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Electrochemical properties of lithium nickel oxide synthesized by the combustion method in an O_2 stream

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Abstract

An appropriate mole ratio of urea/nitrate for preheating to synthesize $LiNiO_2$ was examined by varying the ratio from 1.2 to 9.6. The chemical equation of the combustion reaction was deduced from the XRD analysis result of the mixture after preheating. The XRD pattern of the $LiNiO_2$ sample calcined at 800 °C for 24 h, after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C, shows clear split of the 1 0 8 and 1 1 0 peaks, and the largest value of I_{003}/I_{104}. The sample calcined at 800 °C for 24 h has a relatively high first discharge capacity (164.2 mAh g^{-1}) and a good cycling performance. Derivative $-dx/|dV|$ vs. V curve of the $LiNiO_2$ sample at the voltage range of 2.7–4.4 V for the first cycle exhibits four peaks for charging and discharging, showing that this sample goes through four phase transitions.

Keywords: Lithium ion battery; $LiNiO_2$; Combustion method; Cation disordering

1. Introduction

Transition metal oxides such as $LiMn_2O_4$ [1–3], $LiCoO_2$ [4–6] and $LiNiO_2$ [7–16] have been investigated as potential cathode materials for lithium secondary batteries. $LiMn_2O_4$ is quite inexpensive and does not bring about environmental pollution, but its cycling performance is not good. $LiCoO_2$ has good conductivity and a high operating voltage, and it can be easily prepared. However, it has the disadvantage that it contains an expensive element Co. $LiNiO_2$ is a very promising cathode material since it has a large discharge capacity and is excellent from the viewpoints of economics and the environment. However, its preparation is very difficult as compared with $LiCoO_2$ and $LiMn_2O_4$.

It is known that $Li_{1-z}Ni_{1+z}O_2$ forms rather than the stoichiometric $LiNiO_2$ during preparation [13,17–19]. This phenomenon is called cation disordering. Excess nickel occupies the Li sites, destroying the ideally layered structure and preventing the easy movement of the lithium ions required for their intercalation and deintercalation during cycling. This results in a small discharge capacity and a poor cycling performance.

$LiNiO_2$ synthesized by the solid-state reaction method does not have a large discharge capacity and does not exhibit good cycling performance, probably because it has poor crystallinity, and a smaller fraction of the $LiNiO_2$ phase due to the presence of impurities. On the other hand, the homogeneous mixing of the starting materials can be accomplished by the combustion method, because in this method nitrates as starting materials and urea as a fuel are mixed in distilled water by a magnetic stirrer. This may lead to good crystallinity and a homogeneous particle size when the sample is synthesized.

Combustion synthesis is based on the field of propellants and explosives. Combustion synthesis is a chemical reaction between metal salts and a suitable organic fuel. The reaction accompanies an exothermic and self-sustaining chemical reaction [20]. Its processing feature is that an amount of initial heat is required to start the chemical reaction. Subsequently, the chemical reaction supplies the energy required for the materials to react with each other without the input of external energy [21].

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In this work, $LiNiO_2$ was synthesized by the combustion method in an O_2 stream. An appropriate mole ratio of urea/nitrate for preheating to synthesize $LiNiO_2$ was examined. The chemical equation of the combustion reaction was deduced from the XRD analysis result of the mixture after preheating. The optimum conditions to synthesize $LiNiO_2$ with the best electrochemical properties were investigated. The electrochemical properties such as discharge capacity and cycling performance, and phase transitions of the synthesized samples were then studied.

2. Experimental

In order to synthesize $LiNiO_2$ by the combustion method, lithium nitrate ($LiNO_3$, Aldrich Chemical, purity 98%) and nickel hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, Aldrich Chemical, purity 98%) were used as the starting materials. The starting materials, in the desired proportions, were mixed with urea (NH_2CONH_2, Aldrich Chemical, purity 98%) as a fuel by means of a magnetic stirrer. These mixed samples were preheated in air at 400 °C. For the synthesis of $LiNiO_2$ the preheated mixtures were then calcined in an O_2 stream at 700–850 °C for 6–36 h. The heating and cooling rates were about 100 °C h^{-1}.

The solution of the starting materials mixed with urea at the mole ratio of urea/nitrate of 3.6 was transparent green and viscous. Its color was changed into black as water evaporates. This black solution was preheated in air at 400 °C, resulting in combustion with flame. During combustion, gases were produced. This process ended in several seconds. Fig. 1 shows a photograph of $LiNiO_2$ precursor after combustion reaction at 400 °C. The $LiNiO_2$ precursor prepared likewise was in a form of powder.

The mixtures for the synthesis of $LiNiO_2$ were preheated in air at the mole ratios of urea/nitrate of 1.2–9.6. But the mixtures calcined after preheating only at the mole ratios of urea/nitrate of 2.4 and 3.6 could be collected to obtain XRD patterns. The mixture calcined after preheating at the mole ratio of 1.2 was not in the form of powder but in the form of a mixture not combusted. A very small amount of the mixture or no mixture remained in the crucible after preheating at the mole ratios of 4.8 or 9.6 and then calcining.

The phase identification of the synthesized samples was carried out by X-ray diffraction (XRD) analysis using Cu K_α radiation. A Rigaku III/A X-ray diffractometer was used. The scanning rate was 8° min^{-1} and the scanning range of the diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 80^\circ$. The morphologies of the samples were observed by a field emission-scanning electron microscope (FE-SEM).

To measure the electrochemical properties, electrochemical cells were constructed consisting of the prepared sample as the positive electrode, Li metal as the negative electrode, and 1 M $LiPF_6$ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. A Whatman glass fiber was used as a separator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, the active material, acetylene black and polyvinylidene fluoride (PVDF) binder dissolved in N-methyl-2-pyrrolidone (NMP) were mixed at a weight ratio of 85:10:5 and applied on Al foil. All the electrochemical tests were performed at room temperature with a battery charge–discharge cycle tester at the 0.1*C* rate in the voltage range between 2.7 V and 4.4 V.

3. Results and discussion

The XRD patterns of $LiNiO_2$ calcined at 800 °C for 12 h after preheating at the mole ratios of urea/nitrate of 2.4 and 3.6 at 400 °C are given in Fig. 2. The mixture calcined after preheating at the mole ratio of urea/nitrate of 2.4 contains a phase with an α-$NaFeO_2$ structure (space group: $R\bar{3}m$), and NiO phase as an impurity. However, the mixture calcined after preheating at the mole ratio of urea/nitrate of 3.6 has only a phase with an α-$NaFeO_2$ structure. By considering this result, the preheating of the mixture for the synthesis of $LiNiO_2$ was performed at the mole ratio of urea/nitrate of 3.6.

Fig. 1. Photograph of $LiNiO_2$ precursor after combustion reaction at 400 °C.

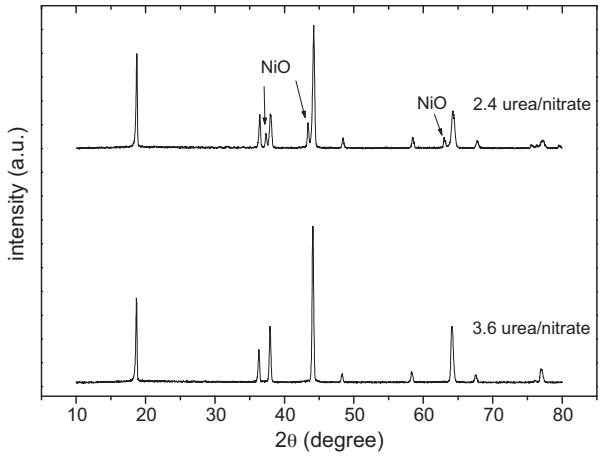

Fig. 2. XRD patterns of $LiNiO_2$ calcined at 800 °C for 12 h after preheating at the mole ratios of urea/nitrate of 2.4 and 3.6 at 400 °C.

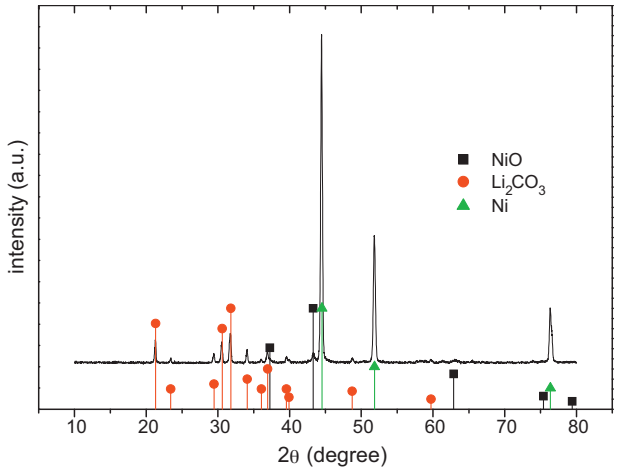

Fig. 3. XRD patterns of $LiNiO_2$ precursor after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C.

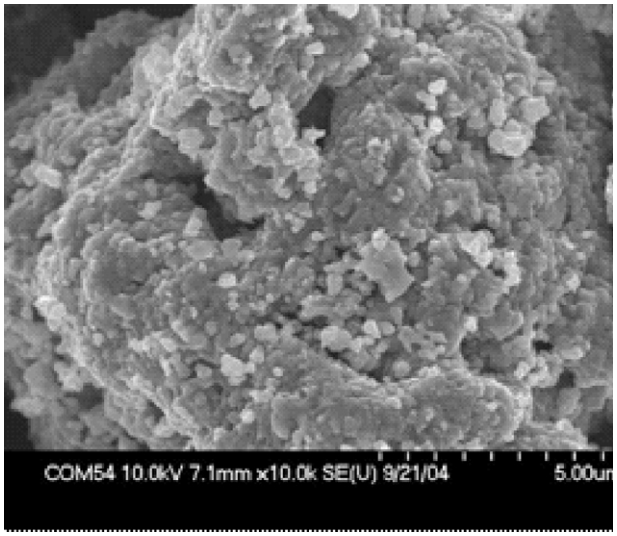

Fig. 5. FE-SEM photograph of $LiNiO_2$ calcined at 700 °C for 6 h.

Fig. 3 presents the XRD patterns of $LiNiO_2$ precursor after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C. The $LiNiO_2$ precursor contains Li_2CO_3, NiO and Ni. The combustion reaction of urea is written by the following equation:

$$CO(NH_2)_2 + 1.5O_2 \rightarrow CO_2 + 2H_2O + N_2 \quad (1)$$

Since the $LiNiO_2$ precursor contains Li_2CO_3, NiO and Ni, the combustion reaction can be written as follows:

$$LiNO_3 + Ni(NO_3)_2{\cdot}6H_2O + mCO(NH_2)_2 + 1.5mO_2 \rightarrow 0.5Li_2CO_3 + (1-n)NiO + nNi + (2m+6)H_2O + (m+1.5)N_2 + ((15+2n)/4)O_2 + (m-0.5)CO_2 \quad (2)$$

where m and n are the number of moles for the added urea and the produced nickel, respectively.

The FE-SEM photograph of $LiNiO_2$ precursor after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C is shown in Fig. 4. The $LiNiO_2$ precursor has large particles with nano-sized particles of smaller than 50 nm on their surfaces. Fig. 3 shows that the $LiNiO_2$ precursor contained Li_2CO_3, NiO and Ni, the peaks of Ni being much stronger than other phases. XRD pattern exhibits more strongly the peaks coming from the surface of samples. It is believed that the nano-sized particles consist of Ni and the large particles contain all of the Li_2CO_3, NiO and Ni phases.

Fig. 5 shows the FE-SEM photograph of $LiNiO_2$ calcined at 700 °C for 6 h. The sample has quite small spherical particles which are agglomerated.

Ohzuku et al. [22] reported that the electrochemically reactive $LiNiO_2$ showed a larger integrated intensity ratio of 0 0 3 peak to 1 0 4 peak (I_{003}/I_{104}) and a clear split of the 1 0 8 and 1 1 0 peaks in their XRD patterns. The degree of cation mixing (displacement of nickel and lithium ions) is low if the value of I_{003}/I_{104} is large and the 1 0 8 and 1 1 0 peaks are split clearly. The cation mixing in layered materials makes sliding between basal planes impossible, resulting in the electrochemical inactivity of the materials. The value of $(I_{006} + I_{102})/I_{101}$, called the R-factor, is known to be smaller as the unit cell

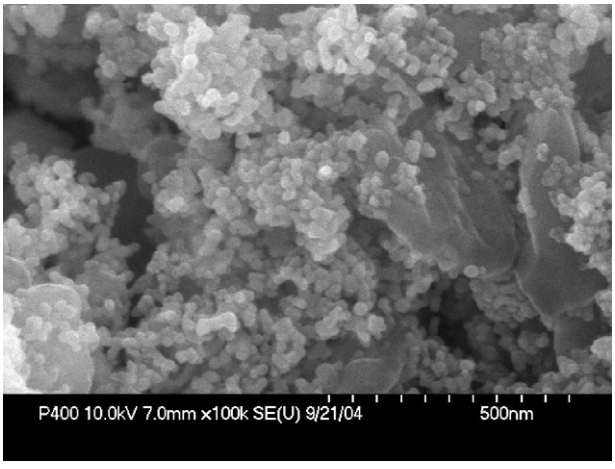

Fig. 4. FE-SEM photograph of $LiNiO_2$ precursor after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C.

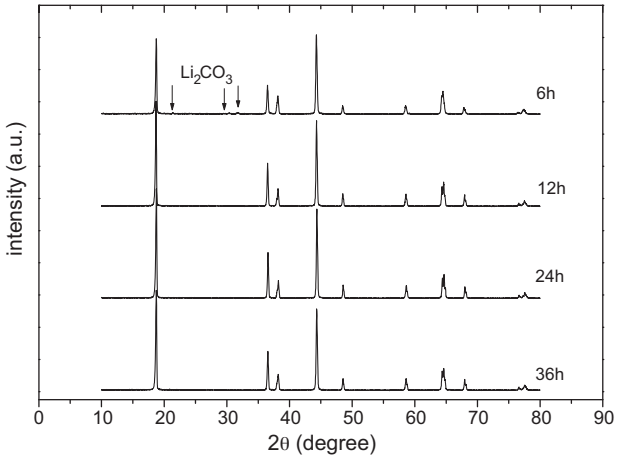

Fig. 6. XRD patterns of $LiNiO_2$ calcined at 800 °C for various times after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C.

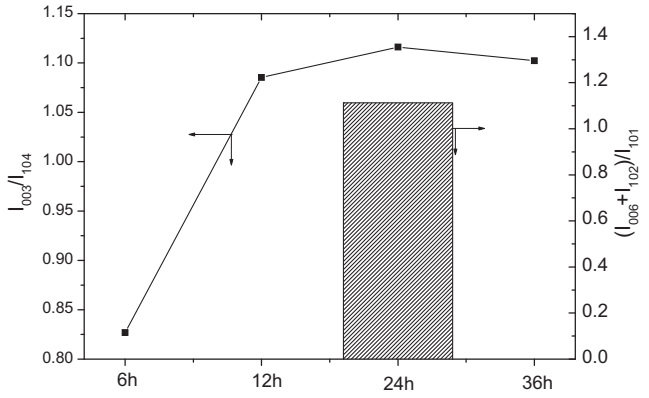

Fig. 7. Variations of I_{003}/I_{104} and $(I_{006} + I_{102})/I_{101}$ values with calcination time at 800 °C for the synthesized $LiNiO_2$.

volume of $Li_yNi_{2-y}O_2$ gets smaller. The *R*-factor increases as *y* in $Li_yNi_{2-y}O_2$ decreases for *y* near 1. This indicates that the *R*-factor increases as the degree of cation mixing becomes larger [7].

The XRD patterns of $LiNiO_2$ calcined at 800 °C for various times after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C are shown in Fig. 6. The sample calcined for 6 h contains a phase with an α-$NaFeO_2$ structure, and Li_2CO_3 as an impurity. The samples calcined for 12 h, 24 h and 36 h have only the phase with an α-$NaFeO_2$ structure. In the sample calcined for 6 h, the 1 0 8 and 1 1 0 peaks are not split clearly. But in the samples calcined for 12 h, 24 h and 36 h, separation of these peaks is observed. The sample calcined for 24 h exhibit the clearest split of the peaks.

Fig. 7 gives the variations of I_{003}/I_{104} and $(I_{006} + I_{102})/I_{101}$ values with calcination time at 800 °C for the synthesized $LiNiO_2$. The value of I_{003}/I_{104} increases rapidly as the calcination time becomes longer from 6 h to 12 h. It is largest at the calcination time of 24 h and then it decreases at the calcination time of 36 h. The value of $(I_{006} + I_{102})/I_{101}$, called *R*-factor, could be calculated for the sample calcined for 24 h. The variation of the I_{003}/I_{104} value with the calcination time shows that the sample calcined for 24 h may have the best electrochemical properties.

The FE-SEM photographs of $LiNiO_2$ calcined at 800 °C for various times are presented in Fig. 8. The sample calcined for 6 h has the smallest particles. The samples calcined for 12 h, 24 h and 36 h have much larger particles than those of the sample calcined for 6 h. The sample calcined for 12 h consists of the particles of 2–3 μm with sharp edges. The sample calcined for 24 h has spherical particles with rounded edges. The sample calcined for 36 h has a little smaller particles than those of the samples calcined for 12 h and 24 h.

Fig. 9 gives the variations, with the number of cycles, of the discharge capacity at 0.1*C* rate in the voltage range between 2.7 V and 4.4 V for the $LiNiO_2$ sample calcined at 800 °C for various times. The first discharge capacities were 135.5, 179.1, 164.2, and 167.1 mAh g^{-1} for the samples calcined for 6, 12, 24 and 36 h, respectively, with the sample calcined for 12 h having the highest first discharge capacity. The sample calcined for 36 h has the second highest first discharge capacity but shows the worst cycling performance. The sample calcined for 6 h has the lowest first discharge capacity but shows the best cycling performance. The sample calcined for 24 h has a relatively high first discharge capacity (164.2 mAh g^{-1}) and a good cycling performance.

The variation of $-dx/|dV|$ with voltage *V* reveals phase transition voltages, where *x* is the *x* in Li_xNiO_2 during charging

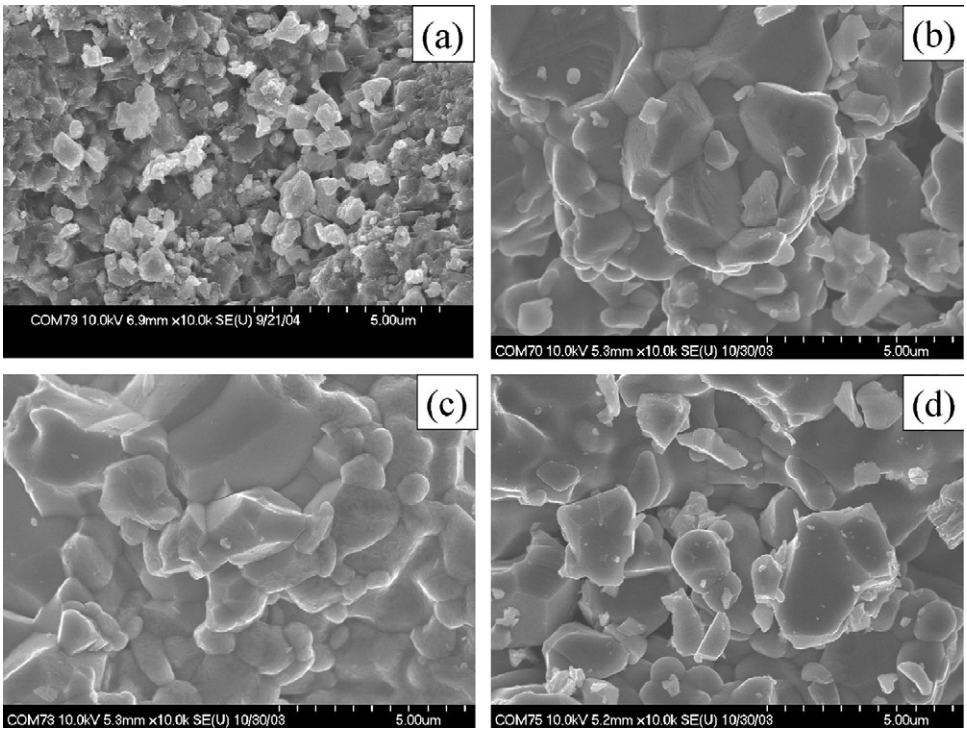

Fig. 8. FE-SEM photographs of $LiNiO_2$ calcined at 800 °C for (a) 6 h, (b) 12 h, (c) 24 h, and (d) 36 h.

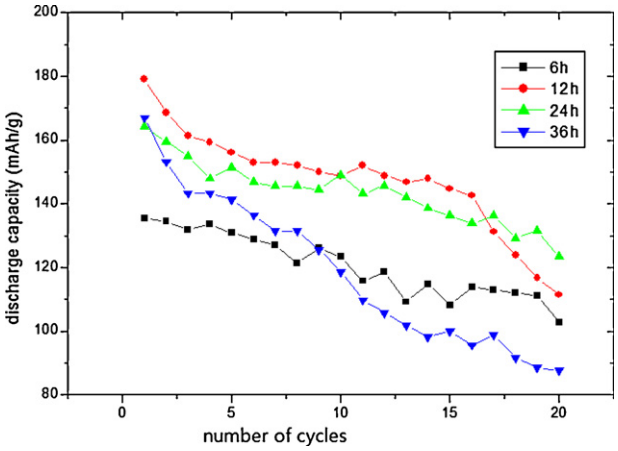

Fig. 9. Variations, with the number of cycles, of the discharge capacity for the $LiNiO_2$ calcined at 800 °C for various times.

and discharging. The sharp peak corresponds to a phase transition at which two phases co-exist and the broad peak corresponds to a phase transition at which one-phase changes continuously [23]. Arai et al. [18] reported that, during charging and discharging, $LiNiO_2$ goes through three phase transitions such as phase transitions from hexagonal structure (H1) to monoclinic structure (M), from monoclinic structure (M) to hexagonal structure (H2), and from hexagonal structure (H2) to hexagonal structure (H3) or vice versa. Ohzuku et al. [22] reported that, during charging and discharging, $LiNiO_2$ goes through four phase transitions such as phase transitions from H1 to M, from M to H2, from H2 to hexagonal structures H2 + H3, and from H2 + H3 to H3 or vice versa. Derivative $-dx/|dV|$ vs. V curve of the $LiNiO_2$ sample at the voltage range of 2.7–4.4 V for the first cycle is presented in Fig. 10. This sample exhibits three peaks for charging curve and four peaks for discharging curve. However, the charging curve has a broad peak between the sharp first and third peaks. Thus during charging and discharging, this sample goes through four phase transitions from H1 to M, from M to H2, from H2 to hexagonal

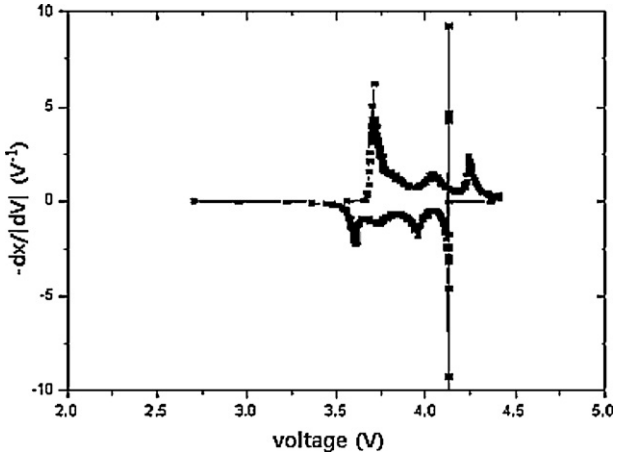

Fig. 10. Derivative $-dx/|dV|$ vs. V curve, where x denotes the value of x in Li_xNiO_2, of the $LiNiO_2$ sample at the voltage range of 2.7–4.4 V for the first cycle.

structures H2 + H3, and from H2 + H3 to H3 or vice versa. During discharging, phase transitions occur at 4.12 V (from H3 to H2 + H3), 3.95 V (from H2 + H3 to H2), 3.72 V (from H2 to M), and 3.60 V (from M to H1).

4. Conclusions

The mixture calcined after preheating at the mole ratio of urea/nitrate of 3.6 has only a phase with an α-$NaFeO_2$ structure. The combustion reaction can be written as:

$$LiNO_3 + Ni(NO_3)_2{\cdot}6H_2O + mCO(NH_2)_2 + 1.5mO_2 \rightarrow 0.5Li_2CO_3 + (1-n)NiO + nNi + (2m+6)H_2O + (m+1.5)N_2 + ((15+2n)/4)O_2 + (m-0.5)CO_2$$

where m and n are the number of moles for the added urea and the produced nickel, respectively. The XRD pattern of the $LiNiO_2$ sample calcined at 800 °C for 24 h, after preheating at the mole ratio of urea/nitrate of 3.6 at 400 °C, shows clear split of the 1 0 8 and 1 1 0 peaks, and the largest value of I_{003}/I_{104}. The sample at 800 °C calcined for 24 h has a relatively high first discharge capacity (164.2 mAh g^{-1}) and a good cycling performance. During discharging of the $LiNiO_2$ sample, phase transitions occur four times at 4.12, 3.95, 3.72, and 3.60 V.

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