

Synthesis by sol–gel method and electrochemical properties of LiNiO₂ cathode material for lithium secondary battery

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Abstract

The optimum conditions for synthesising LiNiO₂ by a sol–gel method and its electrochemical properties are investigated. Single-phase LiNiO₂ powder is synthesised by the sol–gel method using citric acid as chelating agent and LiNO₃, Ni(NO₃)₂·6H₂O as starting materials. The optimum conditions for the synthesis of LiNiO₂ are calcination at 800 °C for 13 h in an oxygen stream after preheating at 600 °C for 5 h in air. The particles of LiNiO₂ powder are generally in the form of a smoothly edged polyhedron and their average size is approximately 3–5 μm. The resulting LiNiO₂ electrode shows relatively large discharge capacities and good cycle performance. The initial discharge capacity and that at the 20th cycle are 168 and 155 mAh g⁻¹ at a current density of 7.5 mA g⁻¹ in a voltage range 3.0–4.2 V. The decrease in the quantity of the intercalated Li ions during the first discharge as compared with that of the de-intercalated Li ions is considered to result from the destruction of the unstable tetrahedral sites and the diminution of Li atoms contained in excess.

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1. Introduction

Transition metal oxides such as LiMn₂O₄ [1–3], LiCoO₂ [4–6], and LiNiO₂ [7–10] have been investigated in order to apply them as positive electrode (cathode) materials for lithium secondary batteries. LiMn₂O₄ is very cheap and does not bring about environmental pollution, but its cycle performance is not good. LiCoO₂ has a large diffusivity and a high operating voltage, and can be easily prepared. It has a disadvantage, however, in that it contains an expensive element, namely, cobalt. LiNiO₂ is a very promising cathode material since it has a large discharge capacity [11] and is relatively excellent in terms of economics and environmental pollution. On the other hand, its preparation is very difficult compared with that for LiCoO₂ and LiMn₂O₄.

In this study, the optimum conditions for synthesis of LiNiO₂ by a sol–gel method are investigated. The thermal behaviour and the phase transformation process from the gel precursor to the final oxide are examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The phase formation is studied by X-ray diffraction

analysis. The electrochemical properties are investigated by charge–discharge experiments.

2. Experimental

In order to synthesise LiNiO₂ by the sol–gel method, lithium nitrate (LiNO₃, Aldrich Chemical) and nickel hexahydrate (Ni(NO₃)₂·6H₂O, Aldrich Chemical) were used as starting materials, and citric acid (C₂H₅O₇, purity 99.5+ %, Aldrich Chemical, reagent grade) as a chelating agent.

The selection of an electrolyte for LiNiO₂ is easy since the charge–discharge potential is low. Its synthesis in a stoichiometric composition is difficult. The important variables affecting the synthesis are temperature, time, atmosphere, and the mole ratio of the chelating agent to metallic ions. The calcination temperature is known to be 750–850 °C. In this work, 800 °C was chosen as the calcination temperature and the time of heat treatment was varied.

When the gel precursor is calcined at 600–800 °C in air, disordered Li_{1-x}Ni_{1+x}O₂ forms. In this state, nickel exists in the stable 2+ state [12–14]. It has been reported [15] that calcination in an oxygen atmosphere leads to better electrochemical properties of the electrode compared with those calcined in air. Thus, calcination was carried out in an

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oxygen atmosphere. Since the chelating agent has ligands which can combine positive ions, the positive ions are distributed homogeneously in the gel precursor. The chelating agent also supplies the heat of combustion during the synthesis of LiNiO_2 . When excess of the chelating agent is added, however, the temperature becomes too high. The increased partial pressures of CO or CO_2 then decrease the oxygen partial pressure. This makes difficult the synthesis of stoichiometric LiNiO_2 . In this work, the mole ratio of the citric acid to total metallic ions was 1.0.

The preparation procedure for LiNiO_2 powder by the sol-gel method is given schematically in Fig. 1. In the procedure, 0.2 M (molality) of metallic ions in aqueous solution is made by dissolving a mixture of lithium nitrate and nickel nitrate (in a mole ratio $\text{Li}^+:\text{Ni}^{2+} = 1:1$) in distilled water at 70–80 °C. This solution is transparent green in colour. A 0.2 M of citric acid is dissolved into 1 l of distilled water at 70–80 °C and is mixed with the 0.2 M metallic ion aqueous solution with a magnetic stirrer at 70–80 °C for 20–24 h. This produces a citrate-metal sol. On drying the citrate-metal sol at 70–80 °C, a gel precursor with a high viscosity is formed. The heating rates are 1 °C min^{-1} for preheating and 2 °C min^{-1} for calcination. After calcination, the samples are cooled in the furnace.

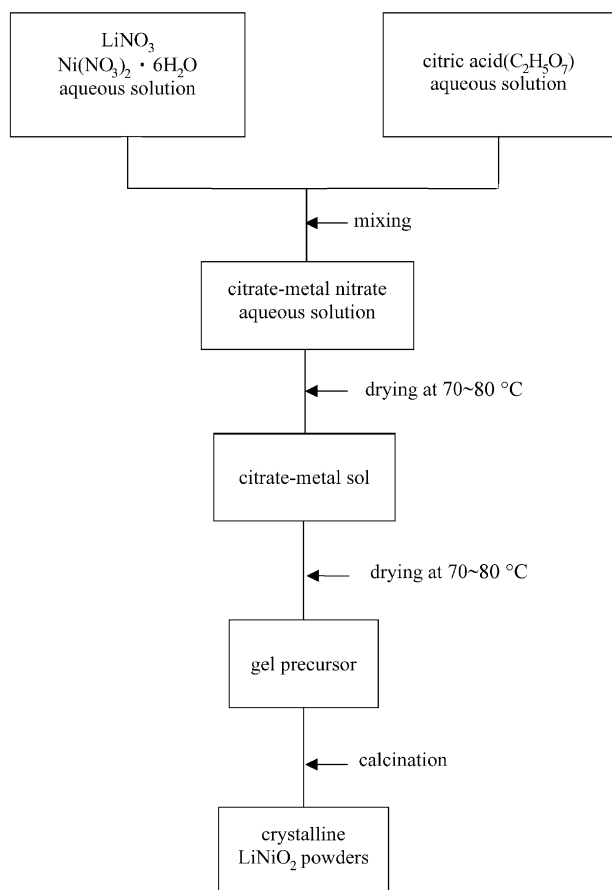


Fig. 1. Preparation procedure for LiNiO_2 powder by sol-gel method.

In order to investigate the optimum conditions for the synthesis of LiNiO_2 , the preheating temperatures were 400, 500, and 600 °C and the times for calcination at 800 °C were 10, 13, and 15 h.

The thermal behaviour of the gel precursors was examined by TGA and DTA at 35–900 °C in air at a heating rate of 5 °C min^{-1} .

The phase identification of the synthesised samples was carried out by X-ray diffraction analysis using Cu $K\alpha$ radiation. A Rigaku III/A diffractometer was used. The scanning rate was 4° min^{-1} and the scanning range of diffraction angle (2θ) was $10^\circ \leq 2\theta \leq 80^\circ$. The morphologies of the samples were observed by means of a scanning electron microscope (SEM).

The diameter of the positive electrode was about 1 cm and its weight was about 0.04 g. The electrochemical cells were assembled, each with the prepared LiNiO_2 as a positive electrode, lithium foil (Cyprus, Foote Mineral, purity 99.9%) as a negative electrode, and an electrolyte (Purelyte, Samsung Chemicals Ltd.) of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and diethylcarbonate (DEC). A glass filter (Wattman GF/A) was used as the separator.

The cells were assembled in an argon-filled dry box. To fabricate the positive electrode, 89 wt.% synthesised oxide, 10 wt.% acetylene black (as a conducting agent), and 1 wt.% granular polytetrafluoroethylene (PTFE) binder were mixed in an agate mortar.

All electrochemical tests were performed at room temperature with a battery charge-discharge cycle tester (WBCS3000, WonATech). The cells were cycled at a current density 7.5 mA g^{-1} between 3.0 and 4.2 V. Cyclic voltammograms were obtained at a scan rate of 10 $\mu\text{V s}^{-1}$ between 3.0 and 4.2 V.

3. Results and discussion

In order to examine the thermal behaviour of the gel precursors and to determine the preheating temperature, TGA and DTA were performed. The TGA and DTA curves at a heating rate of 5 °C min^{-1} are presented in Fig. 2 for the gel precursors dried in a vacuum oven at 80 °C for 24 h. The weight loss continued up to about 560 °C. The TGA curve can be divided into three regions 160–350, 350–380 and 380–560 °C.

The DTA curve exhibits small peaks at about 162, 340 and 370 °C, and a large peak at about 504 °C. The weight loss in the region 35–160 °C is probably due to the evaporation of water.

The X-ray (Cu $K\alpha$) diffraction patterns (Fig. 3) of the powders preheated at 200, 300, 400, 500 and 600 °C for 5 h were obtained in order to investigate phase formations in the gel precursors. The precursor preheated at 200 °C is in an amorphous state; it shows no formation of any compound during the sol-gel process. The precursor preheated at

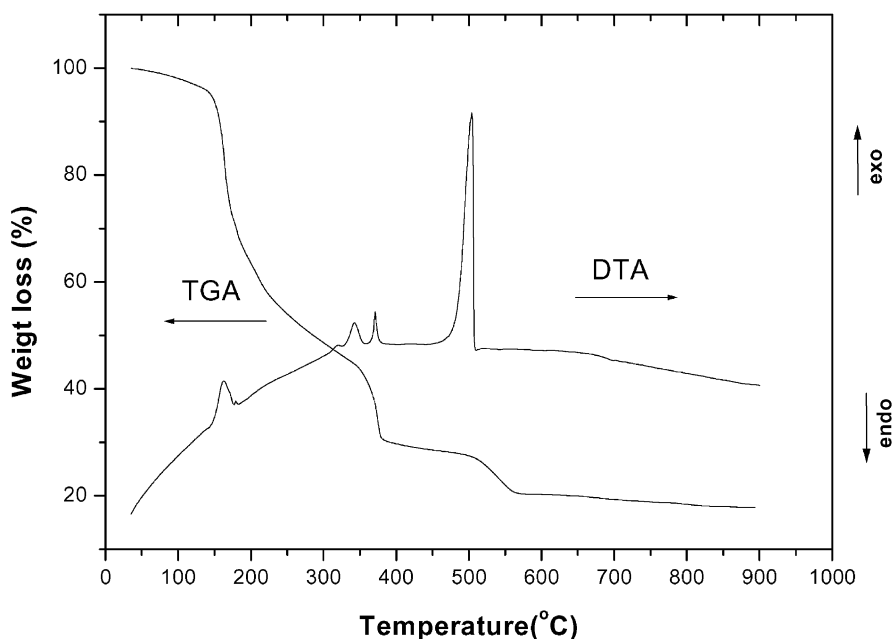


Fig. 2. TGA and DTA curves at heating rate of $5\text{ }^\circ\text{C min}^{-1}$ of precursors dried in vacuum oven at $80\text{ }^\circ\text{C}$.

$300\text{ }^\circ\text{C}$ contains mainly Li_2CO_3 and NiO together with a small amount of LiNO_3 . The precursors preheated at 400 and $500\text{ }^\circ\text{C}$ consist of Li_2CO_3 and NiO phases. The precursor preheated at $600\text{ }^\circ\text{C}$ shows clearly the $(0\ 0\ 3)$ peak of

LiNiO_2 . This indicates that LiNiO_2 forms above about $600\text{ }^\circ\text{C}$. As the preheating temperature increases from 500 to $600\text{ }^\circ\text{C}$, the NiO peaks move to the higher diffraction angle which corresponds to the LiNiO_2 peaks. This is considered to result from the formation of the LiNiO_2 phase from the NiO phase [16].

The precursor preheated at $300\text{ }^\circ\text{C}$ for 5 h contains mainly Li_2CO_3 and NiO (Fig. 3(b)). The largest weight loss (about 55%) in the region $160\text{--}350\text{ }^\circ\text{C}$ corresponds to the $162\text{ }^\circ\text{C}$ peak in the DTA curve and is thus considered to be due to the decomposition of citric acid and the nitrates into Li_2CO_3 and NiO . The weight loss (about 13%) in the region $350\text{--}380\text{ }^\circ\text{C}$, which corresponds to the exothermic reaction around $350\text{ }^\circ\text{C}$, is considered to be due to a compound formed between metal ion and citric acid. The weight loss (about 10%), which corresponds to the largest peak of the exothermic reaction around $504\text{ }^\circ\text{C}$, is considered to be due to the combustion of the residual organic matter in the gel precursor and the formation of the LiNiO_2 phase from the decomposition of Li_2CO_3 and NiO phases, see Fig. 3(e). From these results, the preheating temperatures were chosen as 400 , 500 and $600\text{ }^\circ\text{C}$.

The XRD patterns of the LiNiO_2 powders preheated at 400 , 500 and $600\text{ }^\circ\text{C}$ for 10 h in air followed by calcination at $800\text{ }^\circ\text{C}$ for 10 h in oxygen are shown in Fig. 4. The LiNiO_2 powder preheated at $600\text{ }^\circ\text{C}$ exhibits very weak peaks of Li_2CO_3 . The intensity ratio of the $(0\ 0\ 3)$ peak to the $(1\ 0\ 4)$ peak, viz. $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$, is generally used to examine the crystallinity of the LiNiO_2 phase [17]. The powder preheated at $600\text{ }^\circ\text{C}$ has the largest $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$. It also shows a distinct separation of the $(0\ 0\ 6)$ and $(1\ 0\ 2)$ peaks and a good symmetry of the $(1\ 0\ 8)$ and $(1\ 1\ 0)$ peaks. These

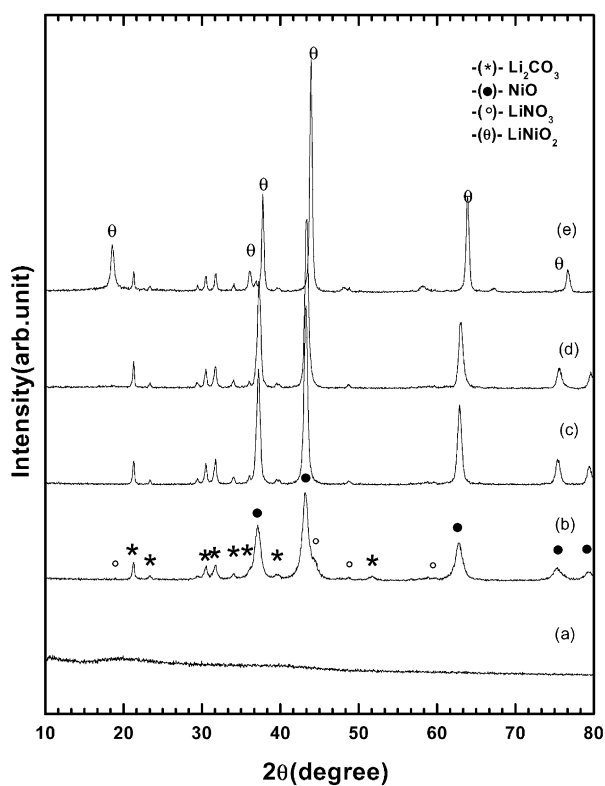


Fig. 3. XRD patterns of LiNiO_2 powders preheated at: (a) $200\text{ }^\circ\text{C}$; (b) $300\text{ }^\circ\text{C}$; (c) $400\text{ }^\circ\text{C}$; (d) $500\text{ }^\circ\text{C}$ and (e) $600\text{ }^\circ\text{C}$.

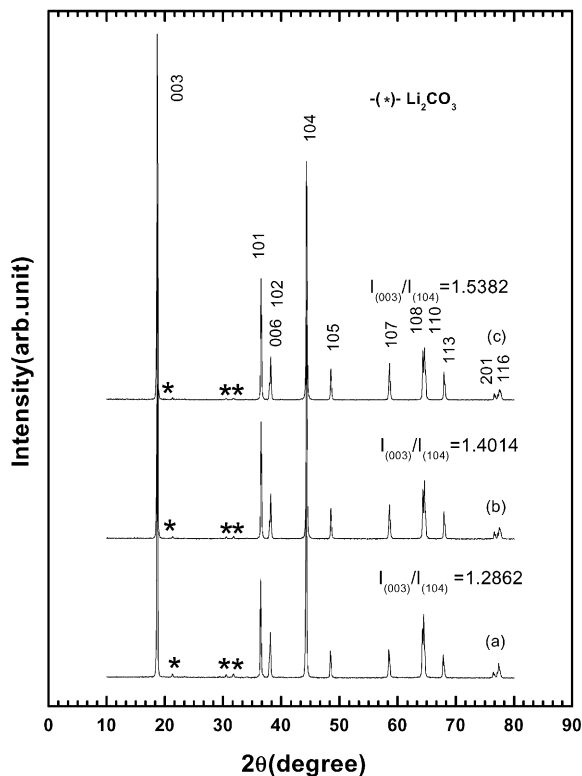


Fig. 4. XRD patterns of LiNiO₂ powders preheated at: (a) 400 °C; (b) 500 °C and (c) 600 °C for 10 h in air followed by calcination at 800 °C for 10 h in oxygen.

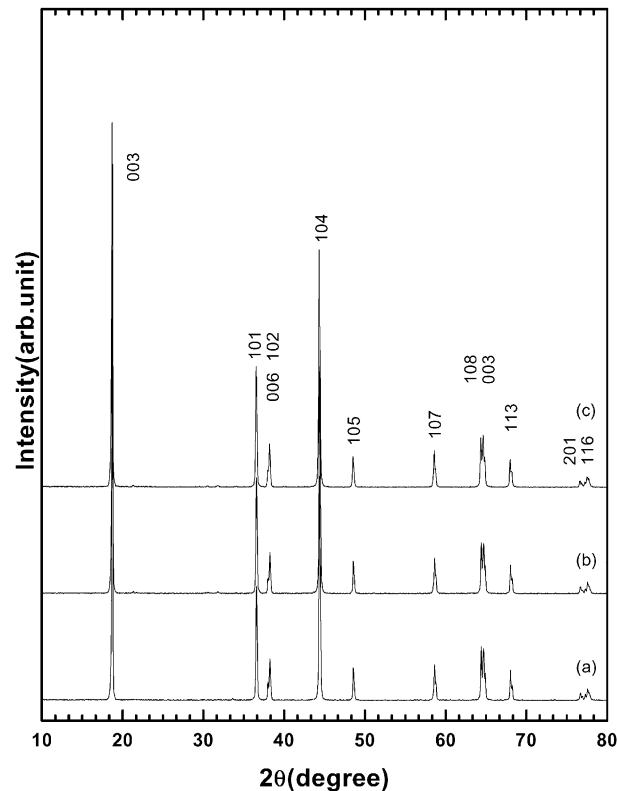


Fig. 5. XRD patterns of LiNiO₂ powders preheated at 600 °C for: (a) 5 h; (b) 7 h and (c) 10 h in air followed by calcination at 800 °C for 10 h in oxygen.

observations show that LiNiO₂ powder preheated at 600 °C has a better crystallinity than powders preheated at the other temperatures.

In order to determine the preheating time at 600 °C, the preheating time was varied. The XRD patterns of LiNiO₂ powder preheated at 600 °C for 5, 7 and 10 h in air, followed by calcination at 800 °C for 10 h in oxygen, are presented in Fig. 5. The $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$ of powder preheated for 5, 7 and 10 h is 1.5918, 1.5868 and 1.5328, respectively. Thus, as the preheating time increases, $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$ decreases. When the preheating time decreases from 7 to 5 h, there is very little difference in $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$. From these results, it was to take 5 h as the preheating time.

The XRD patterns of LiNiO₂ powder calcined at 800 °C for 10, 13 and 15 h in oxygen after preheating at 600 °C for 5 h in air are shown in Fig. 6. The $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$ of LiNiO₂ powder calcined for 10, 13 and 15 h is 1.5937, 1.6189 and 1.5101, respectively. LiNiO₂ powder calcined for 13 h has the largest $I_{(0\ 0\ 3)}/I_{(1\ 0\ 4)}$ value and also shows good symmetry of the (1 0 8) and (1 1 0) peaks.

The variation of discharge capacity at a current density of 7.5 mA g⁻¹ with the number of cycles is given in Fig. 7 for LiNiO₂ electrodes calcined for various times at 800 °C in oxygen after preheating. All the powders exhibit similar cycle performance. The LiNiO₂ powder calcined for 13 h has the largest discharge capacity, viz. an initial value of

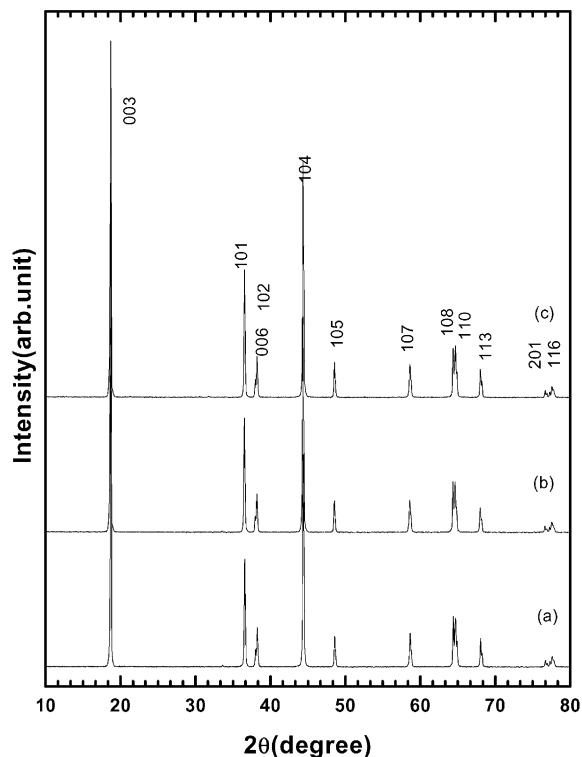


Fig. 6. XRD patterns of LiNiO₂ powders calcined at 800 °C for: (a) 10 h; (b) 13 h and (c) 15 h in oxygen after preheating at 600 °C for 5 h in air.

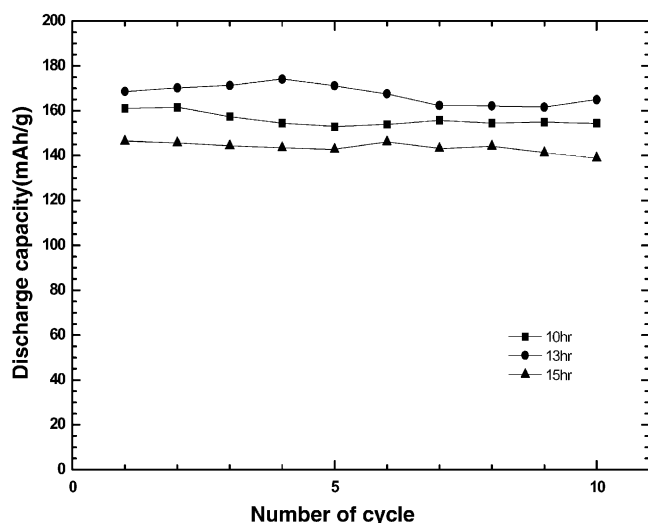


Fig. 7. Variation of discharge capacity at current density 7.5 mA g^{-1} with number of cycles for LiNiO_2 electrodes calcined for various times at 800°C in oxygen after preheating.

168 mAh g^{-1} and a value of 155 mAh g^{-1} on the 20th cycle at a current density of 7.5 mA g^{-1} between 3.0 and 4.2 V.

The results show that the optimum conditions for the synthesis of LiNiO_2 by the sol–gel method are preheating at 600°C for 5 h in air and then calcinating at 800°C for 13 h in oxygen.

Scanning electron micrographs of LiNiO_2 powder preheated at 600°C for 5 h in air and LiNiO_2 powder calcined at 800°C for 10, 13 and 15 h in oxygen after preheating are presented in Fig. 8. The powder preheated at 600°C for 5 h consists of quite small particles of uniform size (Fig. 8(a)). The powders calcined for different times are comprised of particles of similar shape and size. The particles are generally in the form of smooth-edged polyhedra and their average size is approximately $3\text{--}5 \mu\text{m}$.

The first and second charge–discharge curves of the LiNiO_2 electrode prepared by preheating at 600°C for 5 h in air and then calcinating at 800°C for 13 h in O_2 are given in Fig. 9. The curves exhibit two or three plateaux, which indicates that phase transitions occur during intercalation

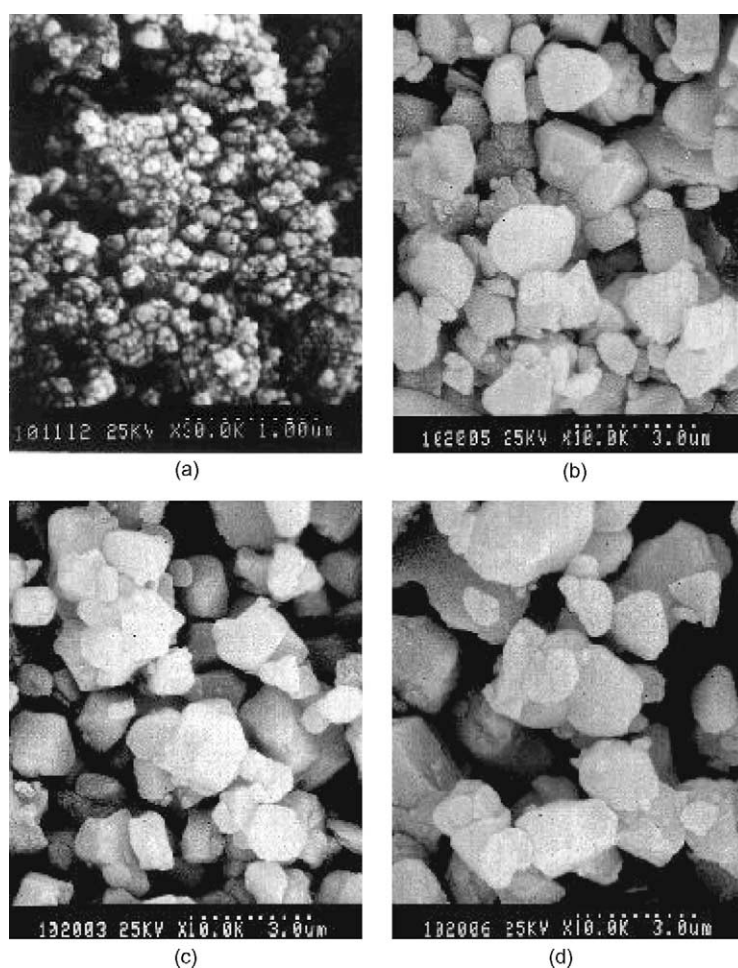


Fig. 8. Electron micrographs of: (a) LiNiO_2 powder preheated at 600°C for 5 h in air; (b) LiNiO_2 powder calcined at 800°C for 10 h, (c) 13 h and (d) 15 h in oxygen after preheating.

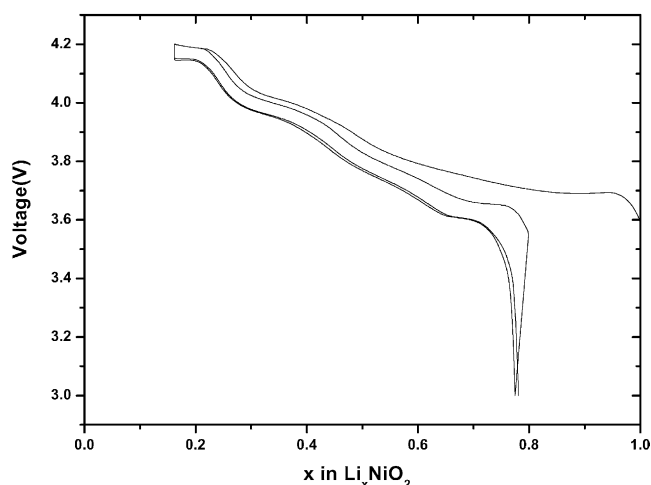


Fig. 9. First and second charge–discharge curves of Li_xNiO_2 electrode prepared by calcining at 800°C for 13 h in oxygen after preheating at 600°C for 5 h in air.

and de-intercalation of Li ions. Compared with the quantity of de-intercalated Li ions during the first charge, that of the intercalated Li ions during the first discharge is much smaller. The initial coulombic efficiency is about 73%. This is because, during the first charge, Li ions not only de-intercalate from stable octahedral (3a) sites but also de-intercalate from unstable octahedral (3a) sites and come out from Li atoms, which may be contained in excess outside the octahedral (3a) sites within the sample. After the first charge (de-intercalation), the unstable tetrahedral sites may be destroyed. These sites cannot then be used for the intercalation of Li ions on the following discharging. The quantity of Li ions which de-intercalate from unstable octahedral (3a) sites and come from the Li atoms outside the octahedral (3a) sites for the following charge will become much smaller as the number of cycles increase.

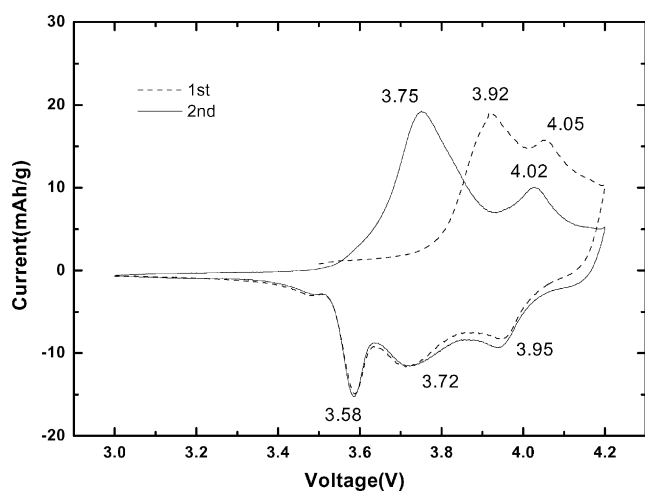


Fig. 10. Cyclic voltammograms for LiNiO_2 electrode prepared by calcining at 800°C for 13 h in oxygen after preheating at 600°C for 5 h in air at a scan rate of $10\ \mu\text{V s}^{-1}$ for initial two cycles.

Cyclic voltammograms are given in Fig. 10 for the LiNiO_2 electrode prepared by preheating at 600°C for 5 h in air and then calcinating at 800°C for 13 h in oxygen. The voltammograms were conducted at a scan rate of $10\ \mu\text{V s}^{-1}$ and are for the initial two consecutive cycles. The main oxidation peaks at 3.92 and 4.05 V during the first charge correspond to transitions in structure of hexagonal (H_1) to monoclinic (M) structure and monoclinic (M) to hexagonal (H_2) [18,19]. The reduction peaks are observed at 3.95, 3.72 and 3.58 V.

4. Conclusions

Single-phase LiNiO_2 powder has been synthesised by a sol–gel method that uses citric acid as a chelating agent and LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as starting materials. The optimum conditions for the synthesis of LiNiO_2 are calcination at 800°C for 13 h in an oxygen stream after preheating at 600°C for 5 h in air. The particles of the LiNiO_2 powder are generally in the form of smooth-edged polyhedra with an average size of approximately 3–5 μm . The LiNiO_2 electrode prepared under the optimum conditions shows a relatively large discharge capacity and good cycle performance. The initial discharge capacity and that at the 20th cycle are 168 and 155 mAh g^{-1} at a current density of $7.5\ \text{mA g}^{-1}$ in the voltage range 3.0–4.2 V. The decrease in the quantity of intercalated Li ions during the first discharge compared with that of the de-intercalated Li ions is considered to result from the destruction of the unstable tetrahedral sites and the diminution of Li atoms contained in excess.

Acknowledgements

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