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Synthesis of $LiNiO_2$ by two-step solid-state method

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$LiNiO_2$ was prepared through two-step solid-state reaction by mechanochemical method and heat treatment, using LiOH (Li_2CO_3) and $Ni(OH)_2$ as starting materials. The influence of grinding speed and time, heat treatment time, and starting materials on the structure of $LiNiO_2$ was studied. The as-milled samples and products were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD). The results show that uniform as-milled samples can be obtained at grinding speed of 580 rpm for 0.5 h, using LiOH and $Ni(OH)_2$ as raw materials. Perfect crystal $LiNiO_2$ has been prepared by calcining the as-milled samples at 700 °C for 15 h. Composite material powders consisting of $Li_2Ni_8O_{10}$ and $LiNiO_2$ have been obtained using Li_2CO_3 as lithium source.

Keywords: *grinding; lithium; solid-state method; mechanochemistry*

1. Introduction

Lithium ion battery is a new kind of “green” chemical cell. Many studies have been focused on the research and development of cathode materials for Li-ion batteries. The development of cathode materials with high capacity, good charge-discharge properties, highly reversible embedded reaction, thermal stability and stabilization of electrolyte is critical for Li-ion batteries. The application of $LiCoO_2$, which is the most common commercial lithium ion battery cathode material, is restricted due to the toxicity and scarcity of Co. $LiNiO_2$, which shows a layered structure, low cost and is environment friendly, is widely used as the material substituting $LiCoO_2$.

The general synthesis methods of $LiNiO_2$ cathode materials include high temperature solid state method [1–5], combustion method [6] and molten salt method [7]. However, these methods are restricted owing to the high temperature, long time, and low uniformity of the products. Many methods for preparation of new materials, such as emulsion method [8], ion exchange method [9], thin film processes [10], sol-gel method [11], voltage prediction method [12], precipitation method [13], hydrolysis of metal alkoxides [14], and refluxing method using acetic acid [15], have been tried safely and economically to synthesize $LiNiO_2$ cathode materials. However, the results are not enough satisfactory to the researchers because of the complex fabrication process and low electrochemical performance of the product.

Mechanochemical technology, which is a well-known method for the preparation of nanomaterials, super thin powders and alloys, is extremely useful for promoting intimate mixing by pulverization of the starting materials during high-energy milling [16]. On the one hand, the impact of high-energy forces originating from the pulverization enhances diffusion of the starting materials and consequently, promotes chemical reactions resulting in metastable structures [16, 17]. On the other hand, the high-energy milling action has been reported to generate nanostructured as well as metastable phases of various compounds [17]. Therefore, these advantages could be very useful for synthesizing $LiNiO_2$ at low temperatures.

In the present work, $LiNiO_2$ was prepared through two-step solid-state reaction by

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mechanochemical method and heat treatment at low temperature. The effect of starting materials, grinding speed and time as well as heat treatment time on the structure of $LiNiO_2$ was studied.

2. Experimental

$LiOH{\cdot}H_2O$, $Ni(OH)_2{\cdot}H_2O$ and Li_2CO_3 (99.9 %) were purchased from Shanghai Runjie Chemical reagent Co., Ltd., Shanghai, China. In general, certain starting materials containing $LiOH{\cdot}H_2O$ (or Li_2CO_3) and $Ni(OH)_2{\cdot}H_2O$ with a molar ratio of Ni/Li equal to 1:1 were first placed in an agate vial. Then, the vial was sealed and subjected to the milling process using the ND2 Mixer/Mill. The weight ratio of balls to powder of 8:1 was used as the mechanochemical process condition. Agate balls with diameters of 20 nm, 10 nm and 6 mm were used in the process. Then, $LiNiO_2$ was synthesized by calcining the as-milled samples for 5 h to 15 h in air at 700 °C.

The as-milled samples of the final products were subjected to X-ray diffraction characterization (XRD, Y500, Fangyuan, China). The general XRD studies were performed in the 2θ range of 10° to 90° at 30 kV and 20 mA at 0.09° step size. A Cu X-ray tube was used as the radiation source in all experiments. Gravimetric/differential thermal analysis was also conducted on the starting materials using the simultaneous thermogravimetry-differential scanning calorimetry instrument (TG/DTA, STA449C, NETZSCH, Germany). A constant heating rate of 10 °C/min was used for the samples subjected to TG/DTA analysis. The morphology of the powders was observed by scanning electron microscopy (SEM, QUANTA 200, FEI, the USA).

3. Results and discussion

The thermogravimetric behavior of the starting materials is shown in Fig. 1. In the TG-DTA curve of $LiOH{\cdot}H_2O + Ni(OH)_2{\cdot}H_2O$ (Fig. 1a), a drastic weight loss is observed at 87 °C, which can be attributed to evaporation of the absorbed water. A subsequent weight loss appeared at 285 °C, which can be assigned to decomposition of the crystal water. The third weight loss, which can be observed at 425 °C, is attributed to decomposition of $Ni(OH)_2$. The last weight loss is observed at 460 °C, which can be assigned to the formation of $LiNiO_2$. In the curve of $Li_2CO_3 + Ni(OH)_2{\cdot}H_2O$ (Fig. 1b), a weight loss is observed at 309 °C, which can be attributed to decomposition of the water contained in the $Ni(OH)_2{\cdot}H_2O$ crystal. A subsequent weight loss is continued beyond 1000 °C. The observed weight loss can be attributed to the decomposition of Li_2CO_3 at 520 °C, followed by the subsequent solid-state reaction between Li_2O_2 and NiO that continues to 1000 °C.

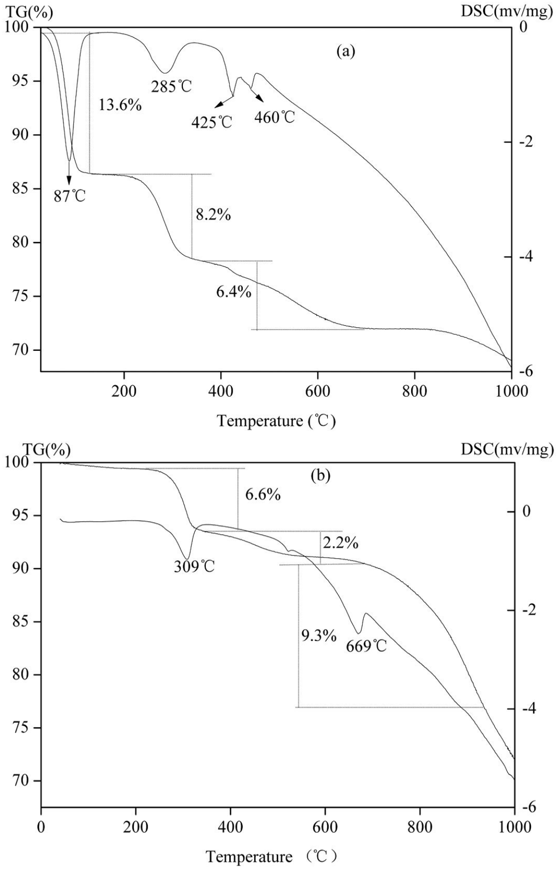

Fig. 1. TG-DTA curves of starting materials (a) $LiOH{\cdot}H_2O + Ni(OH)_2{\cdot}H_2O$, (b) $Li_2CO_3 + Ni(OH)_2{\cdot}H_2O$.

The XRD patterns of the products prepared by two-step solid-state reaction using different starting materials are shown in Fig. 2.

In the XRD pattern of the product originating from Li_2CO_3 and $Ni(OH)_2{\cdot}H_2O$, most of diffraction peaks can be attributed to the characteristic peaks of $Li_2Ni_8O_{10}$. All diffraction peaks in the XRD pattern, originating from $LiOH{\cdot}H_2O + Ni(OH)_2{\cdot}H_2O$, can be assigned to the characteristic peaks of $LiNiO_2$, which implies a well-crystallized nature of the final products. In the mechanochemical process, $LiOH{\cdot}H_2O$ decomposes easily into Li_2O_2 and H_2O. The Li_2O_2 can directly react with NiO which is the main decomposition product of $Ni(OH)_2{\cdot}H_2O$ in the mechanochemical process, to generate $LiNiO_2$. The obtained results demonstrate that $LiNiO_2$ can be fabricated through two-step solid-state reaction method, using $LiOH{\cdot}H_2O$ and $Ni(OH)_2{\cdot}H_2O$ as starting materials. The decomposition enthalpy of Li_2CO_3 is higher than that of $LiOH{\cdot}H_2O$.

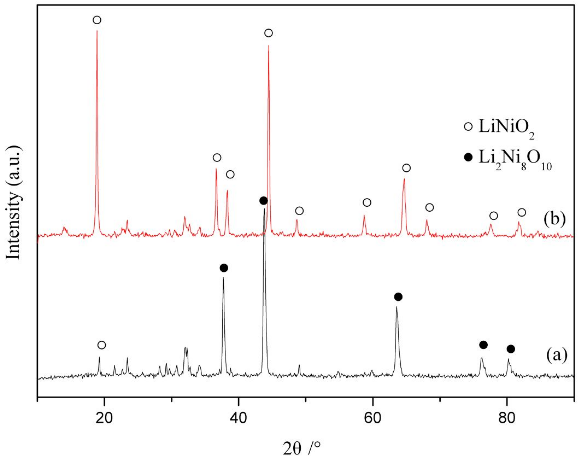

Fig. 2. XRD patterns of the products originating from (a) $Li_2CO_3 + Ni(OH)_2{\cdot}H_2O$ and (b) $LiOH{\cdot}H_2O + Ni(OH)_2{\cdot}H_2O$.

Fig. 3 shows the XRD patterns of the products prepared by mechanochemical process at different grinding speeds. The diffraction peaks in the curve of the sample prepared at 580 rpm are attributed to the characteristic peaks of $LiNiO_2$. However, the diffraction peaks in the curve of the sample prepared at 400 rpm are mainly assigned to the characteristic peaks of $Li_2Ni_8O_{10}$. These results indicate that $LiNiO_2$ can be obtained through mechanochemical process conducted at 580 rpm, followed by heat treatment. The forces exerted on the material through grinding at 580 rpm are more effective than those at 400 rpm, which improves diffusion of the components of the starting materials, thus promoting chemical reactions in heat treatment process [16].

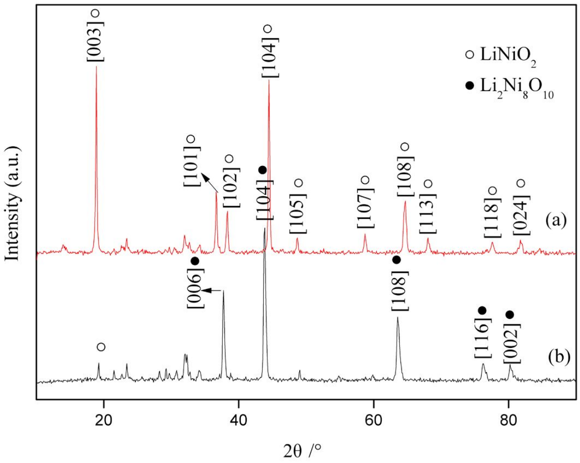

Fig. 3. XRD patterns of samples obtained at different grinding speeds (a) 580 rpm and (b) 400 rpm.

Fig. 4 shows the XRD patterns of the products prepared at different times of mechanochemical process. In Fig. 4 it is observed that the diffraction peak at 2-theta angle of 18.9° starts to evolve at 0 h i.e. in the sample not subjected to the mechanochemical process. However, the characteristic peak of the (0 0 3) plane is lower than that of the (1 0 4). This result implies that the (0 0 3) crystalline plane of $LiNiO_2$ has not completely formed. For 0.5 h sample, distinct peaks have occurred implying a well-crystallized nature of the product. It indicates that $LiNiO_2$ can be prepared through mechanochemical process lasting for 0.5 h. The patterns of other samples show the characteristic peaks of $Li_2Ni_8O_{10}$. Furthermore, the intensity ratio of (0 0 3) to (1 0 4) peaks, $I_{(003)}/I_{(104)}$, is the most important index to evaluate the crystal structure of $LiNiO_2$. When $I_{(003)}/I_{(104)}$ ratio is higher than 1, the product shows a good crystal structure in which nickel and lithium ions are well ordered. In Fig. 4 it can be observed that the $I_{(003)}/I_{(104)}$ ratio of the product obtained at grinding time of 0.5 h is higher than 1. Therefore, the feasible time of mechanochemical process should be 0.5 h.

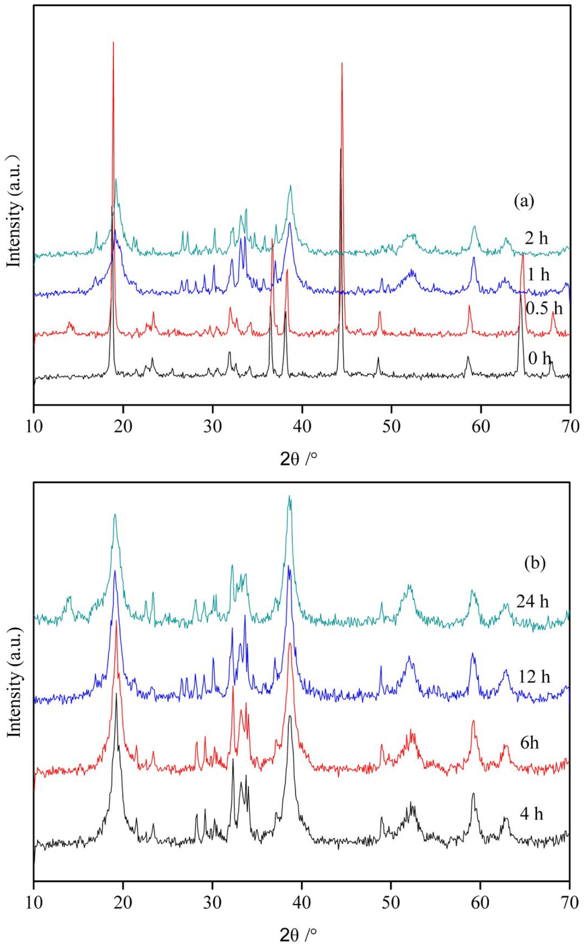

Fig. 4. XRD patterns of samples prepared at different grinding times (a) 0 h to 2 h samples and (b) 4 h to 24 h samples.

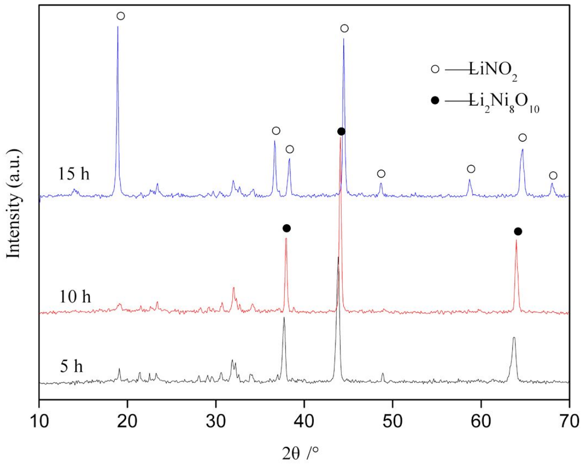

Fig. 5. XRD patterns of samples prepared by heat treatment for different time periods.

Fig. 5 shows the XRD patterns of the products prepared by heat treatment at 700 °C for different times. In Fig. 5 it is observed that a diffraction peak at 2-theta angle of 18.9° starts to evolve for 5 h annealed sample. More peaks are observed for the sample obtained after heat treatment time of 10 h. However, the main composition of the above two products is $Li_2Ni_8O_{10}$. For 15 h annealed sample, distinct peaks, which can be assigned to the characteristic peaks of $LiNiO_2$, can be observed. These results demonstrate that the optimal heat treatment time is 15 h.

Incorporation of lithium ion into an electrode depends on the morphological structure of cathode materials [4]. Therefore, morphological study of cathode materials for Li-ion batteries is essential. Fig. 6 shows the scanning electron microscope images of the product prepared at grinding speed of 580 rpm for 0.5 h, followed by heat treatment at 700 °C for 15. It is observed that the average diameter of $LiNiO_2$ particles is about 15 μm. In addition, single $LiNiO_2$ particle is a microsphere with a good mobility which consequently, improves the energy density of Li-ion batteries.

4. Conclusions

$LiNiO_2$ was prepared through two-step solid-state reaction method. The products were characterized by XRD and SEM. The results indicated that $LiNiO_2$ could be obtained by mechanochemical process at 580 rpm for 0.5 h, followed by heat treatment at 700 °C for 15 h, using $LiOH{\cdot}H_2O$ and $Ni(OH)_2{\cdot}H_2O$ as starting materials. The mechanochemical process can promote chemical reactions between these two materials leading to the preparation of $LiNiO_2$ which can be further improved by heat treatment process.

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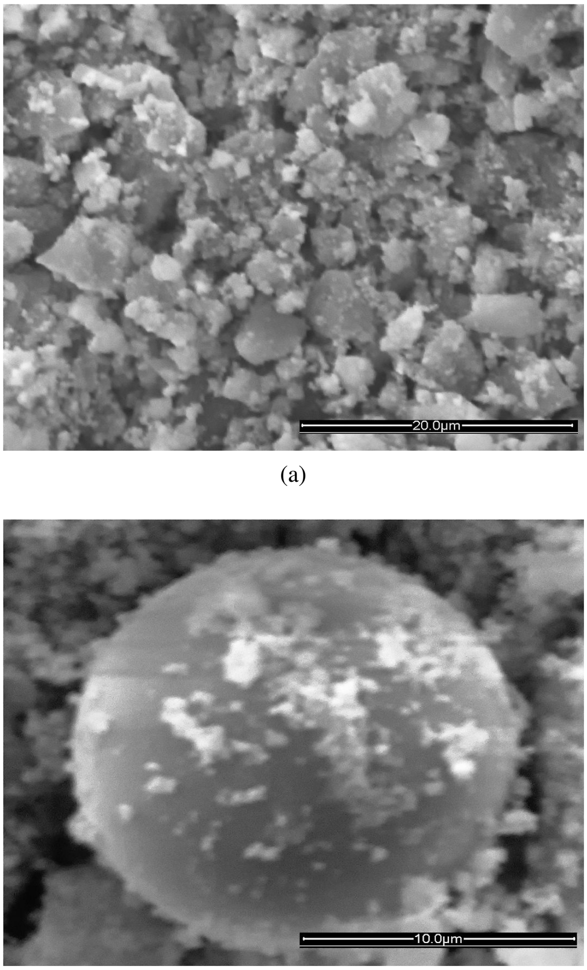

Fig. 6. SEM images of $LiNiO_2$ prepared by two-step solid-state method at different magnifications (a) several particles and (b) a single particle.

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