

Characteristics of Li_xNiO_2 obtained by chemical delithiation

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Abstract

Stoichiometric LiNiO_2 was delithiated using NOPF_6 oxidation or acid leaching. We obtained a highly delithiated compound of $\text{Li}_{0.1}\text{NiO}_2$ by the latter process, whose electrochemical properties were substantially the same as those of Li_xNiO_2 obtained by electrochemical delithiation. The chemically delithiated Li_xNiO_2 sample allowed us to investigate the intrinsic thermal behavior of Li_xNiO_2 , as it was free from any influence of conductive agents or binders. The thermal decomposition mechanism of Li_xNiO_2 is discussed based on the results of X-ray diffraction and thermogravimetric analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Positive electrode; Lithium nickelate; Chemical delithiation; Acid leaching; Thermal decomposition mechanism

1. Introduction

Stoichiometric LiNiO_2 is a promising positive electrode material for lithium battery systems due to its high energy density. There have been numerous studies on the characteristics of its delithiated (lithium extracted) state, namely Li_xNiO_2 ($x < 1$). Among them, thermal behavior is of particular importance [1–6], because it affects battery safety. However, it is difficult to measure the intrinsic thermal behavior, because usual samples obtained by electrochemical delithiation contain conductive agents (such as carbon) and/or binders which have influence on the measurement. Actually, the behavior has been clarified only up to 300°C, due to melting of the binder and decomposing of the carbon at a higher temperature. By contrast, chemically delithiated compounds are free from these additives and are suitable for measuring thermal behavior. There have been several studies on the properties of compounds which were obtained by chemical delithiation of $\text{Li}_{1-\delta}\text{Ni}_{1+\delta}\text{O}_2$ [7–11]. However, as stoichiometric LiNiO_2 only shows a large capacity (hence higher degree of delithiation) [12], it is essential to use stoichiometric samples for evaluating the behavior of interest.

In this study, we report the chemical delithiation of stoichiometric LiNiO_2 using NOPF_6 oxidation and the acid leaching method. The structural, electrochemical and ther-

mal characteristics of the resultant Li_xNiO_2 are discussed in comparison with those of electrochemically obtained samples.

2. Experimental

Stoichiometric LiNiO_2 was synthesized at 700°C using the excess lithium method [12]. We delithiated this LiNiO_2 sample by two chemical methods. One involved oxidizing LiNiO_2 with the oxidizer, NOPF_6 , in acetonitrile in a nitrogen atmosphere. The initial molar ratio of $\text{NOPF}_6/\text{LiNiO}_2$ was 2. The solid product was filtered, washed with acetonitrile and dried in a vacuum. In the second method, the acid leaching process was carried out by adding LiNiO_2 to an aqueous solution of acetic acid, phosphoric acid or sulfuric acid. The initial molar ratio of $\text{H}^+/\text{LiNiO}_2$ was 5. The mixture was stirred at 25°C for 5 h and the product was filtered. The filtrate powder was washed with acetone to remove the water on the surface and dried in a vacuum.

The structure was analyzed using X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (Rigaku RU-200, RAD-rX). We performed the Rietveld analysis with the aid of the computer program RIETAN [13], assuming that the nickelate structure is $[\text{Li}_x\text{Ni}_w]_{3b}[\text{Ni}_{1-w}]_{3a}[\text{O}_2]_{6c}$. The chemical composition of the product was evaluated using inductively coupled plasma emission (ICPE) spectroscopy of lithium and nickel. The nickel oxidation state was analyzed using iodometry.

We examined the electrochemical characteristics using a coin cell [12] with metallic lithium as the negative electrode. The positive electrode mixture consisted of nick-

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elate powder (70 wt.%), acetylene black (AB) (25 wt.%) and polytetrafluoroethylene (PTFE) (5 wt.%). The electrolyte was a 1 mol dm⁻³ LiPF₆ solution in equal volumes of ethylene carbonate and dimethyl carbonate. The quasi open circuit voltage (QOCV) profile was measured by applying an intermittent current of 0.1 mA cm⁻² for 2 h followed by a 2 h rest. The lithium content of the electrode was calculated from the weight of the electrode and the transferred charge. A constant current cycling test was carried out at 0.5 mA cm⁻². With this current density, it typically took 20 h for one discharge (or charge) process.

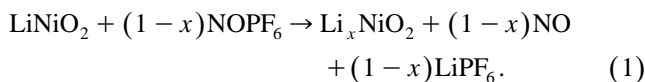
We measured the thermal behavior of Li_xNiO₂ using thermogravimetry (TG) combined with differential scanning calorimetry (DSC) (Rigaku TAS-100). The sample was heated up to 600°C in an argon atmosphere at a heating rate of 10°C min⁻¹.

3. Results and discussion

3.1. Delithiation by NOPF₆ oxidation

The pristine LiNiO₂ sample (sample A) had a layered structure with a hexagonal lattice and an almost completely stoichiometric composition, as shown in Table 1. The iodometric analysis indicated the oxidation state of nickel as being 3.0. The electrochemical characterization of this sample has already been reported [12,14].

Sample B was prepared by oxidizing sample A with NOPF₆. Fig. 1 shows the XRD patterns of samples A and B, indicating that the pristine layered structure of LiNiO₂ is substantially preserved and that this oxidation reaction proceeded in a topotactic manner. Sample B had a monoclinic lattice and the lattice parameters (shown in Table 1) accord well with those of Li_{0.6}NiO₂ obtained by the electrochemical method [12,15]. The following reaction was expected.



The degree of delithiation was low, that is, we obtained the product corresponding to $x = 0.6$ in spite of the excess

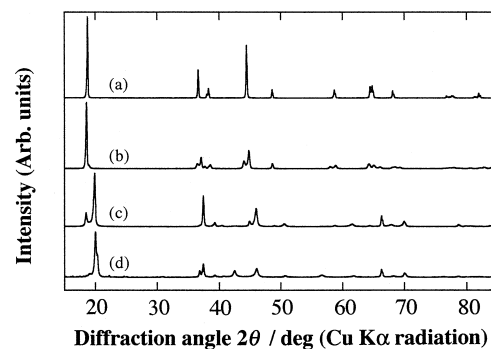
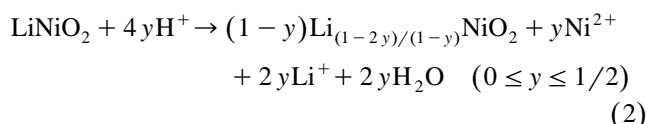


Fig. 1. XRD patterns of samples (a) A, (b) B, (c) E and (d) F.

amount of NOPF₆ used (NOPF₆/LiNiO₂ = 2). This suggests that the delithiation was limited by the oxidizing power of NOPF₆, which is expected to be 3.8 V vs. Li/Li⁺ based on the QOCV curve of this LiNiO₂ sample [12]. This oxidizing power is comparable to that of NOBF₄, with which LiCoO₂ is oxidized to Li_{0.68}CoO₂ [16].

3.2. Delithiation by acid leaching

The acid leaching method allowed further degree of delithiation in comparison to NOPF₆ oxidation. The acid leached product Li_xNiO₂ had various x values, depending on the kind and strength of the acid used. The results are shown in Table 1. The filtrate solution was green, implying that Ni²⁺ was formed. The yield was low for a product with a smaller x value. These facts suggest that the following reaction, namely a disproportionation reaction of nickel ($2\text{Ni}^{3+} \rightarrow \text{Ni}^{4+} + \text{Ni}^{2+}$), occurred.



When the acid concentration of the solution is fixed (1.2 mol dm⁻³), the degree of delithiation was in the order of the strength of the protons in the solution: acetic acid (sample C) < phosphoric acid (sample D) < sulfuric acid (sample E, F). No nickel in the lithium layer was found in the XRD Rietveld analysis and the pristine layered struc-

Table 1
Delithiation condition, structure, and composition of Li_xNiO₂ samples

Sample	Delithiation condition	System ^a	a (Å) ^b	b (Å) ^b	c (Å) ^b	β ^b	x in Li _x NiO ₂ (structure) ^c	Li/Ni ratio (ICPE)
A	(Before delithiation)	Hex	2.875	–	14.19	–	1.0	0.99
B	Excess NOPF ₆ oxidation	Mon	4.981	2.827	5.062	109.73	0.6	–
C	1.2 mol dm ⁻³ acetic acid	Mon	4.973	2.825	5.070	109.66	0.5	–
D	1.2 mol dm ⁻³ phosphoric acid	Hex	2.819	–	14.38	–	0.2	–
E	1.2 mol dm ⁻³ sulfuric acid	Hex1	2.818	–	13.41	–	0.1	0.10
F	3.6 mol dm ⁻³ sulfuric acid	Hex2	2.815	–	14.36	–	0.0	0.04

^aHex and Mon denote hexagonal and monoclinic systems in the unit cell structure, respectively.

^bBased on the structural notation in Ref. [15].

^cDeduced from the structural data of the electrochemical samples in Ref. [12].

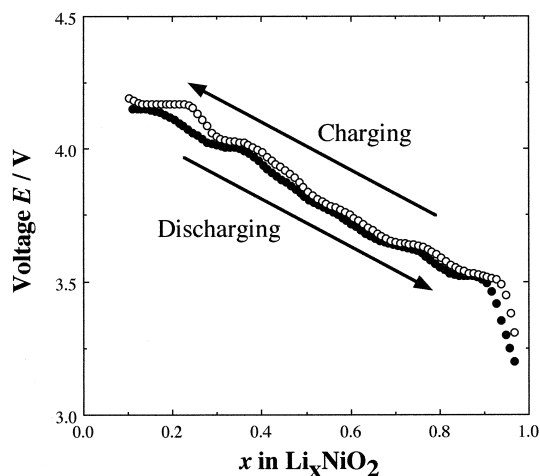


Fig. 2. QOCV profiles of sample E during the first discharging and subsequent charging processes.

ture (CdCl_2 type) was maintained during acid leaching for samples C, D, and E.

The XRD patterns of samples E is shown in Fig. 1(c). The XRD pattern of sample E could be ascribed to a mixture of two layered phases, as shown in Table 1. The major and minor phases had the c axis length of 13.41 Å and 14.36 Å, respectively. The major phase is estimated to be about 80% of the whole nickelate. These data agree well with those for Li_xNiO_2 which is electrochemically obtained at 4.2 V vs. Li/Li^+ [12,15]. Sample E had a Li/Ni value (ICPE measurement) and an oxidation state of nickel (iodometry) of 0.10 and 3.8, respectively. When we take the experimental error in the chemical analysis into consideration, the proton content of this sample seems to be low. This is supported by the fact that sample E showed no weight change up to 200°C and exhibited excellent electrochemical behavior in the non-aqueous electrolyte, as described later. Sample E was stable at room temperature in a dry atmosphere for at least several weeks.

The ICPE measurement revealed that sample F, treated with 3.6 mol dm^{-3} sulfuric acid, had a small Li/Ni value of 0.04. However, the XRD pattern shown in Fig. 1(d) could not be indexed with the CdCl_2 -type structure to which all the other samples belong. This compound may have a CdI_2 -type structure as recently suggested for NiO_2 [17,18]. The assignment of this phase requires further study.

The oxidation states of nickel in samples E and F are ones of the highest values so far obtained by chemical synthesis. Such a highly delithiated state has not been reported in previous studies [7–11], because of the non-stoichiometric nature of their samples. Acid leaching delithiation from LiCoO_2 [10,19] has been reported to produce a lower oxidation state of cobalt (up to $\text{Co}^{3.6+}$). This result accords with the following phenomena which show a low motive force for disproportionation reaction ($2\text{Co}^{3+} \rightarrow \text{Co}^{4+} + \text{Co}^{2+}$). Namely, LiCoO_2 is more easily synthesized from divalent metal salts than LiNiO_2 , showing that

$\text{Co}^{2+}/\text{Co}^{3+}$ has a lower potential than $\text{Ni}^{2+}/\text{Ni}^{3+}$, and an Li_xCoO_2 electrode shows higher voltages than an Li_xNiO_2 electrode, reflecting the fact that $\text{Co}^{3+}/\text{Co}^{4+}$ has a higher potential than $\text{Ni}^{3+}/\text{Ni}^{4+}$.

3.3. Electrochemical behavior of Li_xNiO_2

We examined the electrochemical characteristics of sample E as the positive electrode. Fig. 2 shows the QOCV profiles, assuming that the initial composition was $\text{Li}_{0.1}\text{NiO}_2$. The initial cell voltage was 4.2 V. The x value in Li_xNiO_2 for the first discharging process to 3.0 V and the subsequent charging process to 4.3 V reached almost 1.0 and 0.1, respectively. Fig. 3(a) shows the discharge curves of sample E and electrochemically delithiated $\text{Li}_{0.1}\text{NiO}_2$ [14], both measured as QOCV profiles. Fig. 3(b) is the derivative plot (dx/dE vs. E) of Fig. 3(a). Both figures show that the two profiles are similar. Fig. 4 shows the result of a constant current cycling test at 0.5 mA cm^{-2} . The cycling capacity was about 200 mAh g^{-1} . Good reversibility in the non-aqueous electrolyte suggests that this sample has few protons in the matrix. These results indicate that the chemically delithiated sample shows substantially the same electrochemical behavior as electrochemically delithiated Li_xNiO_2 .

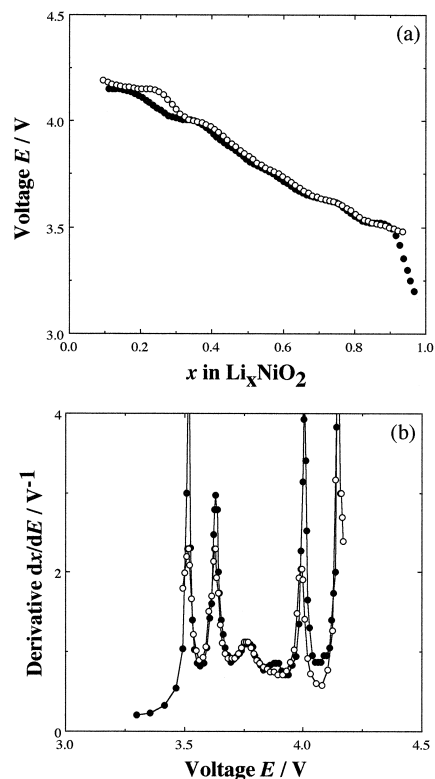


Fig. 3. (a) QOCV profiles and (b) the derivative plots of sample E (black circles) and of electrochemically delithiated $\text{Li}_{0.1}\text{NiO}_2$ (white circles) [14] during discharging.

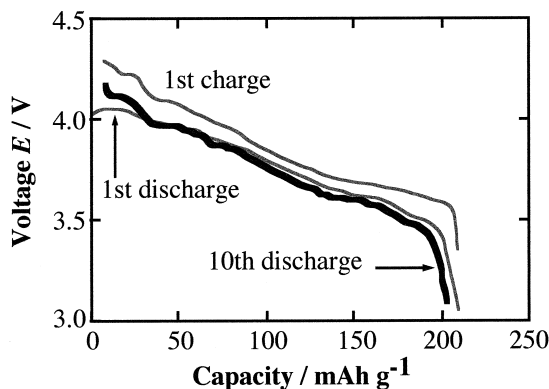


Fig. 4. Discharge-charge profiles of sample E at a current density of 0.5 mA cm⁻² between 3.0 V and 4.3 V.

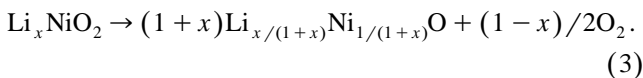
3.4. Thermal behavior of Li_xNiO₂

The thermal behavior of electrochemically delithiated Li_xNiO₂ has been investigated [1–6], and we have recently shown the following using DSC and XRD measurements [5].

(1) When $x \geq 0.4$, endothermic heat is observed at around 220°C and the resulting product has a layered structure.

(2) When $x \leq 0.3$, exothermic heat is generated at around 200°C and the decomposition product has a disordered rock-salt structure, suggesting that the exothermic heat is due to the disordering of the structure.

(3) Structural analysis suggests that the following reaction occurs in both cases:



In this study we observed the thermal behavior of chemically delithiated Li_xNiO₂ using TG-DSC analyses, to find supports for the preceding suggestion. Fig. 5 shows the TG-DSC profile of sample E. The DSC curve shows that the behavior is essentially the same as that of electrochemically delithiated samples of Li_{0.15}NiO₂ [2] and Li_{0.06}NiO₂

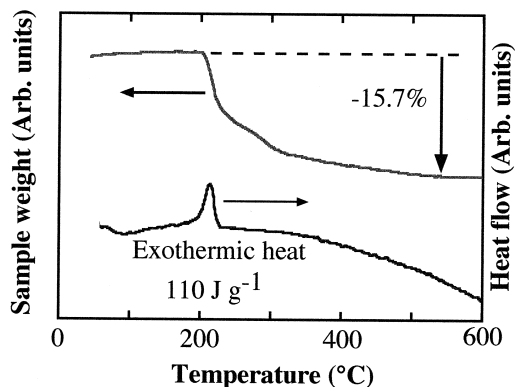


Fig. 5. TG-DSC profiles of sample E in an argon flow with a heating rate of 10°C min⁻¹.

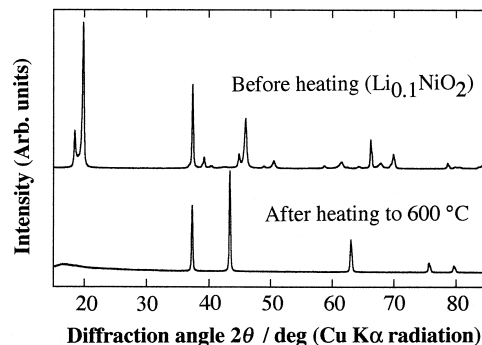


Fig. 6. XRD patterns of samples E (a) before and (b) after heating in the TG-DSC measurement.

[5] up to 300°C, and there was no evident heat generation at a higher temperature. The exothermic heat was about 110 J g⁻¹ with the peak temperature at 213°C. The weight of the sample began to decrease at 200°C and declined gradually and continuously up to about 500°C. The weight loss is due to the oxygen evolution [1], and the final loss at 600°C was 15.7% as shown in the figure. This value agrees well with the expected weight change of 15.8% in the following oxygen evolution reaction.

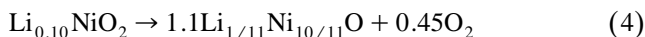


Fig. 6 shows the XRD patterns of sample E both before and after heating. The thermal product had a disordered rock-salt structure with a cubic lattice parameter of $a = 8.36$ (4.18 × 2) Å, which accords with the reported value of Li_{0.1}Ni_{0.9}O in a study of the Li_{1-z}Ni_zO system [20]. Several Li_xNiO₂ samples were examined in the same manner and the reaction mechanism shown above was confirmed not only from the structural data but also from the weight change, the latter of which cannot be correctly measured with electrochemically delithiated samples.

These chemically delithiated samples are useful for examining the characteristics of Li_xNiO₂ free from any additives as described in this study, and can be used to measure not only thermal behavior but also such characteristics as magnetism, conductivity, and electron spin resonance.

4. Conclusion

Stoichiometric LiNiO₂ is chemically oxidized to Li_{0.6}NiO₂ with NOPF₆ and various Li_xNiO₂ compounds ($x \geq 0.1$) are obtained with acid leaching processes. The layered structure is maintained during the chemical delithiation processes. The chemically delithiated Li_{0.1}NiO₂ shows the same electrochemical behavior as electrochemically delithiated Li_xNiO₂. Using these chemically obtained Li_xNiO₂, a reaction mechanism is shown that Li_xNiO₂ is thermally decomposed to produce Li_{x/(1+x)}Ni_{1/(1+x)}O and oxygen.

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