

Research Article

Synthesis and Characterization of LiNiO₂ Nanopowder with Various Chelating Agents

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LiNiO₂ powders were synthesized with acrylic acid, citric acid, oxalic acid, and triethanolamine (TEA) as a chelating agent. Crystallized LiNiO₂ was synthesized in air at a calcinations temperature of 500°C for 12 hours, when the molar ratio of chelating agents to total metal ion (RPM) was 1.0. The TEA-assisted method had the highest intensity ratio of (003)/(104) peaks of X-ray diffraction (XRD) spectrum. The transmission electron microscopy (TEM) analysis indicates that the sample prepared with triethanolamine obtained the smallest particle size with average particle size of only 12 nm. The results indicate that chelating agents have an important role in the intensity ratio of (003)/(104) peaks of XRD spectrum, size and shape of powders.

1. Introduction

Layered oxide LiMO₂ (M = Co, Ni, Mg) has been proposed as a cathode material for lithium secondary batteries. Since the commercialization of LiCoO₂ by Sony in 1990, many efforts have been exerted to find other layered oxide cathode materials to replace it because of the high toxicity of LiCoO₂ [1, 2]. Recently layered oxide LiNiO₂ was accepted as an attractive cathode material because of its various advantages such as lower cost, higher discharge capacity, better reversibility, and nontoxicity [3–7]. Transition metal ions such as nickel and cobalt ions are surrounded by six oxygen atoms forming LiNiO₂ infinite slabs by edge-sharing of the NiO₂ layers in octahedral sites [8]. The ideal layered LiNiO₂ structure has a close-packed oxygen array which is slightly distorted from cubic close packing [8]. Therefore, LiNiO₂ phase has a rhombohedral structure with an $R\bar{3}M$ space group, and the parameters of the unit cell are usually defined in terms of the hexagonal setting. However, obtaining synthesized stoichiometric and ordered layered LiNiO₂ is difficult because decomposition from LiNiO₂ to Li_{1-x}Ni_{1+x}O₂ ($x > 0$) occurs which has a partially disordered cation distribution at the lithium sites. It has been well known that the synthetic condition is important factor to obtain stoichiometric layered LiNiO₂ [9].

The use of a solution-chemistry-based technique for synthesizing materials has several advantages. All these approaches yield molecularly homogeneous intermediate precursors. Despite the variation in the reaction chemistry, the precursor can be designed and synthesized to suitable consist of molecular structures closely resembling the final desired oxide. In this study, a sol-gel method has been used for the preparation of stoichiometric layered LiNiO₂ with submicron and narrow-size distribution particle. Furthermore, the reduced diffusion distance in comparison to the solid state approaches provides the ability to generate fine grained materials with limited coarsening and growth of the particles. We have investigated the optimum condition by examining the effects of chelating agent on structure of layered LiNiO₂ and morphology and size of LiNiO₂ powders.

2. Experimental

2.1. Sample Preparations

2.1.1. Oxalic Acid-Assisted Sol-Gel Method. Stoichiometric amounts of LiNO₃·6H₂O and Ni(NO₃)₂·6H₂O (MERC Co.) were dissolved in aqueous solution. An aqueous solution of oxalic acid was added to obtain a sol, such that the molar

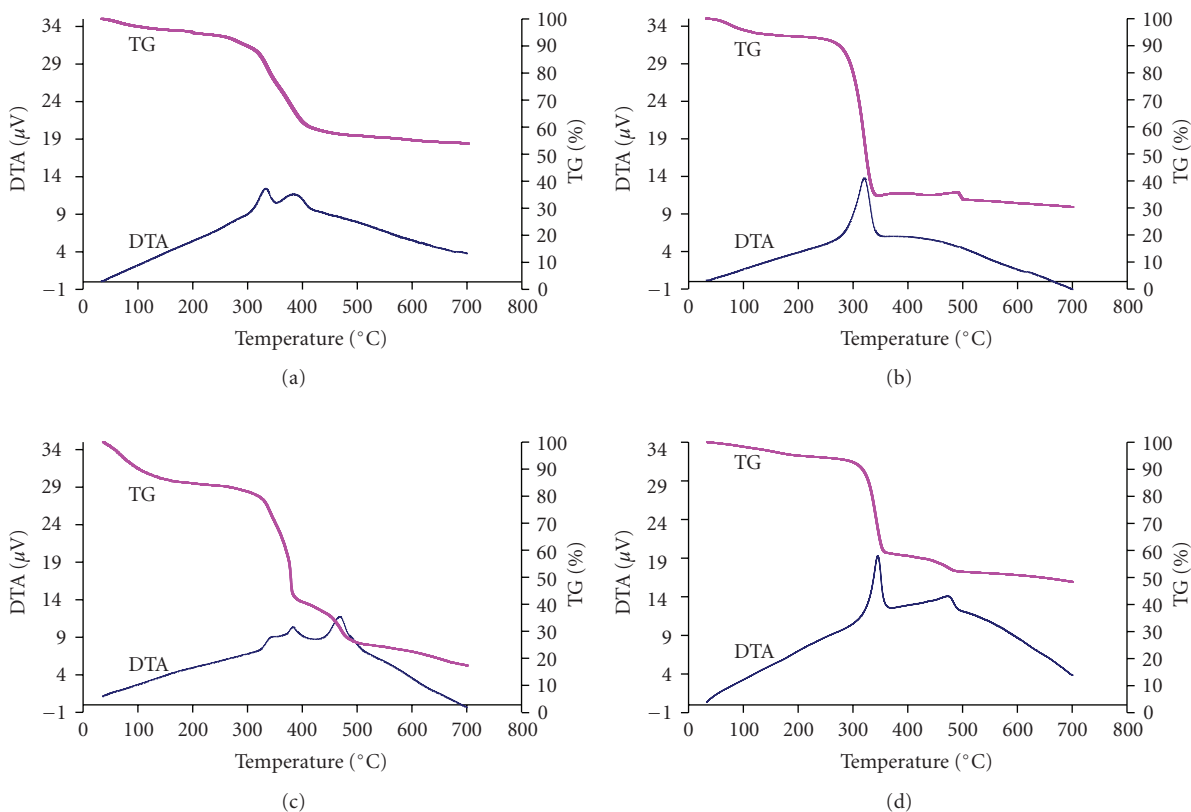


FIGURE 1: TG-DTA curves of the LiNiO_2 precursors prepared by (a) acrylic acid; (b) citric acid; (c) oxalic acid; (d) triethanolamine.

ratio of oxalic acid to total metal ion (RPM) was 1. After stirring for several hours, a transparent sol was obtained. The resulting sol was evaporated at 90°C for several hours to yield a gel. The gel precursor was preheated at 200°C in air for 6 hours and then calcined at 500°C for 12 hours to obtain LiNiO_2 .

2.1.2. Citric Acid-Assisted Sol-Gel Method. Stoichiometric amounts of $\text{LiNO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (MERC Co), with a cationic ratio of $\text{Li}:\text{Ni} = 1$, were dissolved in an aqueous medium. This was mixed well with the aqueous solution of citric acid with $\text{RPM} = 1$. After stirring for several hours, a transparent sol was obtained. The sol was evaporated at 90°C to yield gel precursors. The gel precursors were preheated at 200°C for 6 hours and then calcined at 500°C for 12 hours to obtain LiNiO_2 .

2.1.3. Acrylic Acid-Assisted Sol-Gel Method. Stoichiometric amounts of $\text{LiNO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in water to obtain an aqueous solution. An aqueous solution of acrylic acid was added to this under constant stirring to obtain a sol such that $\text{RPM} = 1$. The resulting sol was evaporated at 90°C for several hours to obtain a gel. The gel precursor was preheated at 200°C for 6 hours in air and then calcined at 500°C for 12 hours to obtain LiNiO_2 .

2.1.4. TEA-Assisted Sol-Gel Method. Stoichiometric amounts of $\text{LiNO}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in water to obtain an aqueous solution. The TEA, with $\text{RPM} = 1$, was added under stirring to obtain a sol. The resulting sol was evaporated at 90°C for several hours to extract out excess water and yield gel. The gel precursor was preheated at 200°C for 6 hours and then calcined at 500°C for 12 hours to obtain LiNiO_2 powder.

2.2. Characterization. The thermal decomposition behavior of the precursors was examined by means of thermogravimetry (TG) and differential thermal analysis (DTA) using a Perkin-Elmer Diamond TG/DTA thermal analyzer simultaneous recording of weight losses (gravimetric thermal analysis) and temperature variations (differential scanning calorimetry). The crystalline phase was identified by powder X-ray diffraction using an Xpert Philips X-ray diffraction analyzer using $\text{Cu K}\alpha$ radiation. The morphologies of the samples were examined by transmission electron microscopy (TEM, Philips CM200) operated at 200 KV.

3. Results and Discussion

3.1. Thermal Analysis. Figure 1 shows the DTA-TG curves of the LiNiO_2 obtained by different complex agents. The TG-DTA curves of precursors prepared by acid acrylic; acid oxalic, acid citric, and triethanolamine are similar.

TABLE 1: Realised heats of the gel precursors prepared by different chelating agents during calcination process.

Chelating agent	ΔQ (KJ/gr)
Acid acrylic	8.4
Acid oxalic	9.6
Acid citric	10.2
Triethanolamine	18.3

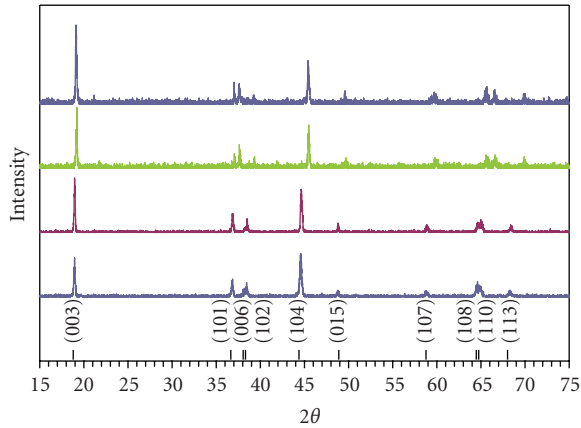


FIGURE 2: XRD patterns of the LiNiO_2 prepared by (a) acrylic acid; (b) oxalic acid; (c) citric Acid; (d) triethanolamine.

The weight loss in temperature 300–500°C corresponds to combustion of organic and inorganic constituents in the gel precursor, such as nitrates and carbonates components [10, 11]. In this stage, a large amount of CO_2 and H_2O released, which occurs with the exothermic peaks at 300–500°C in the DTA curves. For acrylic acid-assisted precursor it seems that the reaction process for synthesizing LiNiO_2 is easier than other solution methods. This is due to the fact that the exothermic peak for acrylic acid-assisted precursor appeared at lower temperature compared to the other samples. Table 1 shows released heats due to combustion of organic and inorganic constitution in the gel precursors accompanied by exothermic peaks in DTA curves. As it is demonstrated in Table 1, the gel obtained by triethanolamine has the highest amount of released heat among the samples. The released heat can help the crystallization of LiNiO_2 nanopowders. It is expected that the crystal sizes increase as the temperature rises. The crystal growth phenomenon is a diffusion control process and time dependent. In our experiments no crystal growth was observed due to temperature rise since the combustion reaction time was not long enough to cause crystal growth.

3.2. XRD Analysis. XRD analyses were carried out on the synthesized LiNiO_2 powders to confirm the phase purity. Figure 2 shows the X-ray diffraction patterns of nanocrystalline LiNiO_2 powders grown by various solution methods. According to the TG-DTA analysis the LiNiO_2 crystal phase

began to form at above 300°C. As shown in Figure 2, all patterns exhibit only peaks for the LiNiO_2 phase with $R\bar{3}M$ structure. Hexagonal cell parameters of the oxides prepared by four different chelating agents, which were calculated by least squares refinement, are given in Table 2. In all the cases, the cell parameters ($a = 2.91 \pm 0.02 \text{ \AA}$, $c = 14.2 \pm 0.03 \text{ \AA}$) as well as unit cell volume were almost identical. They are in good agreement with the literature values [9]. Furthermore, the average crystallite size has been calculated from XRD line broadening with Scherer's equation. As shown in Table 2, when the complex agent used in the solution method was changed, the average crystallite sizes of the prepared samples were changed too. The crystallite sizes range from 9.6 nm to 10.4 nm for various complex agents used in this study. It has been reported that the intensity ratio of (003) and (104) peaks is a key parameter that indicates the degree of the displacement of nickel and lithium [4, 11, 12]. However the extent of the splitting of (108) and (110) peaks is a reliable quantitative criterion for the determination of electrochemical activity of LiNiO_2 [13–15]. The disordering nature which is called cation mixing can seriously degrade the electrochemical performance of the electrode, such as the resistance for the electrochemical intercalation reaction [16, 17]. Table 2 shows the observed values of $I_{(003)}/I_{(104)}$ for the materials synthesized in this study. The LiNiO_2 powder synthesized with TEA-assisted sol-gel method has the highest value of $I_{(003)}/I_{(104)} = 1.8$. In addition, a clear split of the (108) and (104) peaks is observed. This indicates that LiNiO_2 powder synthesized with TEA-assisted sol-gel method has a good crystalline ordering and low cation mixing compared with other materials synthesized in this study. This is because the chelating agent not only works as a complexing agent but also provides the combustion heat necessary for synthesis of LiNiO_2 . According to the DTA analysis, the TEA provided most heat compared with other chelating agents, this causes high crystalline ordering and low cation mixing. And the more combustion heat is generated from TEA to yield LiNiO_2 phase with high crystalline ordering.

3.3. TEM Analysis. Figure 3 shows the TEM images of LiNiO_2 powders synthesized by different chelating agent. The particle size of LiNiO_2 powders prepared by acid acrylic chelating agent is about 180–250 nm which is the largest among all the cases.

For the powders prepared by TEA chelating agent the particle size is the smallest which is about 10–15 nm compared with other powders. This indicates that the average particle size of the products prepared from different chelating agents is different, which is in agreement with the results previously obtained for crystallite size in Table 2.

Furthermore we can conclude that different chelating agents used in sol-gel method have different influences upon particle size of the powders. TEA can be used as surfactant [18]. TEA can be adsorbed on the surface of oxide particles preventing continuous growth of the particles and the prepared powders with small particle size and loose agglomerates. In all the products, chelating agents were used

TABLE 2: Lattice parameters, crystallite size, particle size, and intensity ratio $I_{(003)}/I_{(104)}$ of the LiNiO_2 nanopowder synthesised by different chelating agents.

Chelating agent	a (Å)	c (Å)	$I_{(003)}/I_{(104)}$	Crystallite size (nm)	Particle size (nm)
Acid oxalic	2.91	14.195	1.22	10	70–150
Acid acrylic	2.93	14.23	0.90	10.4	180–250
Acid citric	2.90	14.185	1.40	10.2	80–100
Triethanolamine	2.89	14.187	1.80	9.6	10–15

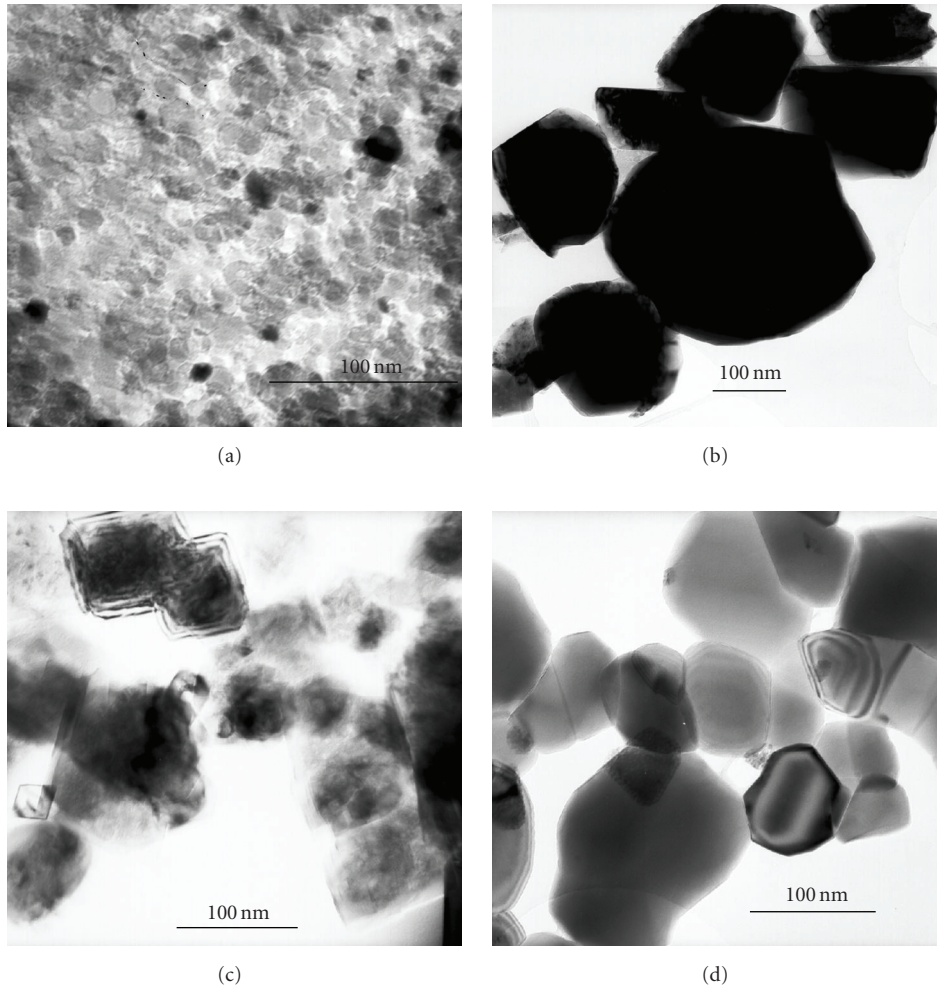


FIGURE 3: TEM of the LiNiO_2 prepared by different chelating agents: (a) triethanolamine; (b) citric acid; (c) oxalic acid; (d) acrylic acid.

to suppress rapid hydrolysis of Ni^{2+} during process of gel formation to form a carbonaceous matrix, which acts as a substrate for the homogeneous mixing of lithium and Nickel metal ion on a molecular scale. Furthermore, all the chelating agents used in our research can serve as a fuel. During the calcination, combustion heat generated due to decomposition of the carbonaceous residue produced from complex agent makes the nucleation process complete at the early stage of the sol-gel process. Upon calcinations in air, the carbonaceous substrate is oxidized to evolve large amounts of gasses, and the accompanying gas evolution helps

breaking down large agglomerated particles and inhibiting the continuous growth of the crystallite, leaving behind a finally divided oxide phase.

TEM images of the single crystal LiNiO_2 prepared with TEA-assisted method are shown in Figure 4(a). The corresponding electron diffraction pattern taken from this LiNiO_2 nanopowder is shown in Figure 4(b). The diffraction spot pattern indicates that the LiNiO_2 nanopowder consists of just one crystal. Here we can conclude that the LiNiO_2 nanopowder obtained in our experiment is single crystal.

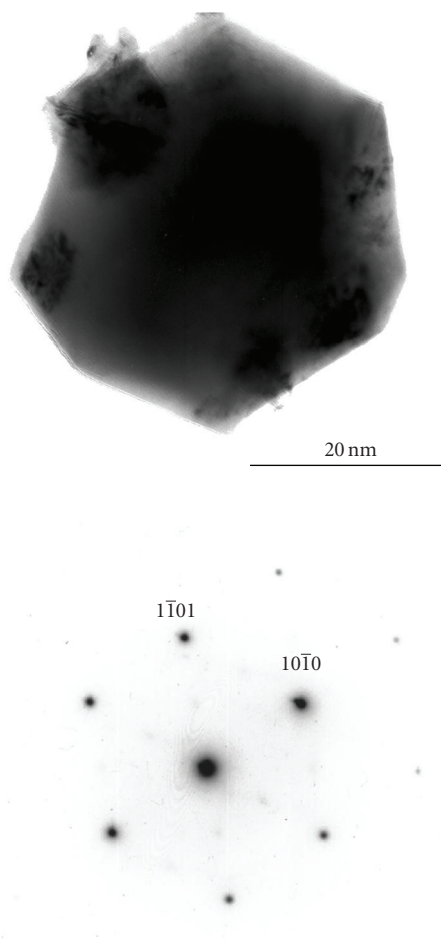


FIGURE 4: TEM photographs of LiNiO_2 single crystal nanopowder image and corresponding electron diffraction pattern.

4. Conclusion

Stoichiometric LiNiO_2 powders were synthesized by a sol-gel method using acrylic acid, citric acid, oxalic acid, and triethanolamine as chelating agents. The quality of the LiNiO_2 powders prepared by a sol-gel method were evaluated by measuring the intensity ratio of (003)/(104) peaks and degree of splitting of (108) and (110) peaks appeared on XRD spectrums. The XRD results indicated that the samples prepared by TEA as a chelating agents have a maximum intensity ratio of (003)/(104) peaks compared with other samples. The TEM results show that different chelating agent have a great effect on size and shape of particles. The sample prepared with TEA had the smallest particle size of 10–15 nm.

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