Research Article

Characterization of LiCoO_2 Nanopowders Produced by Sol-Gel Processing

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LiCoO_2 nanopowders, one of the most important cathode materials for lithium-ion batteries, were synthesized via a modified sol-gel process assisted with triethanolamine (TEA) as a complexing agent. The influence of three different chelating agents including acrylic acid, citric acid, and oxalic acid on the size and morphology of particles was investigated. Structure and morphology of the synthesized powders were characterized by thermogravimetric/differential thermal analyses (TG/DTA), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Results indicate that the powder processed with TEA and calcinated at 800°C had an excellent hexagonal ordering of $\alpha\text{-NaFeO}_2$ -type (space group $R\bar{3}m$). Also, the other three complexing agents had a decisive influence on the particle size, shape, morphology, and degree of agglomeration of the resulting oxides. Based on the data presented in this work, it is proposed that the optimized size and distribution of LiCoO_2 powders may be achieved through sol-gel processing using TEA as a chelating agent.

1. Introduction

In recent years, concerns about energy sources have dramatically increased the demand for high capacity energy storage devices. Lithium metal oxides are the most studied materials for high-capacity cathode to be used in lithium ion batteries. This is mainly due to their attractive properties such as high energy density, high average output voltage, exceptional cycling behavior, high rate capability, and wide working temperature ranges [1–4]. Among this group of materials, LiCoO_2 was the first cathode material commercialized in the early 1990s due to its high energy density and excellent electrochemical stability [5, 6].

Conventionally, LiCoO_2 has been synthesized by solid-state reaction. Problems such as inhomogeneity, abnormal grain growth, and poor control of stoichiometry in solid-state reaction process, however, have led to the development of new approaches for synthesis of LiCoO_2 cathode material. Among processing routes, sol-gel method is a broadly employed technique due to its decisive advantages such as homogeneous mixing, good stoichiometric control, low

synthesis temperature, short heating time, and uniform particle size [4–15].

Predoaň et al. [6] reported producing of LiCoO_2 powder by sol-gel method using inorganic precursors and citric acid as a chelating agent. The bonding of the metallic ions in a chelating complex using carboxylic route was assumed to lead to a highly homogeneous precursor gel and to reduce the particle size of the resulting oxides [6]. Yoon and Kim [9] reported the first preparation of LiCoO_2 using acrylic acid as a chelating agent and showed the advantages of acrylic acid compared to a number of other chelating agents. Wu et al. [10] reported a sol-gel method assisted with triblock copolymer surfactant P123 to synthesize uniform nanosized distributed LiCoO_2 powder.

While a large volume of experimental research has been carried out on sol-gel preparation of LiCoO_2 material, the effects of chelating agents on the size and morphology of the resulting powder have not been systematically studied. An important chelating agent that has not been previously used in producing of LiCoO_2 powders is triethanolamine, $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$, referred to as TEA. TEA reacts with transition

FIGURE 1: TG/DTA data of LiCoO_2 powder prepared by four different chelating agents: (a) oxalic acid, (b) citric acid, (c) acrylic acid, and (d) TEA.

metal ions to form stable complexes. Formation of these complexes prevents rapid hydrolysis and condensation in an aqueous solution. Also, TEA is used as a surfactant in many reactions to prepare powders with good dispersivity [16–18]. Therefore, using TEA as a chelating agent in sol-gel process should have a beneficial impact on the quality of the resulting powder. The main goals of this investigation have been (i) to produce LiCoO_2 nanopowders using TEA as a chelating agent and (ii) to compare the morphology and the size distribution of the resulting powders with those produced by other commonly used chelating agents.

2. Experimental

Equivalent molar ratios of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and LiNO_3 were dissolved in distilled water. During stirring, TEA was added to the solution as a complexing agent and subsequently a clear dark red solution was achieved. The molar ratio of the chelating agent to the sum of metallic ions of the solution (R) was set at 0.5, 1, and 2. The resulting sol was then heated at 90°C for several hours to obtain a viscous gel. The gel was dried at 250°C for 6 hours in air and the resulting powder was calcinated at different temperatures in the range of 400 – 1100°C for 12 hours. To compare the effect of TEA on the size and morphology of LiCoO_2 powders with that of other complexing agents, three different samples with

various complexing agents including acrylic acid, citric acid, and oxalic acid were synthesized via a similar process and $R = 1$. The resulting products were calcinated at 800°C for 12 hours.

Thermal decomposition behavior of the gel precursor was examined by means of a Perkin Elmer TG/DTA A7 thermal analysis unit. Temperature range was selected in the range of 25 to 1100°C and heating rate was set at $5^\circ\text{C}/\text{min}$. X-ray diffraction patterns of the powder samples were obtained using X'pert Philips diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) and scan rate of $2^\circ/\text{min}$. The size and morphology of the powders were studied using a Philips CM200 transmission electron microscope.

3. Results and Discussion

3.1. Thermal Analysis. TG/DTA diagrams of LiCoO_2 powder prepared with four different chelating agents are shown in Figure 1. Weight loss in TGA diagram of the sample synthesized with oxalic acid (Figure 1(a)) occurred in two different regions between 350 – 400°C and 400 – 500°C concurrent with two exothermic peaks at 383°C and 486°C , respectively. The first region is associated with the combustion of nitrates and the remaining organic materials and the second region corresponds to the decomposition of the complexes formed during the sol-gel process. Complexes made with carboxylic

FIGURE 2: XRD data of LiCoO_2 powder produced using TEA calcinated at different temperatures.

FIGURE 3: XRD patterns of the samples synthesized with different values of TEA to metal ions ratio: (a) $R = 0.5$, (b) $R = 2$.

groups (COOH) existing in oxalic acid decompose into other compounds during the calcination process. According to Fey et al. [19], carboxylate mixtures may decompose into several intermediate compounds and their decomposition is facilitated by nitrate ions. Lundblad and Bergman [20] have also discussed the reaction mechanisms of LiCoO_2 formation. They have proposed that Co_3O_4 and carbon dioxide could be products of exothermic combustion reactions. In the DTA diagram of the sample synthesized with citric acid (Figure 1(b)), two exothermic peaks at 346°C and 480°C are observed which are also accompanied with two regions of weight loss between $300\text{--}360^\circ\text{C}$ and $360\text{--}480^\circ\text{C}$ in TGA curve. Combustion and decomposition reactions in a precursor prepared with acrylic acid in TG-DTA curve take place in one step (Figure 1(c)). The exothermic peak of this curve appears at 320°C . As seen, the combustion reaction and complex decomposition temperatures are increased with

changing the chelating agent from acrylic acid to oxalic acid and citric acid, respectively. This is attributed to the increasing of the number of carboxylic groups from 1 to 3 in the sequence. In TG/DTA diagram of TEA, Figure 1(d), two exothermic peaks are seen at 332°C and 348°C , accompanied by a large weight loss of sample between $300\text{--}400^\circ\text{C}$. These thermal events correspond to decomposition of nitrates and complexes. Fey et al. [19] also reported that the exothermicity of the combustion processes triggered the calcination of the oxide product. While thermal transformations were completed at about 400°C , a calcination process at higher temperature is necessary to form a completely crystalline material.

3.2. XRD Results. XRD data of LiCoO_2 synthesized with TEA calcinated in the range of 250°C to 800°C are displayed in Figure 2. The XRD pattern of the powder processed at

FIGURE 4: XRD patterns of powders produced using three common chelating agents: (a) citric acid, (b) oxalic acid, and (c) acrylic acid, calcinated at 800°C for 12 hours.

TABLE 1: Lattice constants and c/a ratio for different temperatures of sample prepared by TEA.

Temp. (°C)	a (Å)	c (Å)	c/a
400	2.828	13.862	4.901
550	2.820	13.871	4.918
800	2.817	14.041	4.984

250°C shows that Co_3O_4 is the main phase formed at this temperature. Co_3O_4 has a normal spinel structure in which the Co^{2+} and Co^{3+} ions occupy tetrahedral and octahedral sites, respectively. According to Antolini [3], substitution of cobalt ions with lithium ions at tetrahedral and octahedral sites leads to the formation of $\text{Li}_x\text{Co}_{3-x}\text{O}_4$. At the final stages of the process at low temperatures, quasispinel LT- LiCoO_2 phase will be produced. This is consistent with the diffraction data presented in Figure 2 for the 400°C-product where LT- LiCoO_2 peaks are clearly present. The c/a ratio of this sample is 4.902. Aspect ratio of the spinel is close to that of the ideal cubic structure based on close packing of oxygen network ($c/a = 2\sqrt{6}$). The c/a ratio is an indicator of the low temperature spinel-related structure formation (space group $\text{Fd}3\text{m}$) [21, 22]. By increasing calcination temperature to 550°C and 800°C, hexagonal distortion in the crystal structure leads to splitting of the spinel (222) diffraction peak into the hexagonal (006) and (012) peaks and also the splitting of the cubic (440) peak into the hexagonal (018) and the (110) peaks. Besides, while the lattice parameter a is decreased, both c and the c/a ratios are known to increased with increasing the calcination temperature [8, 23]. Sun [8] proposed that decreasing the electrostatic binding energy might cause the stabilization of the layered structure and therefore expansion of the c -axis. The lattice constants

TABLE 2: Lattice constants, c/a ratio, and $I_{(003)}/I_{(104)}$ for samples produced using four different chelating agents at 800°C.

Chelating Agent	a (Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$
Acrylic Acid	2.815	14.046	4.989	1.74
Citric Acid	2.806	14.037	5.002	1.47
Oxalic Acid	2.805	14.004	4.992	1.51
TEA	2.817	14.041	4.984	1.71

and c/a ratio for different temperatures are shown in Table 1.

XRD data for the sample calcinated at 800°C show that the pure HT- LiCoO_2 phase with hexagonal $\alpha\text{-NaFeO}_2$ lattice structure has been produced. The c/a ratio of the processed powder shown in Table 2 is in the range of c/a ratio of HT- LiCoO_2 phase reported previously [18]. Splitting of (006)-(102) and (108)-(110) diffraction peaks accompanied with a high (003)/(104) intensity ratio (Table 2) implies an excellent hexagonal ordering of this sample. Integrated intensity ratio of (003)/(104) peaks has been considered to be an important factor indicating the degree of cation ordering in the crystal structure of lithium cobalt oxides. It has been proposed that the electrochemical performance of cathode material is remarkably improved when the (003)/(104) intensity ratio is higher than 1.2 [10, 24, 25].

Figure 2 also shows the diffraction data of a sample calcinated at 1100°C. In this figure, other than the main phase peaks, Co_3O_4 diffraction peaks marked by * are clearly seen. Antolini [3, 26] has discussed decomposition reaction of LiCoO_2 at temperatures higher than 900°C and pointed out that Co_3O_4 diffraction peaks in the XRD pattern occurred as a result of $\text{CoO} \rightarrow \text{Co}_3\text{O}_4$ transition.

FIGURE 5: TEM images of powders processed by sol-gel method using: (a) oxalic acid, (b) citric acid, (c) acrylic acid, and (d) TEA.

The XRD data of samples synthesized with different values of TEA to metal ions ratio ($R = 0.5, 2$) are shown in Figure 3. Diffraction peaks in both of these samples are indexed to HT-LiCoO₂ phase with hexagonal ordering and space group $R\bar{3}m$. However, by using R value of 0.5, 1 and 2, the ratio of $I_{(003)}/I_{(104)}$ changed in the order of 1.06, 1.71, and 1.48, respectively. These intensity changes imply cation disordering of the hexagonal phase. While the combustion heat generated during the decomposition of complexing agent residue facilitates the calcination process, variation of the R value should have an impact on the decomposition and the formation process due to the changes in the partial pressure of oxygen especially during the combustion process [27].

XRD data of powders produced using three commonly used chelating agents calcinated at 800°C for 12 hours are shown in Figure 4. While all diffraction peaks in Figure 4 belong to LiCoO₂ with hexagonal ordering, there are some

diffraction peaks in XRD patterns of powders prepared using oxalic acid and citric acid which are not characteristic of the HT-LiCoO₂ phase. These diffraction peaks are indexed as Co₃O₄ phase which probably remained during the calcination process. Lattice constants, c/a ratio, and $I_{(003)}/I_{(104)}$ for samples produced using four different chelating agents at 800°C are shown in Table 2. As shown in the table, the $I_{(003)}/I_{(104)}$ ratio is considerably lower for citric and oxalic acids compared to that of the other two chelating agents.

3.3. TEM Study. Figure 5 shows bright field images of the powders prepared using different chelating agents. Figure 5(a) illustrates powders processed using oxalic acid and shows agglomeration of product under the experimental condition employed. Figures 5(b) and 5(c) show a rather homogenous distribution of the powder produced using citric and acrylic acids with particle size of about 160 nm

FIGURE 6: (a) Diffraction pattern of LiCoO_2 powder synthesized using TEA at 800°C for 12 hours and (b) indexed pattern.

FIGURE 7: TEM image of a sample processed by TEA and calcinated at 1100°C .

and 300 nm, respectively. The morphology and the size of the powders produced using TEA shown in Figure 5(d) compared to those produced with other chelating materials indicate that TEA has a better effect on producing of powders with suitable distribution and less agglomeration. Diffraction pattern (DP) of the sample synthesized with TEA is shown in Figure 6. In agreement with the XRD data (Figure 2), the DP of this sample clearly identifies the hexagonal structure and $R\bar{3}m$ space group of the LiCoO_2 powders synthesized during the process.

Figure 7 presents TEM image of the sample obtained using TEA calcinated at 1100°C . Decomposition of LiCoO_2 nanopowders at 1100°C can be seen in this image. Decomposition of cathode material followed by releasing oxygen

from the compound leads to degradation as discussed in [3, 26].

The effect of R parameter on the size and morphology of powders was studied using microscopy techniques. Figure 8 shows the morphology of powders produced with different ratio of TEA to sum of metallic ions. It is seen that with decreasing R from 1 to 0.5, the size of powders increased from 65 nm to average particle size of 260 nm. This seems to be related to the reduction of complex numbers formed during the process. With increasing the R ratio from 1 to 2, however, the shape of powders changes from granular to laminar. It is reported that TEA may act as a surfactant in preparation of powders [16–18]. Sugimoto et al. [16, 17] have recently reported TEA to act as a shape controller of TiO_2 as well. They reported that during synthesis of anatase TiO_2 , specific adsorption of TEA onto crystal planes parallel to the c -axis occurred. In the present work, it is suggested that adsorption of TEA residue on the surface of powders may change the powder shape and size.

4. Conclusions

Nanoparticles of LiCoO_2 with highly uniform distribution were synthesized by sol-gel method using TEA and three other chelating agents, that is, acrylic acid, citric acid, and oxalic acid. TEM results indicated that various chelating agents had a key role on the shape, size, morphology, and agglomeration of LiCoO_2 powders synthesized by sol-gel route. Of all powders produced in this study, the powders produced using TEA and calcinated at 800°C for 12 hours had the smallest average particle size of 65 nm and a well-developed layered structure of HT- LiCoO_2 . Results also show that decreasing the R value led to an increase in the size of the final powders. However, increasing the R value affected the morphology of the powders.

FIGURE 8: TEM images of powders synthesized with different R value: (a) 0.5, (b) 2.

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