Lithiation into Chemically Synthesized Li_xNiO_2

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Received June 4, 1998 ; Accepted July 27, 1998

1 INTRODUCTION

A number of synthetic routes have been proposed for obtaining lithium intercalation (insertion) materials for lithium battery systems. Delithiation (lithium extraction) from lithiated compounds is of particular interest, because the product is capable of accommodating lithium in pristine lithium sites with few structural changes. Acid leaching processes using disproportionation reactions¹⁾ are useful methods for chemical delithiation. By contrast, alkaline lithium hydroxide solutions have been recently used as lithiation media.²⁾ On these bases, it seems to be possible to obtain a compound with an arbitrary lithium content by changing the pH value of the ambient solution.

In this study we use stoichiometric LiNiO_2 as the lithiated compound, and examine delithiation and lithiation in acid and alkaline solution, respectively. We describe and discuss the structural and electrochemical characteristics of the products.

2 EXPERIMENTAL

Stoichiometric LiNiO_2 was synthesized as previously reported.³⁾ The delithiation and lithiation processes were carried out by adding the nickelate sample to sulfuric acid and lithium hydroxide aqueous solutions, respectively. The mixture was stirred at 25 °C for 5 h, and the solid product was filtered, washed with acetone, and dried. The Li/Ni ratio in the product was evaluated using inductively coupled plasma emission spectroscopy. The oxidation state of nickel was analyzed using iodometry. The structure was analyzed using X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation (Rigaku RU-200,

RAD-rX), in combination with the computer program RIETAN⁴⁾ for Rietveld analyses. The electrochemical characteristics were evaluated using a coin cell⁵⁾ with metallic lithium as a negative electrode. The positive electrode mixture consisted of the nickelate powder (70 wt%), acetylene black (25 wt%) and polytetrafluoroethylene (5 wt%). The electrolyte was 1 mol/dm³ LiPF_6 solution in equal volumes of ethylene carbonate and dimethyl carbonate. The cell voltage was measured using a quasi open circuit voltage (QOCV) technique, where an intermittent current of 0.1 mA/cm² was applied for 2 h, followed by a 2 h rest.

3 RESULTS AND DISCUSSION

The acid-leached product had various Li/Ni values depending on the strength and the amount of the acid used. The filtrate solution was green and the amount of solid product decreased when the Li/Ni value decreased. These facts suggest that the following reaction occurred.

When a sufficient quantity of acid was used, the Li/Ni value became closer to zero. We obtained the minimum Li/Ni value of 0.1 using 1.2 mol/dm³ sulfuric acid. The iodometric analysis of this sample indicated that the oxidation state of nickel was 3.8 ± 0.1 . The sample weight was unchanged upon heating up to 200 °C. These results indicate that the proton content of this sample is low. This sample is hereafter denoted as $\text{Li}_{0.1}\text{NiO}_2$. The nickel valence in this sample is one of the highest values so far obtained by chemical synthesis. The chemical delithiation of lithium nickelate has been examined previously,^{5,6)} however, such a highly delithiated state has not been reported, possibly because of the non-stoichiometric nature of their samples.

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Key Words: Lithium Battery, Lithium Nickelate, (De)lithiation, Pourbaix Diagram

Figure 1 shows the XRD patterns of $\text{Li}_{0.1}\text{NiO}_2$ and pristine $\text{Li}_{1.0}\text{NiO}_2$. The $\text{Li}_{0.1}\text{NiO}_2$ pattern could be ascribed to a mixture of two layered phases. The hexagonal lattice parameters of the major phase (assumed to be $\text{Li}_{0.0}\text{NiO}_2$) were $a=2.82\text{ \AA}$ and $c=13.4\text{ \AA}$ and those of the minor phase (assumed to be $\text{Li}_{0.3}\text{NiO}_2$) were $a=2.82\text{ \AA}$ and $c=14.4\text{ \AA}$. The major phase was estimated to be about 80% of the whole nickelate. These data are in good agreement with those for the Li_xNiO_2 samples which were electrochemically obtained at the 4.2 V vs. Li/Li^+ .^{3,7)} All the other delithiated products also had a layered structure, and the lattice parameters agreed well with those of electrochemically delithiated compounds with the corresponding Li/Ni value.^{3,7)}

We examined the electrochemical characteristics of $\text{Li}_{0.1}\text{NiO}_2$. Figure 2 shows the QOCV profiles. The initial cell voltage was 4.2 V. The x value in Li_xNiO_2 reached almost 1.0 and 0.1, respectively, for the first discharging process to 3.0 V and the subsequent charging process to 4.3 V. The voltage profile was substantially the same as that of the electrochemically obtained sample.^{3,7)}

This material exhibited good reversibility in the non-aqueous electrolyte as shown in Fig. 2, which implies the proton content in this sample being low.

Figure 3 is a Pourbaix diagram showing the voltages of Li_xNiO_2 ($x=0.0, 1.0$)³⁾ in solutions where the concentration of lithium ion is 1 mol/dm³. This shows that $\text{Li}_{0.0}\text{NiO}_2$ is thermodynamically stable in the aqueous solution only at low pH values of up to 1. The actual $\text{Li}_{0.1}\text{NiO}_2$ sample

Fig. 1 XRD patterns of (a) $\text{Li}_{1.0}\text{NiO}_2$ and (b) $\text{Li}_{0.1}\text{NiO}_2$ both measured with $\text{CuK}\alpha$ radiation.

Fig. 2 QOCV curves of Li_xNiO_2 during the first discharging and charging processes.

Fig. 3 Pourbaix diagram of H_2O and Li_xNiO_2 .

was fairly stable in the ambient moisture in air, suggesting that the oxygen evolution is kinetically slow. Figure 3 also indicates that $\text{Li}_{0.0}\text{NiO}_2$ would accommodate lithium in an alkaline solution. On this basis, we treated $\text{Li}_{0.1}\text{NiO}_2$ with an excess amount of 1.0 mol/dm³ lithium hydroxide solution. The product exhibited the Li/Ni value of 0.5 and had a layered structure. The monoclinic lattice parameters again agreed with those of the electrochemically obtained $\text{Li}_{0.5}\text{NiO}_2$. This result implies that Li_xNiO_2 can be used as an electrode material in a lithium-ion cell with aqueous electrolytes.⁸⁾

In this way it was shown that the x value in Li_xNiO_2 can be controlled by changing the pH value of the ambient solution. Chemically obtained samples are useful for examining the magnetic, electrical or thermal characteristics of Li_xNiO_2 being free of additives such as carbon contained in the electrochemical samples.

Furthermore, we have found that $\text{Li}_{0.1}\text{NiO}_2$ accommodates not only lithium but also sodium and potassium in the corresponding alkaline solution. These results indicate the possibility of synthesizing new intercalation materials for various applications.

4 CONCLUSION

We synthesized various Li_xNiO_2 compounds using acid and alkaline leaching processes. $\text{Li}_{0.1}\text{NiO}_2$ was obtained at a low pH value of 0 and it accommodated lithium in a lithium hydroxide solution. The structural and electrochemical properties of chemically obtained Li_xNiO_2 were essentially the same as those of electrochemically obtained samples.

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