

NiOOH·Li_x (x>0) Synthesized by New Chemical Method with Lithium-Naphthalene Complex Solution for Active Materials of Lithium Secondary Cells

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Abstract

The NiOOH · Li_x (0 < x ≤ 1) positive active material in the discharged state for Li-ion cells has been successfully synthesized by the new chemical method using reduction of NiOOH with lithium-naphthalene organic complex solution. The further lithium insertion by this chemical method was found to provide a novel negative active material with large capacity of 1000 mAh g⁻¹ corresponding to 3.4 Li per formula unit of NiOOH with the reversible potential in the range between 0.6 and 2.4 V vs. Li/Li⁺.

1 Introduction

A world-wide effort has been made to find alternative positive active materials for LiCoO₂, LiNiO₂, and LiMn₂O₄ and negative active materials for carbon in existing Li-ion cells to meet the strong demand of higher energy density for portable phones and electric vehicles. The NiOOH has been a promising candidate as a positive active material for 3-volt-class lithium cells^{1, 2)}, since this material has a layer structure with the feature of high Li-ion diffusion coefficient and shows the delivered discharge capacity of 280 mAh g⁻¹.³⁾ However, the application of this material has to be limited to the positive

active materials for practical cells with metallic lithium as negative active materials, since the NiOOH is the charged state with no lithium source. In this report, lithium was doped into NiOOH by the new chemical method with organic complex solution for the preparation of lithium-contained material as the discharged state. The obtained NiOOH·Li_x (x>0) has been investigated as positive and negative active materials by electrochemical measurements such as X-ray diffraction (XRD) analysis, inductively coupled plasma (ICP), and chemical analysis of KMnO₄ back titration.

2 Experimental

2.1 Synthesis of NiOOH · Li_x (x>0)

The electrode with the composition of 80 mass% of NiOOH, 5 mass% of acetylene black (AB), and 15 mass% of poly-vinylidene fluoride (PVDF) was

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prepared using a foamed-nickel substrate. The complex solution was also prepared by dissolving 0.25 mol dm⁻³ naphthalene and saturated metallic lithium into 1-methoxybutane solvent. The NiOOH electrode was then immersed into the complex solution at various time for the preparation of NiOOH·Li_x (x>0) electrode.

2.2 Electrochemical measurement

Electrochemical behaviors of NiOOH·Li_x (x>0) electrodes were investigated in flooded type glass cells with the mixture electrolyte of 1 mol dm⁻³ LiClO₄ containing ethylene carbonate (EC) and diethyl carbonate (DEC) (1 : 1 in the volume ratio) using metallic lithium as counter and reference electrodes. Charge and discharge tests were conducted at the constant current density of 0.25 mA cm⁻² in the potential range from 1.5 to 4.2 V vs. Li/Li⁺ and 0.3 to 3.0 V vs. Li/Li⁺ for positive and negative electrodes respectively at 25 °C in argon atmosphere.

2.3 Identification of synthesized NiOOH·Li_x (x>0)

The synthesized NiOOH·Li_x (x>0) was identified for the crystalline structure by means of XRD analysis. The quantitative analysis of lithium was determined by inductively coupled plasma (ICP). The oxidation state of nickel was determined by KMnO₄ back titration method using of 0.1 mol dm⁻³ (NH₄)₂Fe(SO₄)₂.

3 Results and discussion

3.1 Open-circuit potential and electricity charged of Li-doped NiOOH electrode

The change in open-circuit potential of NiOOH electrode treated at different immersion times is shown in Fig. 1. The potential is found to shift toward less-noble direction with immersion time. This means that the reduction of active material is promoted in the solution. The first charge curves of NiOOH electrodes treated at different immersion times are shown in Fig. 2. The electricity charged is found to be strongly dependent on the immersion time. This fact indicates that the amount of doped lithium increases with the immersion time.

3.2 Charge-discharge characteristics of Li-doped NiOOH electrode

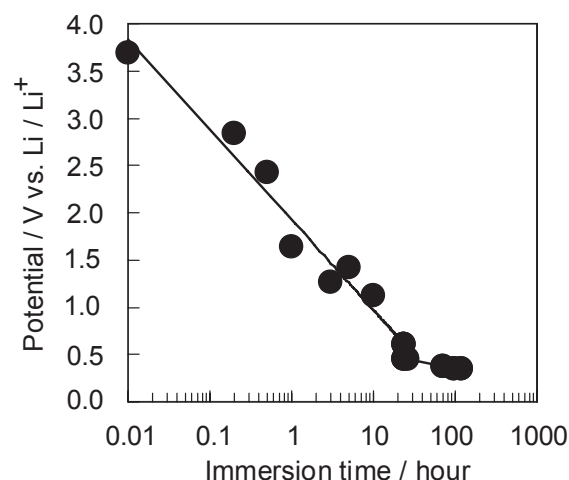


Fig. 1 Change in the open-circuit potential of Li-doped NiOOH electrode with immersion time.

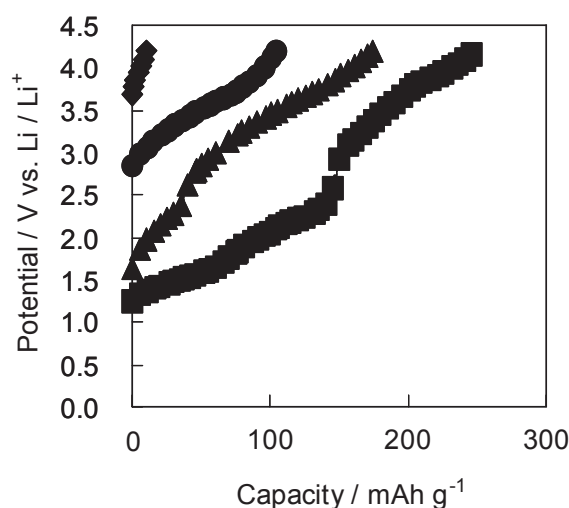


Fig. 2 The first charge curve of NiOOH·Li_x (x ≥ 0) electrodes treated for various immersion time. Immersion times are ◆ : 0 h, ● : 0.2 h, ▲ : 1 h, and ■ : 3 h.

The potential behavior of Li-doped NiOOH electrode with open-circuit potential of 2.8 V vs. Li/Li⁺ is shown in Fig. 3. The electricity charged of this electrode is found to be 104 mAh g⁻¹ and the subsequent discharge capacity is 96 mAh g⁻¹. The value of charging efficiency was 92.3%. The discharge profile for non doped NiOOH electrode is shown in Fig. 4 for reference of the doped electrode. The discharge behavior is found to be the same as the Li-doped electrode and its delivered capacity

is also found the similar value of 96 mAh g^{-1} in the potential region of $4.2 - 1.5 \text{ V vs. Li/Li}^+$.¹⁾ Therefore, the Li-doped electrode with the open-circuit potential of $2.8 \text{ V vs. Li/Li}^+$ is considered to be attributed to $x=1$ of $\text{NiOOH}\cdot\text{Li}_x$. Furthermore, the potential behavior of Li-doped NiOOH electrode with the less noble open-circuit potential of $0.6 \text{ V vs. Li/Li}^+$ corresponding to the immersion time of 24 hours

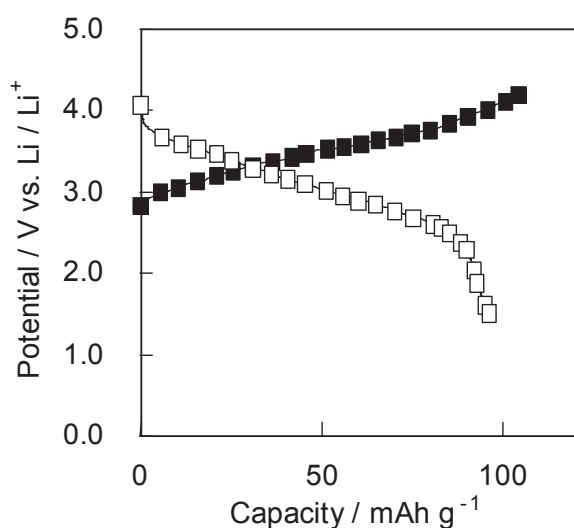


Fig. 3 Charge-discharge profiles of Li-doped NiOOH electrode with open-circuit potential of $2.8 \text{ V vs. Li/Li}^+$ obtained by chemical method with 0.2 h immersion.

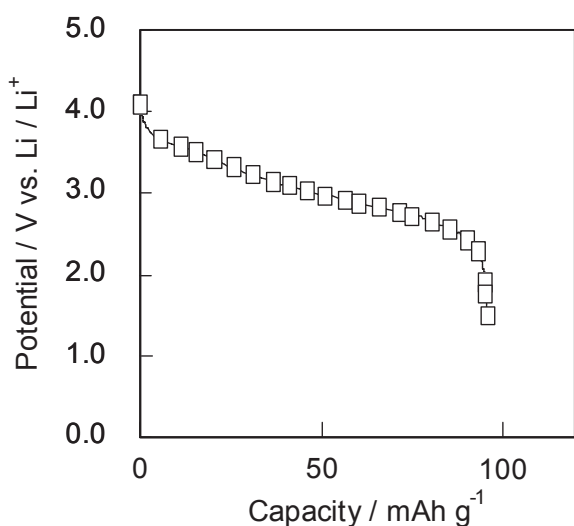


Fig. 4 Discharge profile of NiOOH electrode.

is shown in **Fig. 5**. The potential behavior of this electrode is totally different from one of the former electrode of the Li-doped NiOOH electrode with open-circuit potential of $2.8 \text{ V vs. Li/Li}^+$. That is to say, this electrode is found to show the large capacity of over 1000 mAh g^{-1} corresponding to 3.4 Li per formula unit of NiOOH with the reversible potential range between 0.6 and $2.4 \text{ V vs. Li/Li}^+$. This behavior shows that this electrode may be the new negative active material rather than the positive one.

3.3 Identification of Li-doped NiOOH

XRD patterns of Li-doped NiOOH with various immersion times are shown in **Fig. 6**. The peaks of $2\theta = 19^\circ$ and 38.5° are attributed to (001) and (002) index number of NiOOH respectively. The peak of $\text{Ni}(\text{OH})_2$ is also detected at around $2\theta = 33^\circ$. The NiOOH peaks gradually become to broaden with increasing the immersion time and the peak disappears in the case of the electrode with open-circuit potential of $0.6 \text{ V vs. Li/Li}^+$. The change in half-width of NiOOH X-ray diffraction peak (001) is shown as the function of open-circuit potential in **Fig. 7**. The value of half-width of peak (001) shows to be stable by the open-circuit potential of $2.8 \text{ V vs. Li/Li}^+$, but drastically increases beyond its value. The phenomenon is considered to be the lithium insertion

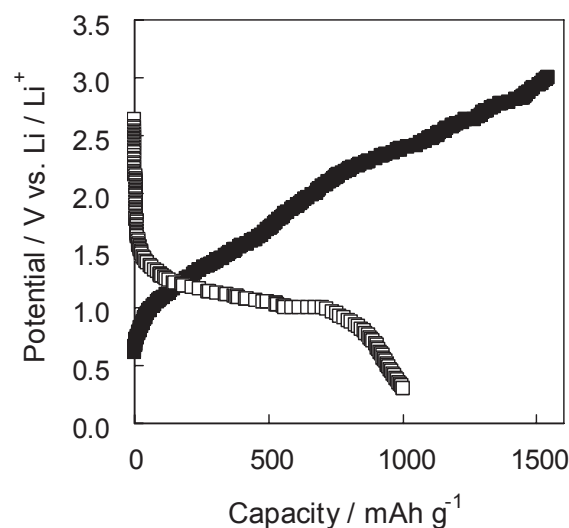


Fig. 5 Charge-discharge profiles of Li-doped NiOOH electrode obtained by chemical method with 24 h immersion.

mechanism beyond $x=1$ of $\text{NiOOH}\cdot\text{Li}_x$ resulting in the amorphousization of its the crystalline structure. The change in Li/Ni mole ratio of Li-doped NiOOH by ICP analysis is shown as a function of open-circuit potential in Fig. 8. The value of Li/Ni mole ratio tends to increase as the open-circuit potential shifts toward less-noble potential. The value reaches to

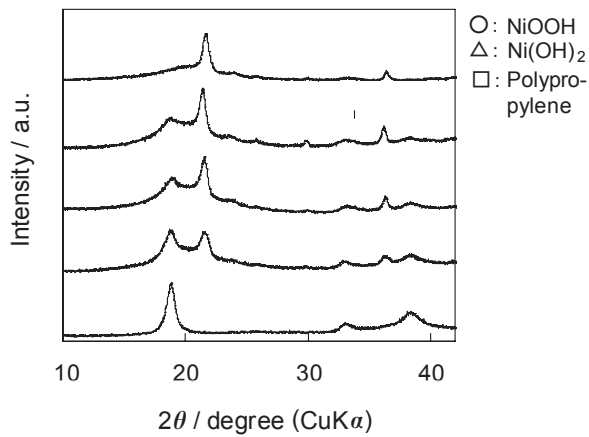


Fig. 6 XRD patterns of $\text{NiOOH}\cdot\text{Li}_x$ electrode with various immersion time and open-circuit potential of (a) 24 h, 0.6 V, (b) 3 h, 1.4 V, (c) 1 h, 1.6 V (d) 0.5 h 2.4 V, and (e) 0 h, 3.7 V vs. Li/Li^+ respectively.

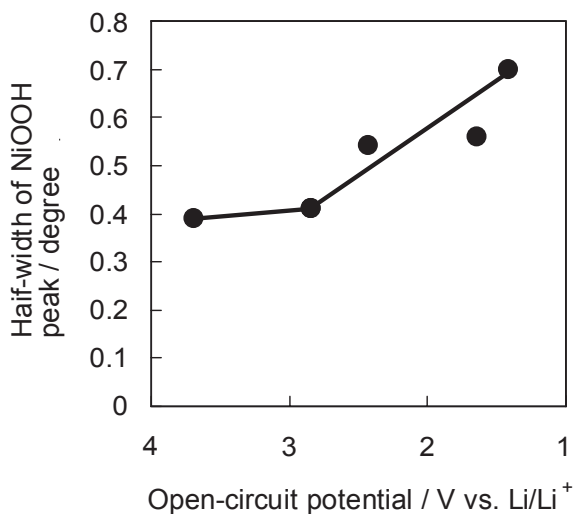


Fig. 7 The value of half-width for NiOOH peak of $2\theta = 19^\circ$ as a function of open-circuit potential.

1 as the open-circuit potential shifts to 2.8 V vs. Li/Li^+ . The change in nickel oxidation state for Li-doped NiOOH electrode by KMnO_4 back titration method is also shown in Fig. 9. The oxidation state of nickel in the case of 2.52 V vs. Li/Li^+ seems to be changed from trivalent to divalent. The change of the oxidation state of nickel seems to be promoted

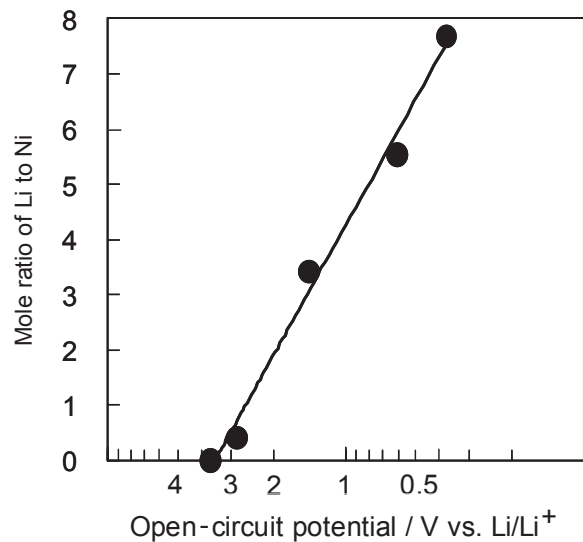


Fig. 8 Mole ratio of Li to Ni for Li-doped NiOOH as a function of open-circuit potential by ICP analysis.

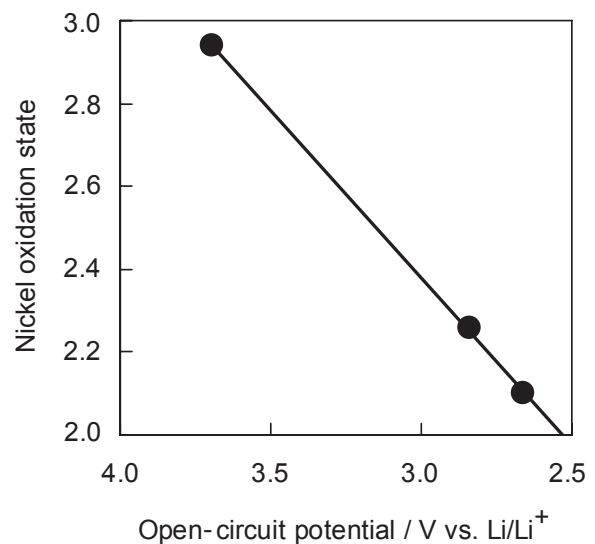


Fig. 9 Change in nickel oxidation state for Li-doped NiOOH electrode as a function of open-circuit potential.

by the immersion time judging from the potential change of Li-doped NiOOH electrode as shown in Fig. 1. The sudden change of discharge behavior is observed when the open-circuit potential shifts to less-noble beyond 2.8 V vs. Li/Li⁺ as shown in Fig. 5. This is considered to be caused by the lithium insertion beyond $x = 1$ of NiOOH·Li_x resulting in the amorphousization of its the crystalline structure as mentioned before. The amount of electricity discharged is beyond 1000 mAh g⁻¹ and the value of electricity charged is beyond 1500 mAh g⁻¹ as shown in Fig. 5. This further lithium insertion by this chemical method seems to provide a novel negative active material with large capacity of 1000 mAh g⁻¹ corresponding to 3.4 Li per formula unit of NiOOH with the reversible potential in the range between 0.6 and 2.4 V vs. Li/Li⁺.

4 Conclusions

The NiOOH·Li_x ($0 < x \leq 1$) positive active material in the discharged state for Li-ion cells has been

successfully synthesized by the new chemical method using reduction of NiOOH with lithium-naphthalene organic complex solution. The sudden change of discharge behavior of this electrode with amorphousization was observed, when more than 1 Li per unit formula was inserted into NiOOH. The further lithium insertion beyond $x > 1$ seems to provide a novel negative active material with large capacity of 1000 mAh g⁻¹ corresponding to 3.4 Li per formula unit of NiOOH with the reversible potential in the range between 0.6 and 2.4 V vs. Li/Li⁺.

References

- 1) J. Maruta, H. Yasuda, Y. Fujita, and M. Yamachi, *Electrochem. Soc. Proc.*, Vol. 97-18, 151 (1997).
- 2) H. Sasaki, H. Yasuda, and M. Yamachi, *GS news Technical Report*, 60 (1), 12 (2001).
- 3) J. Maruta, H. Yasuda, and M. Yamachi, *The 38th Battery Symposium in Japan*, p.99 (1997).