Low-temperature synthesis of lithium nickelate positive active material from nickel hydroxide for lithium cells

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Abstract

A novel method of synthesizing lithium nickelate has been proposed by chemical oxidation of nickel hydroxide in a aqueous LiOH solution at lower temperature than 100°C. In this new process ''direct-oxidation method'', the oxidation of $Ni(OH)_2$ and a subsequent ion-exchange reaction successively took place in the same medium. The conversion yield of the ion-exchange process has not been complete and the product has seemed to remain some amount of proton in its structure. In order to increase the reaction rate and its conversion ratio, it was preferable that the reaction was allowed to proceed at higher temperature range 80–100°C, however, electrochemical activity of the product was drastically deteriorated with a lapse of reaction time at those temperature. Co doping in $Ni(OH)_2$ was found to be effective in depression of the capacity decrease in the long-time reaction. In addition, the product prepared by the direct-oxidation method has a possibility of a further high-capacity active material based on two-electron redox reaction in the range from Ni^{2+} to Ni^{4+}. It has exhibited larger discharge capacity than 310 mA h g^{-1} with a smooth potential change between two plateaux corresponding to Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox couples. Its cycle performance has also been superior to that of $LiNiO_2$ prepared by the other synthetic methods. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Several transition metal oxides such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ have been regarded as suitable compounds as positive active materials for lithium-ion cells. Although $LiNiO_2$ exhibits the highest energy density of them, its commercialization has been outstripped by the others. $LiCoO_2$ and $LiNiO_2$ have layered structure where lithium and transition metal ions fill alternating layers of octahedral sites in a cubic-close packed lattice of oxygen ions. Those are generally synthesized by solid-state reaction between a nickel source and a lithium source at high temperature such as 450°C to 900°C. Compared with $LiCoO_2$, $LiNiO_2$ is difficult to obtain in pure phase because of instability of trivalent nickel species and facility of disordering of cationic distribution at lithium site in its

structure. To synthesize well-ordered $LiNiO_2$, a number of attempts have been carried out at the optimization of heat-treatment condition.

On the other hand, new processes, which do not involve high-temperature solid-state reaction, have been proposed in the field of soft chemistry such as hydrothermal reaction, ion-exchange reaction, etc. [1–3]. The low-temperature syntheses seem to have the advantages of facility of synthetic process and depression of the structural disordering which often occurs in high-temperature synthesis. Those low-temperature syntheses involve ion-exchange reaction of NiOOH, which has an analogous layered structure to that of $LiNiO_2$, with lithium ion. NiOOH as the starting material can easily accept some impurities such as alkaline cation and water molecule in its inter-layer space. Therefore, a synthetic process which does not start from NiOOH seems to be preferable for preparation of highly pure $LiNiO_2$. In this report, a novel low-temperature synthesis of lithium nickelate and Co-doped lithium nickelate in direct oxidation of $Ni_{1-x}Co_x(OH)_2$ has been proposed as a method which skips the formation of NiOOH.

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2. Experimental

2.1. Synthesis of lithium nickelate and cobalt-doped lithium nickelate by the direct-oxidation method

$Ni_{1-x}Co_x(OH)_2$ ($x = 0$, 0.05, 0.10, and 0.15) were dispersed in a 4-M LiOH solution. The excess amount of $Na_2S_2O_8$ as an oxidizing agent was then added into the dispersion stirred. The green color of $Ni_{1-x}Co_x(OH)_2$ was turned to black immediately in the beginning of the reaction. The dispersion was bubbled with oxygen gas during those processes to avoid the formation of Li_2CO_3 by the reaction of LiOH with CO_2 contained in air. Reaction time and temperature were selected variously for investigation into the optimal condition. After the reaction, the product was washed and dried.

2.2. Characterization

The reaction products have been characterized by XRD, galvanostatic tests and cyclic voltammetry. Average valence of the transition metals in the product has been determined by redox and chelate titration using $KMnO_4$ and EDTA, respectively. The electrochemical tests have been performed in flooded-type cell by using electrodes which were prepared by coating of paste consisted of the obtained product as an active material, acetylene black as a conducting additive, polyvinylidenedifluoride (PVdF) as a binder on aluminum mesh as a current collector. Mixed solution of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) containing 1 M $LiClO_4$ has been used as an electrolyte.

3. Results and discussion

3.1. Reaction mechanism in conventional low-temperature syntheses of lithium nickelate

Conventional low-temperature syntheses of $LiNiO_2$ have been carried out by using NiOOH and solutions containing lithium ion either under hydrothermal condition or at atmospheric pressure. In those methods, the mechanism of $LiNiO_2$ formation are based on ion-exchange reaction of NiOOH with lithium ion, as shown in:

$$NiOOH + Li^+ \rightleftarrows LiNiO_2 + H^+ \qquad (1)$$
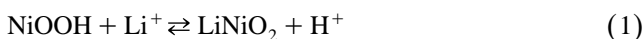
NiOOH is known to have two types of phases, i.e., β-NiOOH and γ-NiOOH. β-NiOOH has analogous structure to that of $Ni(OH)_2$ which is well-ordered layered structure containing little amount of any impurities. On the other hand, γ-NiOOH has a layered structure containing some impurities such as alkaline metal ions and water molecules in its inter-layer space. Owing to the presence of the impurities, the layers are disorderly stacked, and the

inter-layer space is expanded. Therefore, β-NiOOH is preferable as the starting material for synthesis of highly pure $LiNiO_2$. It has been, however, difficult to control the reaction condition to obtain pure β-NiOOH. NiOOH is prepared by oxidation of divalent Ni species, especially $Ni(OH)_2$, with a strong oxidizing agent, as shown in:

$$Ni(OH)_2 + Ox. \rightleftarrows NiOOH + Red. + H^+ + e^- \qquad (2)$$
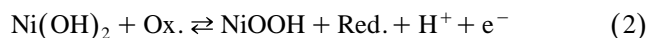
It is preferable that this oxidation proceeds in an alkaline medium because NiOOH is more stable in a solution at higher pH value. Since alkaline metal cations are easy to be inserted into NiOOH as mentioned above, the purity of $LiNiO_2$ prepared from NiOOH tends to be low. To solve this problem, two ideas will be presented. One is to increase the purity of NiOOH by optimization of the reaction condition. The other is to apply a new process which skips the formation of NiOOH. The former method will be hard to succeed however far the reaction condition is optimized, because sources of the impurities are indispensable to process of the reaction. The latter idea will be rather promising and has not realized yet.

To return the conventional process, the first step, i.e., the oxidation shown in Eq. (2), is carried out in alkaline solution, and the second process, i.e., the ion-exchange reaction shown in Eq. (1), is allowed to proceed in a solution containing lithium ion. As a lithium salt dissolved in this solution, LiOH will be the best choice because the equilibrium moves toward the product as both lithium concentration and/or pH value are high. If LiOH solution, which is both alkaline and containing lithium salt, is used as a reaction medium, those two reactions are expected to occur successively in the same solution, as shown in:

$$Ni(OH)_2 + Ox. + Li^+ \rightleftarrows LiNiO_2 + Red. + 2H^+ + e^- \qquad (3)$$

If the reaction takes place, $LiNiO_2$ is able to be directly synthesized in one step from $Ni(OH)_2$, which is a nickel source easily available. Furthermore, the elimination of disadvantages involved in the formation of NiOOH will be expected. This new synthetic process has been called the
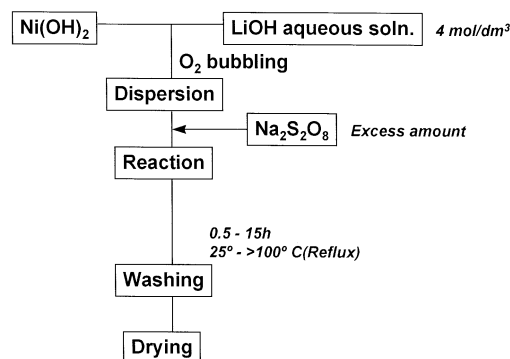
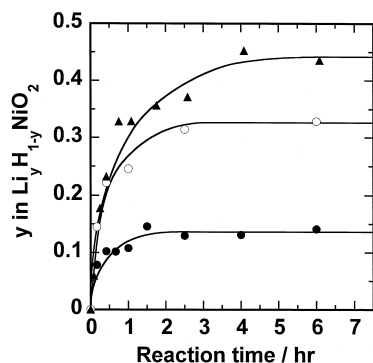Scheme 1. Process flow diagram of the direct-oxidation process.

Fig. 1. Time course of product in the ion-exchange reaction of NiOOH with Li$^+$ ion in 1 M (#), 3 M ()) or 4.5 M (%) LiOH solution at 80°C.

''direct-oxidation'' method and discussed in the following section.

3.2. Synthesis of lithium nickelate by the direct-oxidation method

Scheme 1 shows the process flow diagram of the direct-oxidation method according to the reaction shown in Eq. (3). Na$_2$S$_2$O$_8$ was used as a oxidizing agents in this process. Reaction conditions which strongly affect the yield of lithium nickelate will be LiOH concentration, temperature and time.

In the same way as the conventional ion-exchange synthesis, LiOH concentration should be as high as possible because the direct-oxidation method probably involve ion-exchange process in its successive reaction. Fig. 1 shows the dependence of reaction yield on LiOH concentration in ion-exchange reaction of NiOOH with lithium ion at 80°C. The conversion ratio increased as LiOH concentration was increased, and this behavior has been consistent with the balance of the equilibrium according to Eq. (1). Although this result has been attributed to the ion-exchange reaction, the similar tendency is expected in the direct oxidation. In this experiment, LiOH concentration has been fixed at 4M according to the above-mentioned idea.
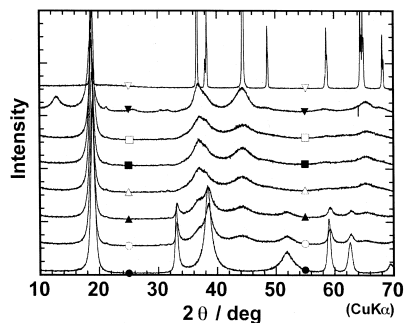

Fig. 3. Variation in X-ray diffraction pattern for product in the reaction of Ni(OH)$_2$ with Na$_2$S$_2$O$_8$ in 4 M LiOH solution at 50°C: #, Ni(OH)$_2$;), reacted for 0.5 h; %, for 1.0 h; +, for 2.0 h; !, for 3.0 h; ', for 6.0 h; &, for 15.0 h; ,, LiNiO$_2$ prepared by solid-state reaction.
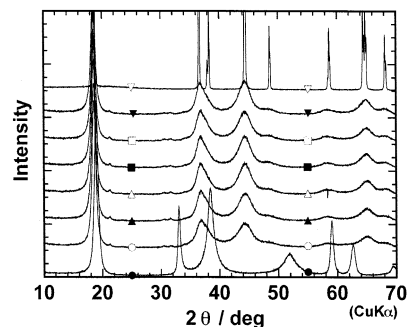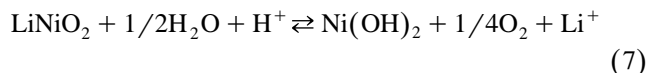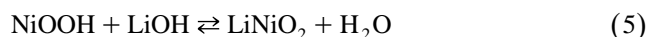
Reaction temperature will strongly relate to the reaction yield as well. The following equations are assumption of possible main and side reactions in the direct-oxidation process. The main successive reaction is divided into oxidation of Ni(OH)$_2$ and ion-exchange reaction as shown in Eqs. (4) and (5).

$$Ni(OH)_2 + 1/2S_2O_8^{2-} \rightleftarrows NiOOH + HSO_4^- \qquad (4)$$

$$NiOOH + LiOH \rightleftarrows LiNiO_2 + H_2O \qquad (5)$$

$$NiOOH + 1/2H_2O \rightleftarrows Ni(OH)_2 + 1/4O_2 \qquad (6)$$

$$LiNiO_2 + 1/2H_2O + H^+ \rightleftarrows Ni(OH)_2 + 1/4O_2 + Li^+ \qquad (7)$$

$$4OH^- \rightleftarrows O_2 + 2H_2O + 4e^- \qquad (8)$$

In the oxidation, lower temperature is known to be preferable to obtain β-NiOOH prior to the γ phase. The subsequent ion-exchange reaction, however, should be allowed to proceed at higher temperature for good yield and rapid proceeding of the reaction. On the other hand, several side reaction as shown in Eqs. (6)–(8) are possible to
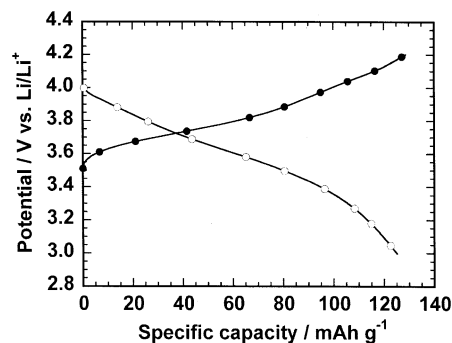

Fig. 2. Variation in X-ray diffraction pattern for product in the reaction of Ni(OH)$_2$ with Na$_2$S$_2$O$_8$ in 4 M LiOH solution at 25°C: #, Ni(OH)$_2$;), reacted for 0.5 h; %, for 1.0 h; +, for 2.0 h; !, for 3.0 h; ', for 6.0 h; &, for 15.0 h; ,, LiNiO$_2$ prepared by solid-state reaction.

Fig. 4. First charge–discharge characteristics of LiNiO$_2$ prepared by the direct-oxidation method in mixed solution of EC, DEC and DMC containing 1 M LiClO$_4$ at a current density of 0.89 mA cm^{-2}.
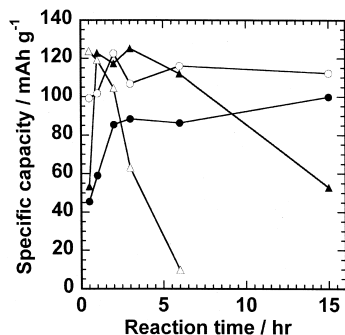
Fig. 5. Initial discharge capacity of product by the direct-oxidation method at 25°C (#), 50°C (), 80°C (%) or > 100°C (+).

Fig. 7. Variation in X-ray diffraction pattern for product in the reaction of Ni(OH)$_2$ with Na$_2$S$_2$O$_8$ in 4 M LiOH solution at 80°C: #, Ni(OH)$_2$;), reacted for 0.5 h; %, for 1.0 h; +, for 2.0 h; !, for 3.0 h; ', for 6.0 h; amp;, for 15.0 h; ,, LiNiO$_2$ prepared by solid-state reaction.

take place in competition with the main reactions. Water molecules take part in all side reactions shown here. Eqs. (6) and (7) describe re-reduction of the obtained NiOOH and LiNiO$_2$ by water, i.e., regeneration of Ni(OH)$_2$ starting material. Eq. (8) indicates the oxidation of water, not of Ni(OH)$_2$. In other words, it is an undesirable consumption of an oxidizing agent. Those side reactions, including formation of γ-NiOOH, will be depressed at lower temperature, but the main ion-exchange reaction needs to proceed at higher temperature. Thus, an optimal temperature exists in the balance of those reactions.

Fig. 2 shows the change in X-ray diffraction pattern of product with a lapse of time in the direct oxidation at 25°C. Compared with LiNiO$_2$ prepared by solid-state reaction at high temperature, the obtained compound exhibits similar but broader pattern, and that is same characteristics as LiNiO$_2$ obtained from the other low temperature syntheses. The broadness of the X-ray pattern implies partial disordering of the structure due to the remaining of proton which was not extracted. In the beginning of the reaction, unreacted Ni(OH)$_2$ existed while NiOOH was not detected. In addition, γ-NiOOH was produced at the end of the reaction. Those results indicate the main ion-exchange reaction was not sufficiently rapid to complete prior to the other side reactions. Fig. 3 represents the change in X-ray diffraction pattern of the product in the direct oxidation at 50°C. Since both unreacted Ni(OH)$_2$ and γ-NiOOH were not produced, the main reaction seems to proceed domi-
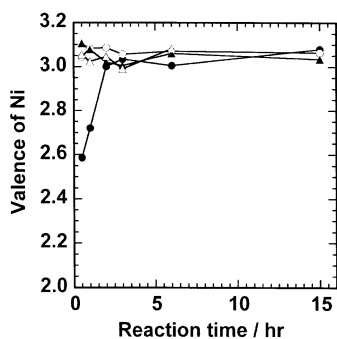
nantly at 50° C. Disordering of the structure, however, seems to still exist as the broadness of the diffraction peaks did not reduce.

The obtained materials were subjected to galvanostatic charge–discharge test. Fig. 4 exhibits a first charge–discharge characteristics of the product by the direct-oxidation method. Its electrochemical behavior has been similar to that of LiNiO$_2$ prepared by the other methods. This test's result indicates that the product is identified as LiNiO$_2$ or its analogue. According to the X-ray diffraction patterns shown in Fig. 2 and Fig. 3, the product appears to contain a little amount of proton and its composition will be described as Li$_{yz}$H$_{(2-y)z}$NiO$_2$ ($0 < y \leq 2$, $0 < z < 1$). Fig. 5 represents the dependence of initial discharge capacity of the product on its reaction conditions. In the reaction at 25°C or 50°C, the capacity of product increased as reaction time became longer. This tendency is consistent with the reaction proceeding in the direction of the product. On the other hand, however, the discharge capacity drastically deteriorated with a lapse of reaction time at high temperature such as 80°C and above 100°C. As this reason, an influence of the side reactions, as shown in Eqs. (6)–(8), may be proposed. Fig. 6 describes the variation in nickel oxidation state of the same products shown in Fig. 5. Since both NiOOH and LiNiO$_2$ are trivalent nickel

Fig. 6. Time course of Ni oxidation state in product by the direct-oxidation method at 25°C (#), 50°C (), 80°C (%) or > 100°C (+).
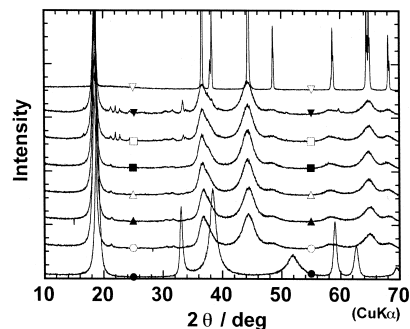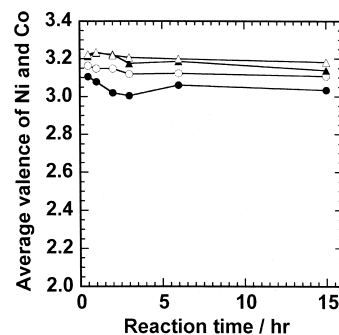

Fig. 8. Time course of average oxidation state of Ni and Co in product by the direct-oxidation method at 80°C from 0% (#), 5% ()), 10% (%) or 15% (+) Co-doped Ni(OH)$_2$.
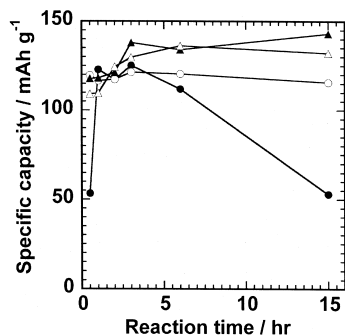
Fig. 9. Initial discharge capacity of product by the direct-oxidation method at 80°C from 0% (#), 5% (◯), 10% (△) or 15% (+) Co-doped $Ni(OH)_2$.

species, the target value of Ni valence is 3.0. If the side reaction shown in Eqs. (6)–(8) occurs, this value decreases. As the result, nickel in the all samples was trivalent, except in the beginning of the reaction at 25°C. It suggests that the oxidation was nearly completed and the side reactions shown in Eqs. (6)–(8) did not take place. Fig. 7 shows change in X-ray diffraction pattern of the product in the reaction at 80°C. The main product seems to be $Li_{yz}H_{(2-y)z}NiO_2$ $(0 < y \leq 2, 0 < z \leq 1)$, similar to that in the synthesis at 50°C. At the end of the reaction, the other peaks, which are identified as LiOH and Li_2SiO_3, appeared in the XRD pattern. Lithium silicate seems to be produced by reaction of lithium hydroxide with glass vessel used as the reactor. Since the amounts of those impurities have been small, their presence does not seem to be the main factor of the deterioration.

3.3. Effect of cobalt doping

In conventional high-temperature syntheses of $LiNiO_2$, cobalt doping has been known to effective technique to stabilize its structure and depress a disordering of the cationic distribution. Cobalt-doped $Ni(OH)_2$ has been used in the direct-oxidation method as well in order to depress
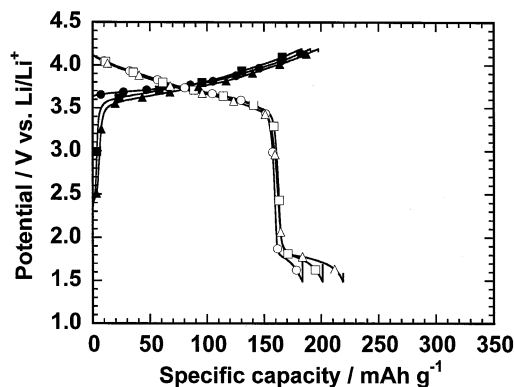

Fig. 10. Initial electrochemical characteristics of $LiNiO_2$ prepared by solid-state reaction in mixed solution of EC, DEC and DMC containing 1 M $LiClO_4$ at a current density of 0.89 mA cm^{-2} in the potential range 1.5–4.2 V vs. Li/Li^+: #, ◯), 1st cycle; !, ', 2nd cycle; %, +, 3rd cycle.
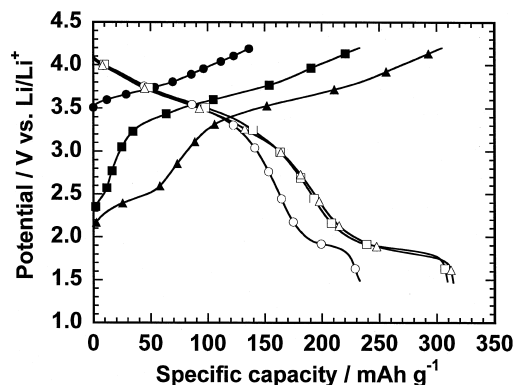

Fig. 11. Initial electrochemical characteristics of $LiNiO_2$ prepared by the direct-oxidation method in mixed solution of EC, DEC and DMC containing 1 M $LiClO_4$ at a current density of 0.89 mA cm^{-2} in the potential range 1.5–4.2 V vs. Li/Li^+: #, ◯), 1st cycle; !, ', 2nd cycle; %, +, 3rd cycle.

the capacity degradation by long-time reaction. Fig. 8 represents the time course of the mixed oxidation state of Ni and Co in the products obtained by the direct-oxidation method from Co-doped $Ni(OH)_2$ at 80°C. The metals were trivalent in the all products, and the valences in Co-doped samples were slightly higher than those in the non-doped products. It suggests that trivalent state of nickel has been stabilized by the Co doping. In comparison between those initial discharge capacity, Co doping has been found to be effective in the depression of the capacity deterioration, as shown in Fig. 9. This result implies that the Co-doping
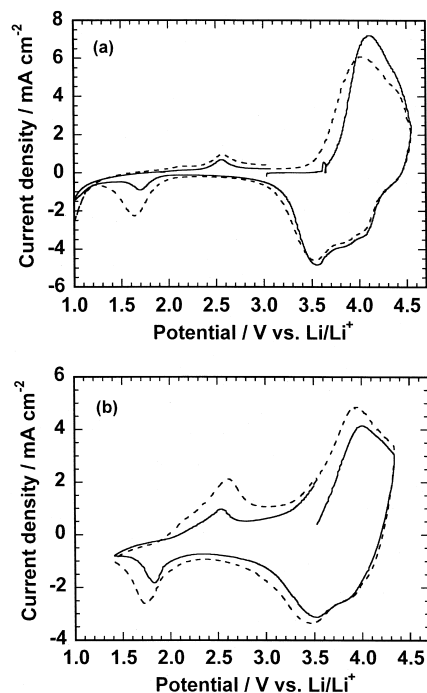

Fig. 12. Cyclic voltammogram of $LiNiO_2$ prepared (a) by solid-state reaction or (b) by the direct-oxidation method in mixed solution of EC, DEC and DMC containing 1 M $LiClO_4$ at sweep rate of 10 mV min^{-1}: S, 1st cycle; –, 2nd cycle.
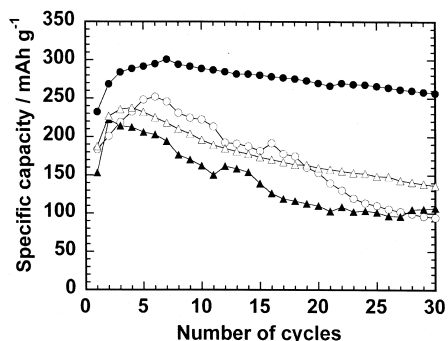
Fig. 13. Representative cycle performances of Li$_y$NiO$_2$ (0 < y ≤ 2), prepared by the direct-oxidation method (#), HT solid-state reaction (◯), LT ion-exchange reaction (%) or LT hydrothermal reaction (+), in mixed solution of EC, DEC and DMC containing 1 M LiClO$_4$ at a current density of 0.89 mA cm^{-2} in the potential range 1.5–4.2 V vs. Li/Li$^+$.

effect relates to stabilization of lithium nickelate in the same case as HT-LiNiO$_2$.

3.4. Two-electron redox reaction in the range between Ni^{2+} and Ni^{4+}

Meanwhile, LiNiO$_2$ which is trivalent nickel species has been known to be also discharged to a divalent compound with further intercalation of lithium, according to:
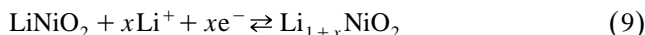
$$LiNiO_2 + xLi^+ + xe^- \rightleftarrows Li_{1+x}NiO_2 \qquad (9)$$

Fig. 10 shows an initial charge–discharge characteristics of LiNiO$_2$ prepared by solid-state reaction in the range between Ni^{2+} and Ni^{4+}. In this figure, two potential plateaux, which correspond to redox couples of Ni^{3+}/Ni^{4+} and Ni^{2+}/Ni^{3+}, appear with a large potential gap of approximately 1.5 V. In addition, the discharge capacity due to the Ni^{2+}/Ni^{3+} couple is extremely small. Therefore, the use of the range Ni^{2+}/Ni^{3+} subsequent to the Ni^{3+}/Ni^{4+} couple has been difficult as a practical active material. On the other hand, lithium nickelate prepared by the direct oxidation exhibited smoothly connected two plateaux due to Ni^{3+}/Ni^{4+} and Ni^{2+}/Ni^{3+} redox couples, as shown in Fig. 11. Furthermore, Ni^{2+}/Ni^{3+} redox

couple showed markedly high capacity. The total discharge capacity between the Ni^{2+} and the Ni^{4+} exceeded 310 mA h g^{-1}. Thus, this compound seems to have a possibility as a high-capacity active material based on two-electron redox reaction. Those cyclic voltammograms also represent the two redox couples and the deference of electrochemical activity in Ni^{2+}/Ni^{3+} couple, as shown in Fig. 12.

Lithium nickelate prepared by the direct oxidation exhibited good cycle performance as well, as shown in Fig. 13. This figure also indicates that lithium nickelate obtained from the other synthetic method, such as low-temperature ion-exchange process both at atmospheric pressure and under hydrothermal condition, and a high-temperature heat treatment, have been not durable against volumetric change during redox reaction in the range between Ni^{2+} to Ni^{4+}.

4. Conclusion

One-step synthesis of lithium nickelate by direct oxidation of Ni(OH)$_2$ (the direct-oxidation method) has been proposed as a novel low-temperature synthetic method. Reaction condition should be further optimized because the product seems to remain a little amount of proton in its structure. The improved lithium nickelate has the possibility of a high-capacity active material based on two-electron redox reaction. Co doping in Ni(OH)$_2$ depressed proceeding of the side reactions which deteriorated electrochemical activity of the product.

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