was indicated that the reaction was not completed. Fig. 2(c) and (d) shows SEM images of LiCoO_2 . Li ions affect the growth rate of LiCoO_2 . However, excess Li precursor could affect the formation of impurities such as H_2O and CO_2 that leading to the loss of Li ions [9]. Excess LiOH is decomposed to Li^+ ions and hydroxyl groups. These hydroxyl groups are easily composed to hydrogen ions and carbon ions in air during the sintering process to form H_2O and CO_2 gas.

LiOH coated Co_3O_4 nanoparticles

A predetermined amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ was added to the recycled Co_3O_4 nanoparticles to adjust the Li/Co molar ratio in the range of 1.00–10.00. Fig. 3 presents XRD patterns of LiOH reacted with Co_3O_4

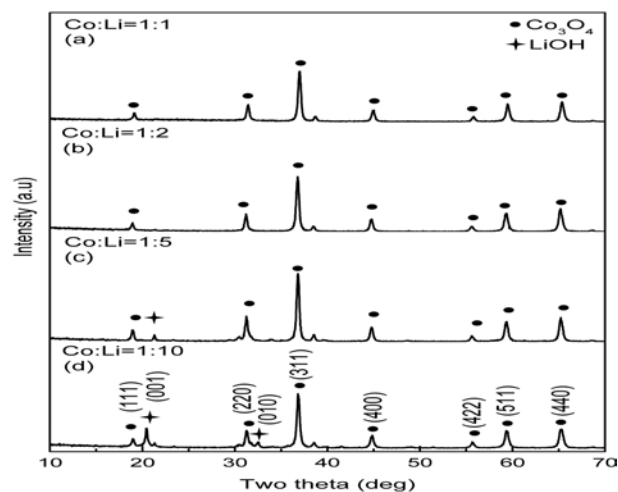


Fig. 3. X-ray diffraction patterns of LiOH coated Co_3O_4 nanoparticles prepared by the sonochemical method (20 kHz, 200 W) with different molar ratios of Li/Co . (a) $\text{Li}/\text{Co} = 1.00$, (b) $\text{Li}/\text{Co} = 2.00$, (c) $\text{Li}/\text{Co} = 5.00$ and (d) $\text{Li}/\text{Co} = 10.00$.

nanoparticles. In the case of a Li/Co molar ratio of less than 5.00 (Fig. 3(a) and (b)), only a Co_3O_4 peak was observed. However, with a Li/Co molar ratio exceeding 5.00 (Fig. 3(c) and (d)), LiOH peaks were observed with Co_3O_4 phase. These results indicate that LiOH reacted with the Co_3O_4 nanoparticles to form LiOH -coated Co_3O_4 nanoparticles. Fig. 4(a) and (b) are TEM images of LiOH coated Co_3O_4 nanoparticles with different molar ratios ($\text{Li}/\text{Co} = 1$ (Fig. 4(a)), $\text{Li}/\text{Co} = 10$ (Fig. 4(b)). In Fig. 4(b), a thickness of the LiOH coating layer of 5–7 nm is observed. The surface of the Co_3O_4 nanoparticles

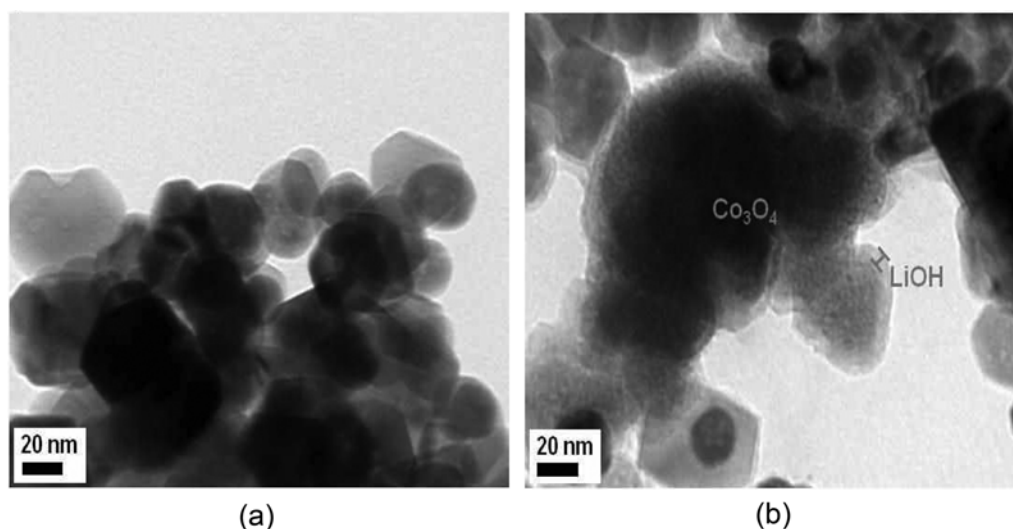


Fig. 4. TEM images (a) LiOH-coated Co_3O_4 nanoparticles ($\text{Li}/\text{Co} = 1.00$) and (b) LiOH-coated Co_3O_4 nanoparticles ($\text{Li}/\text{Co} = 10.00$) deposited from an ethanol dispersion of the nanoparticles on an amorphous carbon-coated copper grid and dried at room temperature.

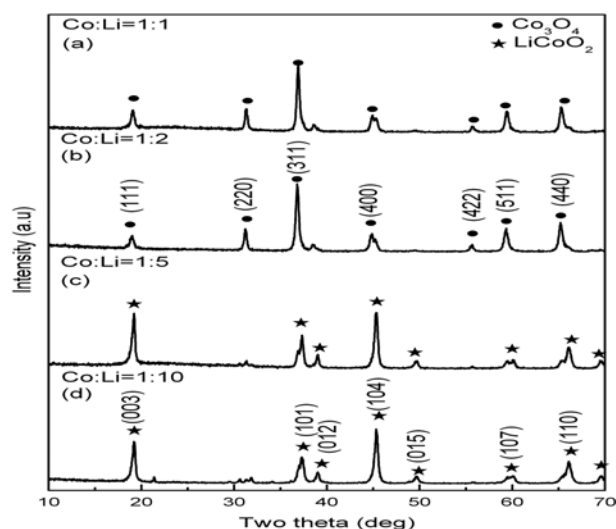


Fig. 5. X-ray diffraction patterns of LiCoO_2 nanoparticles ($\text{Li}/\text{Co} = 1.00$ - 10.00) prepared at 500°C for 3 h.

reacted with LiOH continuously due to the hydroxyl radical oxidation of $\text{LiOH} \cdot \text{H}_2\text{O}$ under sonochemical conditions [18-19]. The sonochemical method is widely used for the degradation of oxidized particles, particle agglomeration and surface modification. These reactions are attributed to the surface coating due to the cavitation at high frequency by collapse of bubbles in the liquid phase [20].

Synthesis of LiCoO_2 nanoparticles

Nano-sized LiCoO_2 could be synthesized by a chemical surface coating reaction with LiOH at a low temperature of about 500°C . Fig. 5 shows XRD patterns of LiCoO_2 nanoparticles with different molar ratios ($\text{Li}/\text{Co} = 1.00$ - 10.00) fabricated by sintering at 500°C for 3 h. For the LiCoO_2 nanoparticles obtained with a Li/Co molar ratio less than 5.00 (Fig. 5(a) and (b)), only a Co_3O_4 peak was observed. However, with a Li/Co

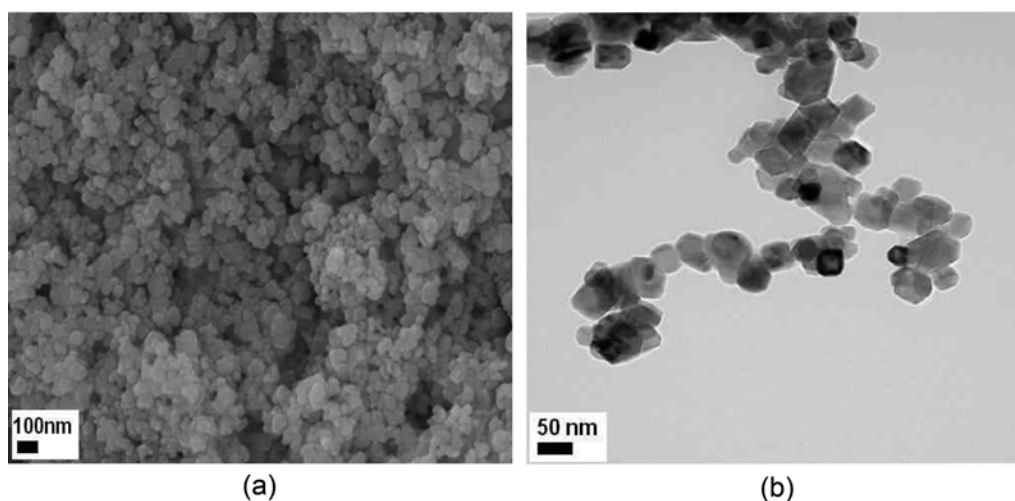


Fig. 6. (a) SEM and (b) TEM images of LiCoO_2 nanoparticles prepared at 500°C for 3 h.

molar ratio exceeding 5.00 (Fig. 5(c) and (d)), the Co₃O₄ peak decreased with an increasing Li/Co ratio and LiCoO₂ peaks were indexed. These results indicate that the Li ions move into Co₃O₄ via thermal diffusion during oxidation at high temperature [21]. Diffusion of Li ions was believed to lead to the formation of LiCoO₂ nanoparticles. Fig. 6 shows SEM and TEM images of the LiCoO₂ nanoparticles obtained by sintering at 500 °C. Their sizes were about 35-45 nm, which are similar to the size of the Co₃O₄ nanoparticles. A key advantage of this process is that it allows the synthesis of nano-sized LiCoO₂ at a lower temperature.

Conclusions

In conclusion, LiCoO₂ particles were synthesized using recycled Co precursors extracted from a waste hard metal acidic solution. Nano-sized LiCoO₂ particles were synthesized from LiOH-coated Co₃O₄ with different Li/Co molar ratios. A LiOH layer is observed as the LiOH·H₂O is increased due to the collapse of cavitation bubbles during application of the sonochemical method which were sintered at a lower temperature (500 °C) than the usual synthetic process. Micro-sized LiCoO₂ particles were prepared by a sintering reaction with different Li/Co molar ratios. The particle size of the LiCoO₂ microparticles was 6-7 μm (Li/Co = 1.00) and 8-9 μm (Li/Co = 1.05). In this study, we have investigated the synthesis of LiCoO₂ with different concentrations of Li using recycled Co phase as a precursor. The proposed synthetic method using recycled Co precursors is expected to serve as an effective material recycling system producing high quality cathode materials for lithium rechargeable cells.

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