Synthesis of LiNiO$_2$ cathode by the combustion method

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Abstract

To determine optimum conditions for the synthesis of LiNiO$_2$ by the combustion method, syntheses were carried out in air and under oxygen at various calcination temperatures and for different times. The electrochemical properties of the prepared samples were then investigated. The optimum conditions are preheating at 400 °C for 30 min in air in the mole ratio of urea to nitrate 3.6 and calcination at 750 °C for 36 h under O$_2$. The LiNiO$_2$ synthesized under these conditions had a first discharge capacity of 189 mAh g^{-1} at 0.1 C-rate and relatively good cycling performance. This sample has a larger value of I_{003}/I_{104} (smaller cation mixing) and a smaller R-factor (larger hexagonal ordering). Cycling performance was investigated in various voltage ranges. The first discharge capacity increased as the upper limit of the voltage range rose. The first discharge capacity was small but cycling performance was good when the sample was cycled in the voltage range with the lowest upper limit.

1. Introduction

The transition metal oxides such as LiMn$_2$O$_4$ [1–3], LiCoO$_2$ [4–6] and LiNiO$_2$ [7–10] have been investigated as the cathode materials for lithium secondary batteries. LiMn$_2$O$_4$ is very cheap and does not bring about environmental pollution, but its cycling performance is not good. LiCoO$_2$ has a large diffusivity and a high operating voltage and 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 high discharge capacity [11] and is relatively good from cost and environmental perspectives. On the other hand, its preparation is very difficult as compared with LiCoO$_2$ and LiMn$_2$O$_4$.

LiNiO$_2$ synthesized by the solid-state reaction method does not have a high discharge capacity and has poor cycling performance, probably because it has poor crystallinity and non-uniform particle size. On the other hand, homogeneous mixing of the starting materials is possible in the combustion method because the starting materials are liquid. This may lead to good crystallinity and uniform particle size.

In this work the combustion method was employed to synthesize LiNiO$_2$ as a cathode material with high discharge capacity. Syntheses were carried out in air and under oxygen at various calcination temperatures and for different times to determine the optimum conditions for synthesis.

2. Experimental

In order to synthesize LiNiO$_2$ by the combustion method, lithium nitrate (LiNO$_3$, Aldrich chemical) and nickel hexahydrate (Ni(NO$_3$)$_2$· 6H$_2$O, Aldrich chemical) were used as starting materials. The starting materials of the desired composition were mixed with urea in a mole ratio of urea to nitrate 3.6 homogeneously by a magnetic stirrer. These mixed samples were preheated at 400 °C for 30 min in air, and then calcined at 700–850 °C for 6–48 h in air and under oxygen. The heating and cooling rates were about 100 °C h^{-1}. The samples prepared by preheating and calcination in air exhibited impurity peaks in X-ray diffraction (XRD) patterns and lower discharge capacities than the samples prepared by preheating in air and calcination under oxygen. Therefore we prepared the sample by preheating in air and calcination under oxygen.

The phase identification of the synthesized samples was carried out by X-ray diffraction analysis using CuK$_\alpha$ radiation. A Rigaku III/A X-ray diffractometer was used. The scanning rate was 8 °C min^{-1} and the scanning range of diffraction angle (2θ) was 10° ≤ 2θ ≤ 80°. The morphologies of the samples were observed by a field emission-scanning electron microscope (FE-SEM). To measure the electrochemical properties, the cells consisted of the prepared sample as a positive electrode, Li metal as a negative electrode and an electrolyte of 1 M LiPF$_6$ in a 1:1 (volume ratio) mixture of ethylene

carbonate (EC) and diethyl carbonate (DEC). A Whatman glass fiber was used as separator. The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, active material, acetylene black and polyvinylidene fluoride (PVDF) binder with N-methyl-2-pyrrolidone (NMP) were mixed in a weight ratio 85:10:5 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 a potential range from 2.7 to 4.4 V.

3. Results and discussion

Figure 1 gives the X-ray powder diffraction patterns of $LiNiO_2$ calcined at 700 °C for 6 h and at 750–850 °C for 12 h under O_2, after preheating at 400 °C for 30 min in air. The sample calcined at 700 °C for 6 h had the phase with $R\bar{3}m$ structure and impurities (Li_2CO_3 and NiO). The samples calcined at 750–850 °C for 12 h had only the phase with $R\bar{3}m$ structure, and their X-ray powder diffraction patterns were similar.

Figure 2 shows the FE-SEM photographs of $LiNiO_2$ calcined at 750–850 °C for 12 h. The particles of the sample calcined at 750 °C had small spherical shape with uniform size. The particles of the sample calcined at 800 °C were of 2–3 μm size with smaller particles attached to them. The particles of the sample calcined at 800 °C were larger than those of the sample calcined at 750 °C. The particles of the sample calcined at 850 °C
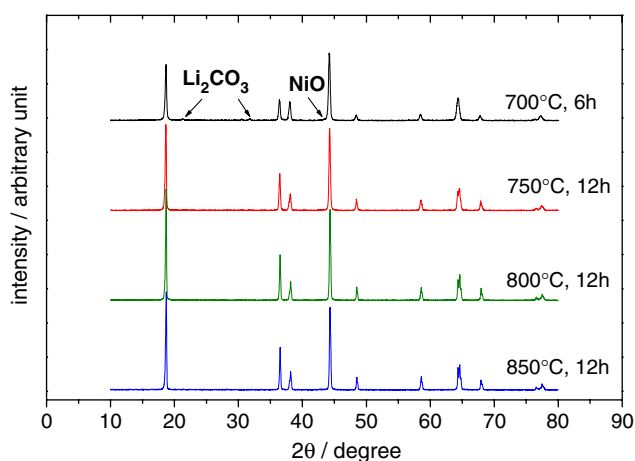
had the largest size, and the particles were rounded. The particles calcined at 850 °C were clustered. As the calcination temperature rose, the particles grew. Above 800 °C, the particles grew very rapidly.

Figure 3 gives the X-ray diffraction (XRD) patterns of $LiNiO_2$ calcined at various times at 750 °C. All the samples had the phase with $R\bar{3}m$ structure. The $R\bar{3}m$ structure is distorted in the c-axis direction. This is reflected by the split of 006 and 102 peaks, and of 108 and 110 peaks in the XRD patterns. The 108 and 110 peaks were split for all the samples, but the 006 and 102 peaks were split only for the samples calcined for 24 and 36 h.

Figure 4 gives variations of the ratios of XRD peak intensities (I) with calcination time at 750 °C for the $LiNiO_2$ synthesized by the combustion method. It is generally known that the cation mixing is small if the intensity ratio of the 003 peak to the 104 peak (I_{003}/I_{104}) is large. The cation mixing has strong influences on the electrochemical properties. The value of I_{003}/I_{104} increases as the calcination time becomes longer from 12 to 36 h, and then it decreases at the calcination time 48 h. The value of $(I_{006} + I_{102})/I_{101}$, called the R-factor, is known to be smaller when the hexagonal ordering is high. The sample calcined for 36 h has a smaller R-factor than that calcined for 24 h.

Figure 5 shows the FE-SEM photographs of the $LiNiO_2$ calcined for various times at 750 °C. The sample calcined for 12 h has the smallest and the most uniform particles. The particle size increases as the calcination time becomes longer from 24 to 48 h. The sample calcined for 48 h was agglomerated.

Figure 6 gives the variations, with the number of cycles, of the discharge capacity for the $LiNiO_2$ calcined for various times. The discharge capacity was calculated on the basis of the mass of the used active cathode material $LiNiO_2$. The first discharge capacities were 183, 189 and 170 mAh g^{-1} for the samples calcined for 24, 36 and 48 h, respectively. The sample calcined for 48 h has the lowest first discharge capacity and that calcined for 36 h has the highest. From the 13th cycle, the discharge capacity of the sample calcined for 24 h becomes smaller than that of the sample calcined for 48 h. The sample calcined for 36 h has higher discharge capacity than the other samples from the first cycle through the 20th cycle, and has relatively good cycling performance. This agrees well to the points that this sample has a larger value of
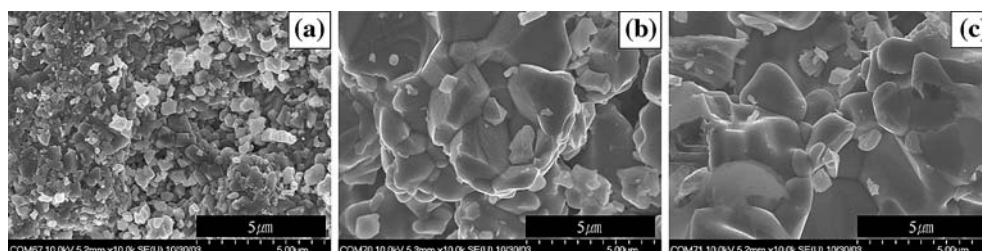

Fig. 1. XRD patterns of $LiNiO_2$ calcined at various temperatures for 6 and 12 h.

Fig. 2. FE-SEM photographs of $LiNiO_2$ calcined at various temperatures for 12 h; (a) 750 °C, (b) 800 °C and (c) 850 °C.

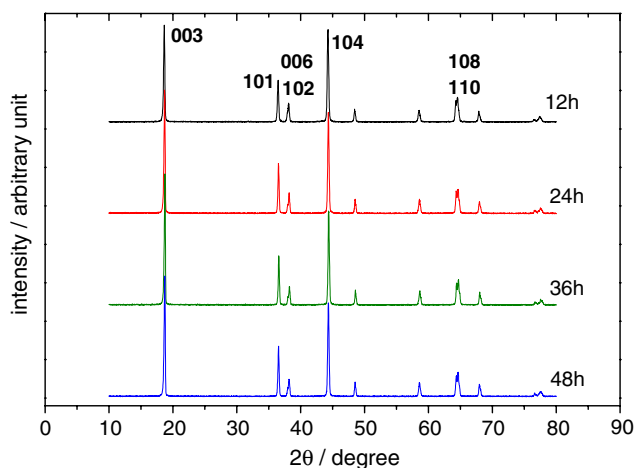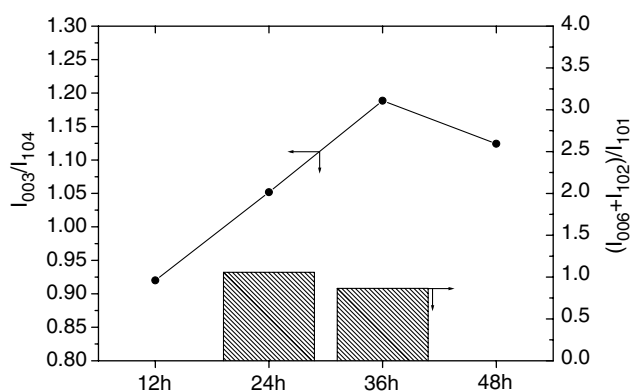I_{003}/I_{104} (smaller cation mixing) and a smaller R-factor (larger hexagonal ordering) than the other samples.

These results suggest that the optimum temperature and time to synthesize $LiNiO_2$ by the combustion method are 750 °C and 36 h, respectively.

Figure 7 shows the variations of discharge capacity with number of cycles in the various voltage ranges (2.7–4.2, 2.7–4.3, 2.7–4.4 and 2.7–4.9 V) for the $LiNiO_2$ calcined at 750 °C for 36 h. The first discharge capacity increases as the upper limit voltage of the voltage range rises. The first discharge capacities are 146, 165, 189 and 209 mAh g^{-1}, respectively, in these voltage ranges. The higher the upper limit of the voltage range, the higher the discharge capacity through all the cycles.

Figure 8 shows the variations, with the number of cycles, of the discharge capacities of $LiNiO_2$ synthesized by the combustion method (voltage range 2.7–4.4 V, 0.1 C-rate) of this work, by the sol–gel method (voltage range 3.0-4.2 V, 0.05 C-rate) [12], and by the solid-state reaction method (voltage range 2.8–4.3 V, 0.1 C-rate) [13]. The $LiNiO_2$ synthesized by the combustion method has the highest first discharge capacity (189 mAh g^{-1}), followed in order by electrodes synthesized by the sol–gel method (169 mAh g^{-1}) and by the solid-state reaction method (145 mAh g^{-1}). From the fourth cycle the $LiNiO_2$ synthesized by the sol–gel method has higher discharge capacity than that by the combustion method, but they have similar cycling performance from the fourth cycle. The $LiNiO_2$ synthesized by the solid-state reaction method has the lowest discharge capacity than those synthesized by the other methods, and shows bad cycling performance. The small discharge capacity and the bad cycling performance of $LiNiO_2$ synthesized by the solid-state reaction method are considered to result from bad crystallinity and poor uniformity of particle
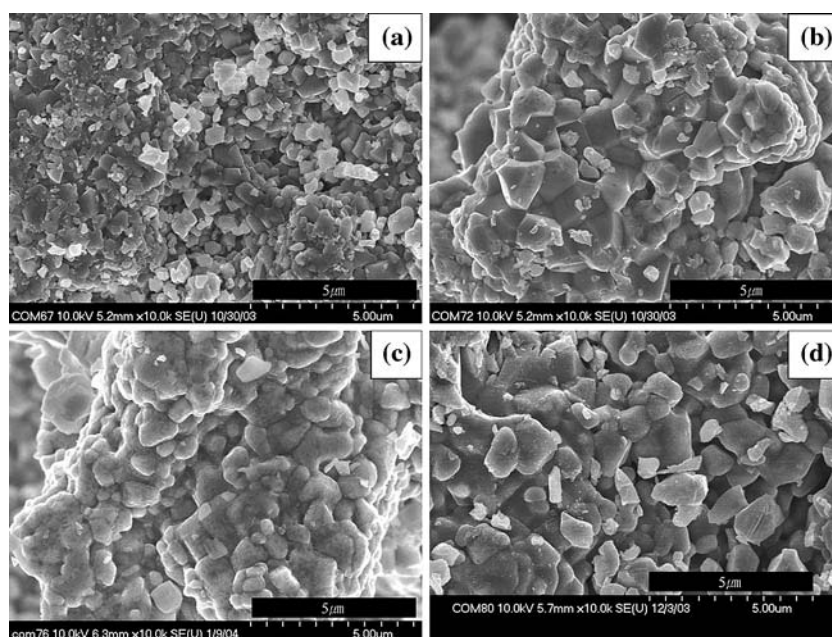

Fig. 3. XRD patterns of $LiNiO_2$ calcined at various times at 750 °C.

Fig. 4. Variations of the ratios of XRD peak intensities for $LiNiO_2$ with calcination times at 750 °C.

Fig. 5. FE-SEM photographs of $LiNiO_2$ calcined for various times at 750 °C; (a) 12 h, (b) 24 h, (c) 36 h and (d) 48 h.
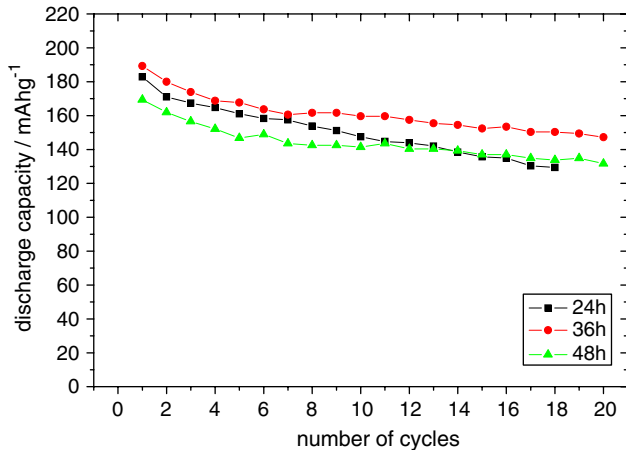
Fig. 6. Variations, with the number of cycles, of the discharge capacity, for LiNiO$_2$ calcined for various times.
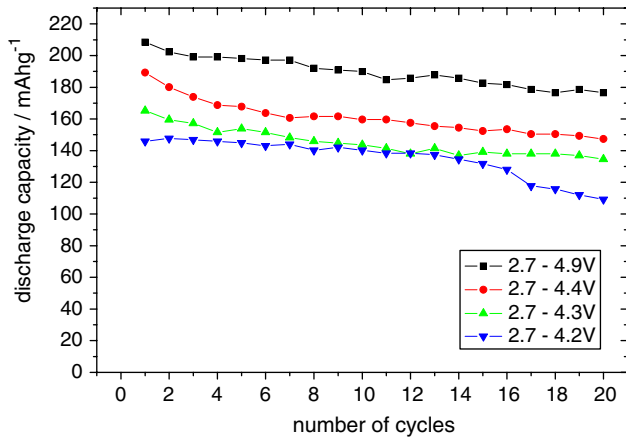

Fig. 7. Variations of the discharge capacity with the number of cycles in the various voltage ranges for LiNiO$_2$ calcined at 750 °C for 36 h.
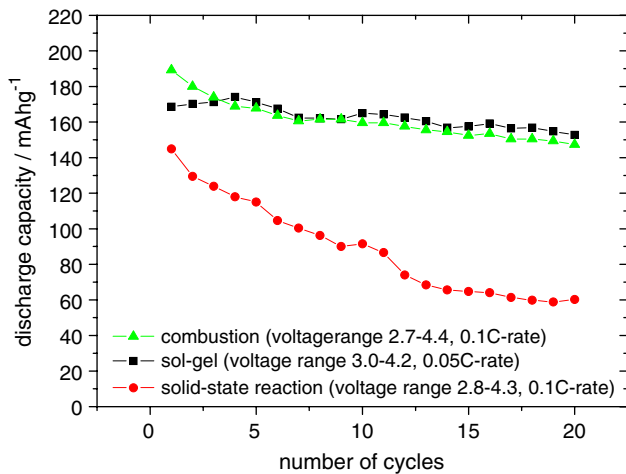

Fig. 8. variations, with the number of cycle, of the discharge capacity of LiNiO$_2$ synthesized by combustion method, sol–gel method and solid-state reaction method.

size. Since the voltage ranges and the C-rates are different, a direct comparison is not possible. However, it is considered that the LiNiO$_2$ electrode synthesized by the combustion method has the highest first discharge capacity, relatively high discharge capacity and relatively good cycling performance.

Figure 9 shows the variation of $-dx/|dv|$ for the first cycle as a function of voltage for the LiNiO$_2$ samples synthesized by the combustion method (of this work), the sol–gel method and the solid-state reaction method. Here x is the value of x in Li$_x$NiO$_2$ during charging and discharging. The peaks correspond to the voltage at which phase transitions occur during charging or discharging. The voltages of the peaks are related to the voltages of plateaus of the voltage vs. x in Li$_x$NiO$_2$ during charging or discharging. The voltages of the peaks for discharging of LiNiO$_2$ synthesized by the combustion method are 4.12, 3.95 and 3.60 V. Those of LiNiO$_2$ synthesized by the sol–gel method are 4.15, 3.96 and 3.61 V. LiNiO$_2$ synthesized by the solid-state reaction method exhibits a clear peak at 3.61 V, but the peak near 3.95 V is not clear and no peak can be found near 4.12 V. This is probably related to the lower discharge capacity of the LiNiO$_2$ sample synthesized by the solid-state reaction method. The peaks for LiNiO$_2$ synthesized by the combustion method and the sol–gel method are more prominent than those for LiNiO$_2$ synthesized by the solid-state reaction method. This is also considered to be related to the charge and discharge capacities of the samples.

4. Conclusions

The optimum conditions for the synthesis of LiNiO$_2$ by the combustion method are preheating at 400 °C for 30 min in air in the mole ratio of urea to nitrate 3.6 and calcination at 750 °C for 36 h under O$_2$. The LiNiO$_2$ synthesized under these conditions had a first discharge capacity of 189 mAh g^{-1} at the 0.1 C-rate and relatively
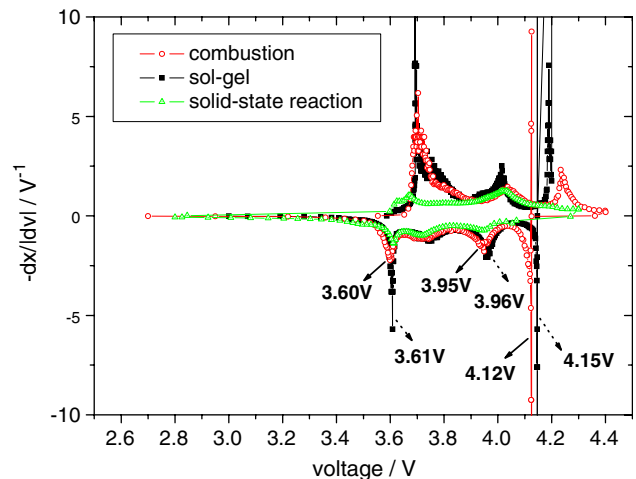

Fig. 9. Variation of $-dx/|dv|$ for the first cycle as a function of voltage for LiNiO$_2$ synthesized by combustion method (of this work), sol–gel method and solid-state reaction method.

good cycling performance. This sample has a larger value of I_{003}/I_{104} (smaller cation mixing) and a smaller R-factor (larger hexagonal ordering). Cycling performance was investigated in various voltage ranges. The first discharge capacity increased as the upper limit of the voltage range rose. The first discharge capacity was small but cycling performance was good when the sample was cycled in the voltage range with the lowest upper limit.

Acknowledgement

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