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Effects of cathode fabrication conditions and cycling on the electrochemical performance of $LiNiO_2$ synthesized by combustion and calcination

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Abstract

$LiNiO_2$ was synthesized by the combustion method with various excess lithium amount z in $Li_{1+z}NiO_2$ ($z = 0.04$, 0.08, 0.10, 0.12, and 0.15). The sample with $z = 0.10$ has the largest first discharge capacity of 195 mAh/g at 0.1 C rate and voltage range 2.7–4.4 V with the weight ratio of active material:acetylene black:binder = 85:10:5. The $LiNiO_2$ cathodes, in which the excess lithium amount z for the synthesis of $LiNiO_2$ was 0.10, were fabricated with various weight ratios of active material:acetylene black:binder (85:10:5, 85:12:3, and 90:7:3). The cathode with the ratio of active material:acetylene black:binder 85:10:5 has the best electrochemical properties. The variation, with C-rate, of discharge capacity vs. number of cycles curve for the $LiNiO_2$ cathode with the weight ratio of active material:acetylene black:binder = 85:10:5 was investigated. At 0.1 C rate, the $LiNiO_2$ cathode has the largest first discharge capacity, the discharge capacity degradation rate of 0.70 mAh/g/cycle and a discharge capacity at $n = 50$ of 134 mAh/g.

Keywords: $LiNiO_2$; Combustion method; Discharge capacity; Cathode fabrication conditions; $I_{0\,0\,3}/I_{1\,0\,4}$; R-factor

1. Introduction

Transition metal oxides such as $LiMn_2O_4$ [1–3], $LiCoO_2$ [4–6], and $LiNiO_2$ [7–10] have been intensively investigated for their use as cathode materials of lithium secondary batteries. $LiMn_2O_4$ is comparatively inexpensive and does not bring about any environmental pollution, but its cycling performance is not adequate. $LiCoO_2$ has a large diffusivity and a high operating voltage, and it can be easily prepared. However, it has the disadvantage that it contains Co, an expensive element. $LiNiO_2$ is a very promising cathode material since it has a large discharge capacity [11] and is excellent from the economic and environmental viewpoints. On the other hand, its preparation is very difficult compared with $LiCoO_2$ and $LiMn_2O_4$.

It is known that nonstoichiometric $Li_{1-x}Ni_{1+x}O_2$ forms rather than the stoichiometric $LiNiO_2$ during preparation [12] due to cation mixing. Excess nickel occupies the Li sites, destroying the ideally layered structure and preventing the lithium ions from undergoing the easy movement required for intercalation and deintercalation during cycling. This results in a small discharge capacity and poor cycling performance.

$LiNiO_2$ 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 distribution. 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 distribution.

In this work, $LiNiO_2$ was synthesized by the combustion method with various excess lithium amount z in $Li_{1+z}NiO_2$. The $LiNiO_2$ cathodes were fabricated with various weight ratios of active material:acetylene black:binder, and their electrochemical properties were investigated.

2. Materials and methods

The optimum conditions to synthesize $LiNiO_2$ by the combustion method, studied in our previous work [13], were preheating at 400 °C for 30 min in air and calcination at 750 °C

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for 36 h in an O_2 stream. $LiNiO_2$ was synthesized under these conditions. Aldrich Chemical's $LiNO_3$ and $Ni(NO_3)_2{\cdot}6H_2O$ were used as starting materials. Excess lithium was added to compensate for the evaporated lithium during preparation. The excess lithium amount z in $Li_{1+z}NiO_2$ was 0.04, 0.08, 0.10, 0.12, and 0.15. The starting materials, in the desired proportions, were mixed with urea by a magnetic stirrer. The mole ratio of urea to nitrate was 3.6. The heating rate and the cooling rate were about 100 °C/h. The phase identification of the synthesized samples was carried out by the X-ray powder diffraction analysis (Rigaku D/MAX 2500 powder diffractometer) using Cu Kα radiation, scanning rate of 6 °/min and diffraction angle 2θ of $10^\circ \leq 2\theta \leq 80^\circ$. The electrochemical cells consisted of $LiNiO_2$ as a positive electrode, Li foil as a negative electrode, and an electrolyte [Purelyte (Samsung General Chemicals Co., Ltd.)] prepared by dissolving 1 M $LiPF_6$ in an 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The positive electrode consisted of synthesized materials, acetylene black, and polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidinone (NMP) with weight ratios of 85:10:5, 85:12:3, and 90:7:3. A Whatman glass-filter was used as a separator. The coin-type (2016) cells were assembled in an argon-filled dry box. All of the electrochemical tests were performed at room temperature with a potentiostatic/galvanostatic system. The cells were cycled between 2.7 and 4.4 V at the rates of 0.1 C, 0.2 C, and 0.5 C.

3. Results and discussion

Fig. 1 shows the 1st and 2nd charge–discharge curves of $LiNiO_2$ synthesized with excess lithium $z = 0.08$ at 0.1 C rate in a voltage range of 2.7–4.4 V. This $LiNiO_2$ cathode was fabricated with a weight ratio of active material:acetylene black:binder = 85:10:5. The lengths of plateaus in the charge and discharge curves are proportional to charge and discharge capacities. The first charge capacity is quite larger than the first discharge capacity, which is revealed by the difference in x of the first charge and discharge curves. The charge and discharge curves exhibit several plateaus in the charge and discharge curves. This indicates that phase transitions occur at several different voltages in the electrode with $z = 0.08$.

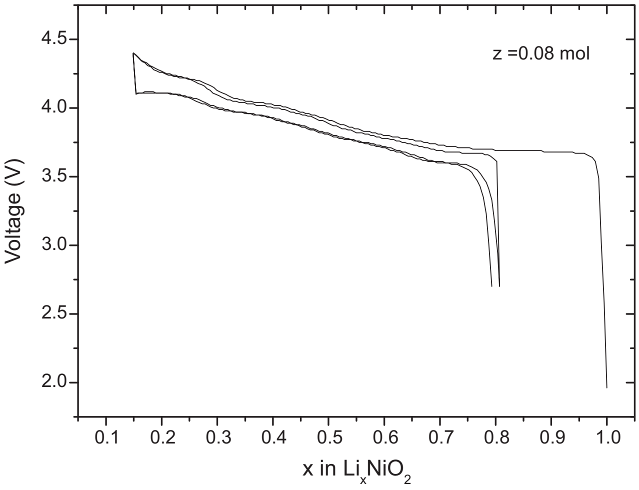

Fig. 1. The 1st and 2nd charge–discharge curves of $LiNiO_2$ synthesized with excess lithium $z = 0.08$ (0.1 C rate, voltage range 2.7–4.4 V, weight ratio of active material:acetylene black:binder = 85:10:5).

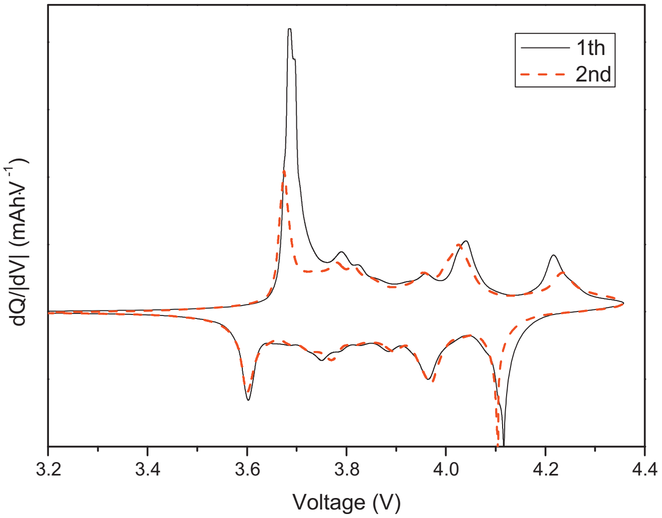

Fig. 2. dQ/|dV| vs. V curves of the 1th and 2nd charge–discharge cycles for $LiNiO_2$ synthesized with excess lithium $z = 0.08$.

dQ/|dV| vs. V curves of the 1th and 2nd charge–discharge cycles for $LiNiO_2$ synthesized with the amount of excess lithium $z = 0.08$ are presented in Fig. 2. Here Q is the charge capacity and V is the voltage. It is reported that phase transitions occur from a hexagonal structure phase to a monoclinic structure phase or vice versa, and from a hexagonal structure phase to another hexagonal structure phase or vice versa during charging and discharging of $LiNiO_2$ [14–16]. The dQ/|dV| vs. V curves show several peaks, indicating that phase transitions occur at several different voltages in the electrode with $z = 0.08$.

The variation of discharge capacity vs. number of cycles n curve with the amount of excess lithium z ($z = 0.04$, 0.08, 0.10, 0.12, and 0.15) for the synthesis of $LiNiO_2$ (0.1 C rate, voltage range 2.7–4.4 V, and weight ratio of active material:acetylene black:binder = 85:10:5) is shown in Fig. 3. The excess lithium z corresponds to the value of z in $Li_{1+z}NiO_2$. The sample with $z = 0.10$ has the largest first discharge capacity (195 mAh/g at a rate of 0.1 C), and the discharge capacity of 155 mAh/g at $n = 25$. It shows relatively good cycling performance with the discharge capacity degradation rate of 1.56 mAh/g/cycle. The first discharge capacity decreases in the order of $z = 0.08$, 0.12, 0.15, and 0.04. The samples with $z = 0.08$, 0.10, 0.12, and 0.15 have similar cycling performances. The sample with $z = 0.04$ has the smallest first discharge capacity (158 mAh/g), but has the best cycling performance with the discharge capacity degradation rate of 0.54 mAh/g/cycle.

Fig. 4 presents the variation of the discharge capacity at 0.1 C rate with the number of cycles for the $LiNiO_2$ cathodes with various weight ratios of active material:acetylene black:binder (voltage range 2.7–4.4 V). The excess lithium amount z for the synthesis of $LiNiO_2$ was 0.10. The sample with the weight ratio of active material:acetylene black:bin-