Reaction Mechanism of LiNiO$_2$ Synthesized in Oxygen Atmosphere by Pechini Method

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Pechini process was known as an excellent method for the synthesis of LiNiO$_2$ powder. Compared with the result of solid state reaction using NiO and Li$_2$CO$_3$ as reactants, Ni$_2$O$_3$ was the new compound found in Pechini-processed powder. In the present work, the role of Ni$_2$O$_3$ and the reaction mechanism for the synthesis of Pechini-processed LiNiO$_2$ were studied. XRD and DTA/TG analysis were used to investigate the phases present and the thermal reaction in the Pechini process studied. It was found that Ni$_2$O$_3$ was obtained from nickel citrate and nickel acetate which released a large amount of heat during calcination. Based on the thermodynamic calculation, Ni$_2$O$_3$ is not a stable compound in the oxidizing environment. As a result, Ni$_2$O$_3$ decomposes into NiO, and the decomposed NiO reacts with Li$_2$CO$_3$ and forms LiNiO$_2$ at 700°C. An isothermal kinetics study was performed on the mixture of NiO, Ni$_2$O$_3$ and Li$_2$CO$_3$ at 700°C. The result indicates that the decomposition of Ni$_2$O$_3$ into NiO takes place at the beginning hour of the isothermal reaction. Consequently, NiO and Li$_2$CO$_3$ are consumed due to the formation of LiNiO$_2$. Based on the results obtained, the reactions for Pechini-processed LiNiO$_2$ may be described by the following reactions:

$$\text{Citrate complex} \rightarrow \text{Li}_2\text{CO}_3 + \text{NiO} + \text{Ni}_2\text{O}_3$$

$$\text{Ni}_2\text{O}_3 \rightarrow 2\text{NiO} + \frac{1}{2} \text{O}_2$$

$$\frac{x}{2} \text{Li}_2\text{CO}_3 + (2-x)\text{NiO} + \frac{x}{4} \text{O}_2 \rightarrow \text{Li}_x\text{Ni}_{2-x}\text{O}_2 + \frac{x}{2} \text{CO}_2 \quad (0 < x \leq 1)$$

This reaction is rationalized on the basis of the instability of Ni$_2$O$_3$ and the structural similarity between NiO and LiNiO$_2$.

Key-words: X-ray diffraction, Lithium compound, Oxides

1. Introduction

LiNiO$_2$ as cathode in lithium ion batteries provides the advantage of being inexpensive and environmentally benign, but suffers from the difficulty in stoichiometric powder synthesis, inferior capacity and unacceptable performance fade.$^{11-6}$ In order to improve the performance of LiNiO$_2$, the soft chemical process which mixes cations in an atomic scale by forming polymeric precursors was widely used. Among them, the Pechini method has received much attention. In this method, various cations are chelated with an organic acid and ethylene glycol.$^{17-10}$ After heating to the moderate temperature, polyestification occurs and most of the excess water is removed. Then, a solid polymeric ‘resin’ is formed. Finally, the “resin” is calcined at a high enough temperature to remove all organic substances. After calcination, a homogenous, well-crystallized and stoichiometric oxide is expected. This process provides a good stoichiometric ratio of reactants. LiNiO$_2$ powder in submicron range has been developed using Pechini method. An improved performance for Pechini-processed LiNiO$_2$ was observed due to shortened diffusion path of lithium ion in LiNiO$_2$ cathode.$^{11,12}$

Li$_2$CO$_3$, NiO, and Ni$_2$O$_3$ were observed from the decomposition of lithium nickel precursor at 300°C, when LiNiO$_2$ was synthesized using Pechini method. To examine the role of Ni$_2$O$_3$ and detailed reaction mechanism for LiNiO$_2$ synthesized by Pechini method in O$_2$ atmosphere, XRD, DTA/TG and isothermal reaction kinetics were conducted.

2. Experimental procedure

2.1 LiNiO$_2$ synthesized by Pechini method

To synthesize LiNiO$_2$ powder using Pechini method, citric acid (99.5%, FERAK), ethylene glycol (99.7%, TEDIA), nickel nitrate (99+%, Merck) and lithium nitrate (99+%, ACROS) were used as starting materials. Nickel nitrate and lithium nitrate were first dissolved in de-ionized water. Subsequently, citric acid, and ethylene glycol with desired ratio were added and formed homogenous solution. After water was removed, the solution was dehydrated into gels, which were then calcined at the temperatures ranging from 200°C to 700°C for various periods of time in O$_2$ atmosphere.

For the sake of comparison, LiNiO$_2$ was also synthesized in O$_2$ atmosphere using solid state reaction method, in which NiO and Li$_2$CO$_3$ were used as starting materials. Same heating and calcinations procedures as Pechini process were used.

2.2 Characterization of calcined LiNiO$_2$ powder from Pechini-process

A Setarm differential thermal analyzer (model TGA 92) was used to examine thermal reaction and corresponding weight change of dried, ground resins with a heating rate of 2°C/min in the range from 25°C to 900°C in O$_2$ atmosphere. X-ray diffraction (XRD) analysis was conducted on calcined powder using Shimadzu X-ray Diffraction System (model XD–D1) with monochromated Cu K$_\alpha$ radiation. The accelerating voltage and current were set at 30 kV and 30 mA, respectively, with a 20 scan speed of 1° min$^{-1}$ from 10° to 80°. The volume fraction ($\alpha$) of individual phases was calculated from the integrated intensity of XRD patterns which were collected with a step of 0.01° and counting time of 1 s.

3. Results and discussion

3.1 Decomposition of lithium nickel citrate obtained from Pechini method

After mixing citric acid, ethylene glycol and nitrate salts
using Pechini method and followed by drying at 120°C, a homogeneous lithium nickel citrate gel was obtained. Subsequently, the dried gel was calcined at various temperatures. Figure 1 shows the XRD traces for lithium nickel citrate calcined at the temperatures between 200°C and 700°C in O₂ for 12 h. For citrate calcined below 200°C, an amorphous phase was observed as shown in Fig. 1(a). As the temperature increased to 300°C, the reflections from Li₂CO₃, NiO and Ni₂O₃ were observed due to the decomposition of lithium nickel precursors. Subsequently, Li₂CO₃ reacted with NiO or Ni₂O₃, and layer-structured LixNi₂-xO₂ was formed at 700°C as shown in Fig. 1(c). However, it is interesting to note that the phase of Ni₂O₃ was not observed when LiNiO₂ was synthesized in pure O₂ using a solid-state method with Li₂CO₃, Li₂O and NiO as starting materials. Until now, it is still not clear how Ni₂O₃ reacts with Li₂CO₃ and forms LiNiO₂. Thus, the objective of this study is to investigate the role of Ni₂O₃ in the formation of LiNiO₂, when a Pechini method is adopted in an oxygen-containing atmosphere.

3.2 Origin of Ni₂O₃

As shown previously, Ni₂O₃ was observed when LiNiO₂ was synthesized using Pechini method in O₂. To find out the mechanism for the formation of Ni₂O₃, Li citrate was first excluded and various sources of Ni were studied. The sources of Ni including Ni citrate (Pechini method), Ni(CH₃COO)₂, Ni(NO₃)₂·6H₂O, and NiO were heated at 400°C for 12 h in pure O₂. The corresponding XRD results are shown in Fig. 2. In Figs. 2(a) and (b), Ni₂O₃ and NiO were formed when Ni citrate and Ni(CH₃COO)₂ were used as starting materials. However, only NiO phase was observed when Ni(NO₃)₂·6H₂O, and NiO as starting materials as shown in Figs. 2(c) and (d). Then the DTA-TG analysis was also conducted for the decomposition of various Ni sources in O₂. As shown in Fig. 3, Ni citrate and Ni(CH₃COO)₂ exhibit exothermic behavior and Ni₂O₃ is formed as shown in Figs. 2(a) and (b), and Figs. 3(a) and (b). Violent exothermic reaction was caused by the self burning of hydrocarbon chains of Ni citrate and Ni(CH₃COO)₂. The weight loss of Ni citrate and Ni(CH₃COO)₂ is caused by the removal of water during dehydration of (-CH₂-CHOH-) at temperatures below 300°C as shown in Figs. 3(a) and (b). At about
the violent exothermic peak from self burning was observed. The released heat enhances the conversion of Ni citrate to NiO and Ni$_2$O$_3$. At temperatures higher than 450°C, all the DSC and TG traces for precursors heated in oxygen become nearly flat lines which indicates that neither thermochemical reaction nor weight loss has occurred. Table 1 summaries the result of thermal analysis for various nickel sources. Summarily, the violent exothermic reaction gives rise the oxidation of nickel acetate and nickel citrate to higher valent nickel (III) by overcoming the high activation energy of Ni$_2$O$_3$.

On the other hand, the decomposition of Ni(NO$_3$)$_2$$\cdot$6H$_2$O is an endothermic reaction. The final product NiO forms at about 350°C as shown in Figs. 2 (c) and 3 (c). The result indicates that no excess heat is available to enhance the formation of Ni$_2$O$_3$. In Fig. 3 (d), when NiO was used as the starting material neither weight loss nor thermal reaction observed. NiO is stable up to 1000°C. The result indicates that Ni$_2$O$_3$ could not be obtained from NiO even when NiO was heated in O$_2$ atmosphere. Hence, NiO is the stable phase in oxygen atmosphere. This result is consistent with the XRD trace observed from the solid-state reaction.

The formation of Ni$_2$O$_3$ may be expressed by the following reaction

$$2\text{NiO} + \frac{1}{2} \text{O}_2 \rightarrow \text{Ni}_2\text{O}_3$$

(1)

The thermodynamic data for heat capacity and entropy of Ni$_2$O$_3$ are not readily available. Although the exact free energy change for the formation of Ni$_2$O$_3$ is not available, approximation may be made from $\Delta H$ and $\Delta S$. The $\Delta H_{298}$ was calculated to be around $-1.0 \times 10^4$ J/mol. The entropy change can be approximated by the elimination of oxygen. Thus, $\Delta S$ is close to $-1.0 \times 10^2$ J/molK. Therefore, the Gibbs free energy for Eq. (1) should be positive and this reaction is not spontaneous. That is the reason why Ni$_2$O$_3$ was not observed in solid-state reaction using NiO as starting material.

Again, Ni$_2$O$_3$ was obtained when Ni citrate and Ni acetate were heated in O$_2$. It is believed that Ni$_2$O$_3$ is a meta-stable phase. Thus, the decomposition of Ni$_2$O$_3$ into NiO is expected. In this study, the mixture of Ni$_2$O$_3$ and NiO which was obtained as Ni citrate was heated from 400°C to 800°C for 12 h. Figure 4 shows the volume fraction ($\phi$) of NiO which is estimated from XRD integrated peak intensity of the reflections of NiO and Ni$_2$O$_3$ located at about $2\theta = 43.2^\circ$ and $44.85^\circ$, respectively. The fraction formed of NiO follows a parabolic behavior. At 400°C, the fraction of NiO was about 20%, when temperature was extended to 600°C, 80% of NiO obtained. When the temperature was raised to 800°C, almost 100% NiO was obtained. This result confirms the fact that Ni(III)$_2$O$_3$ is unstable and easily transforms to Ni (II)O in an oxygen-rich atmosphere as the temperature increases.

### 3.3 Formation mechanism of lithium nickel oxides processed by Pechini method

Since Ni$_2$O$_3$ is present during the synthesis of LiNiO$_2$ by the Pechini method, it is important to study the role of Ni$_2$O$_3$ on the formation of LiNiO$_2$. As shown in Fig. 1, when precursor formed by the Pechini method was calcined at various temperatures, it was found that Ni$_2$O$_3$ appeared at 300°C and then reacted with Li$_2$CO$_3$ to form LiNiO$_2$. Two possible reaction routes may have taken place for the formation of LiNiO$_2$. One is the direction reaction between Li$_2$CO$_3$ and Ni$_2$O$_3$ since the Ni is trivalent in both Ni$_2$O$_3$ and LiNiO$_2$. Another possible route is that Ni$_2$O$_3$ may convert into NiO and then react with Li$_2$CO$_3$ to form LiNiO$_2$.

#### 3.3.1 Reaction between Ni$_2$O$_3$ and Li$_2$CO$_3$

In order to clarify the reaction between Ni$_2$O$_3$ and Li$_2$CO$_3$, the following reactions were conducted. Ni$_2$O$_3$ was first obtained by decomposition of Ni citrate at 400°C in O$_2$. The decomposed products contain Ni$_2$O$_3$ and NiO as shown in Fig. 2(a). Subsequently, the following two reactions were studied using different starting materials.

1. **Reaction A**: In this reaction, the starting materials used were NiO, Ni$_2$O$_3$ and Li$_2$CO$_3$ and heated at 700°C for various periods of time in O$_2$.

2. **Reaction B**: In this reaction, the starting materials used were NiO and Li$_2$CO$_3$. Same heating procedure as reaction A was used. The result of this reaction was compared with reaction A to examine the effect of NiO$_2$ on the formation of LiNiO$_2$.

#### 3.3.1.1 XRD analysis of reaction A

After the reaction was completed, the volume fraction of individual phases was determined based on the integrated intensity of reflection from XRD. Figure 5 shows the XRD

### Table 1. Summary for the Thermal Decomposition for Various Nickel Salts

<table>
<thead>
<tr>
<th>Calculating temperature (°C)</th>
<th>Starting materials</th>
<th>Decomposed compound at temperature &gt;350°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>200-350°C</td>
<td>Ni(CH$_3$COO)$_2$</td>
<td>Ni$_2$O$_3$, NiO</td>
</tr>
<tr>
<td></td>
<td>Ni(NO$_3$)$_2$•6H$_2$O</td>
<td>Ni$_2$O$_3$, NiO</td>
</tr>
<tr>
<td></td>
<td>NiO</td>
<td>Ni$_2$O$_3$, NiO</td>
</tr>
<tr>
<td></td>
<td>NiO</td>
<td>Ni$_2$O$_3$, NiO</td>
</tr>
</tbody>
</table>

Fig. 4. XRD intensity ratio of [NiO/(NiO+Ni$_2$O$_3$)] at various temperatures for 12 h.
reflections of reaction A after NiO, Ni$_2$O$_3$ and Li$_2$CO$_3$ were heated in O$_2$ at 700$^\circ$C for up to 12h. It was observed that Ni$_2$O$_3$ and NiO coexist during the first 5h reaction. However, the reflection of Ni$_2$O$_3$ abruptly decreases as time increases. On the contrary, LixNi$_{2-x}$O$_2$ appears in about 1h. The reflection intensity of LixNi$_{2-x}$O$_2$ and NiO increases significantly, while Ni$_2$O$_3$ decreases abruptly at the beginning hour. As the reaction extended to 12h, the reflection of Ni$_2$O$_3$ is no longer available. The reflection intensities from Li$_2$CO$_3$ and NiO also decreased rapidly. Subsequently, the (003) reflection of rhombohedral phase of LixNi$_{2-x}$O$_2$ appears at 2$\theta$=18.7$^\circ$. It is suggested that lithium and nickel cations diffuse to alternate cation layers of NiO, and the R$3m$ (x>0.6) is formed as shown in Fig. 5 (f). In the ideal stoichiometry, the Li$^+$ and Ni$^{3+}$ cations are supposed to be orderly arranged along the [111] direction of the rock salt cubic lattice, leading to a 2D layered structure material (R$3m$). The displacement between Ni$^{3+}$ ions at octahedral 3a sites and Li$^+$ ions at 3b sites in space group R$3m$ weakens the intensity of the (003) line, while such a displacement does not affect the intensity of the (104) line at about 2$\theta$=44.1$^\circ$. The phenomenon was demonstrated by the calculation of structure factor in the previous study.\(^{11}\)

3.3.1.2 XRD analysis of reaction B

Figure 6 shows the XRD patterns from the products of reaction B when Li$_2$CO$_3$ and NiO were heated in O$_2$ at 700$^\circ$C for up to 12h. This result shows that as holding time increases, the intensity of XRD peaks of Li$_2$CO$_3$ decreases. The reflections of NiO also shift to the higher angle, indicating that lattice parameter of NiO decreases. This result suggests that the valence of nickel is increased from Ni$^{2+}$ ($r_{Ni^{2+}}$=0.068 nm) to Ni$^{3+}$ ($r_{Ni^{3+}}$=0.056 nm) when Li inserts into NiO lattice as shown LixNi$_{2-x}$O$_2$. This structure is similar to NaCl (Rock salt) structure. This result indicates that Li and Ni randomly occupy original Ni sites before 5h. When the reaction extended to 12h, the characteristic reflection (003) of R$3m$ structure was found in Fig. 6 (f). When both reactions A and B extended for 12h at 700$^\circ$C, rhombohedral LixNi$_{2-x}$O$_2$ was observed. I(003)/I(104) ratio which is commonly used to describe the layered structure was found to be 0.37 and 0.39 for Fig. 5(f) and Fig. 6 (f), respectively. Thus, similar layered LixNi$_{2-x}$O$_2$ was obtained when either Ni$_2$O$_3$ or NiO was used as the source of Ni.

3.3.2 Kinetics study of reactions A and B

The kinetics of reactions A and B was studied based on the volume fraction ($\alpha$) of individual phases. The volume fraction was estimated from the integrated intensity of different phases. In Fig. 7, the fraction ($\alpha$) of LixNi$_{2-x}$O$_2$ was plotted as a function of reaction time, for reactions A and B conducted at 700$^\circ$C. The formation of LixNi$_{2-x}$O$_2$ from both reactions at constant temperature follows a parabolic behavior as time increased. It was found that the reaction rates of A and B are nearly the same. Thus, the reaction mechanism should be the same for both reactions.

The kinetics resemblance between reactions A and B can be further examined from the variation of volume fractions ($\alpha$) of NiO, Ni$_2$O$_3$ and LixNi$_{2-x}$O$_2$. Figure 8 shows the
relationship between fractions (α) of NiO, Ni2O3, LixNi2-xO2 and reaction periods in reaction A. A significant change for individual phases was observed in the beginning hour. In this period, the amount of Ni2O3 phase reduces from 75% to 15%. On the other hand, NiO, LixNi2-xO2 phase increases from 25% to 45% and 0% to 35%, respectively. This result indicates that Ni2O3 decomposes into NiO first. Then, NiO and Li2CO3 react and form LixNi2-xO2. With reaction time extended to 12 h, only LixNi2-xO2 phase increased gradually from 35% to 70%. Both Ni2O3 and NiO decreased from 15% to 1% and 45% to 25%, respectively. The decomposition of Ni2O3 into NiO was verified by heating Ni2O3 at 700°C in O2. The amount of converted NiO was plotted as a function of reaction time as shown in Fig. 9. The decomposition of Ni2O3 into NiO takes place rapidly in the first two hours. Subsequently, the decomposition of Ni2O3 reaches equilibrium. Thus, the amount of NiO obtained was leveling off as the time increased. When Ni2O3 was heated with Li2CO3 shown in Fig. 8, the amount of NiO increased first due to the decomposition of Ni2O3. Subsequently, NiO actively reacts with Li2CO3 and forms LixNi2-xO2. The amounts of NiO are gradually consumed as the reaction continues.

From the kinetics study shown here, it may be concluded that the presence of Ni2O3 does not enhance the formation of LiNiO2, although the valence of Ni is the same as that in LiNiO2. It is believed that the structure resemblance between NiO and LiNiO2 is the determining factor in the formation of LiNiO2. The structure of NiO provides an excellent skeleton for the formation of LiNiO2. As the reaction continues, the symmetry of lithiated NiO is gradually lowered from Fm3m to R3m. The schematics of the structure variation are shown in Fig. 10. First, the Li and Ni ions occupy randomly in the octahedral sites of oxygen, and the structure belongs to Fm3m shown in Fig. 10(a). As Li and Ni ions form an ordered arrangement along the [111] direction, the symmetry of structure decrease and a layered structure with symmetry of R3m was obtained as shown in Fig. 10(b).

Considering the instability of Ni2O3 at high temperature and the requirement of structure similarity, the synthesis of LiNiO2 using Pechini method from citrate salt can be expressed as following equations.

\[
\text{Citrate complex} \rightarrow \text{Li}_2\text{CO}_3 + \text{NiO} + \text{Ni}_2\text{O}_3 \quad (2)
\]

\[
\text{Ni}_2\text{O}_3 \rightarrow 2\text{NiO} + \frac{1}{2} \text{O}_2 \quad (3)
\]

\[
\frac{x}{2} \text{Li}_2\text{CO}_3 + (2-x)\text{NiO} + \frac{x}{4} \text{O}_2 \rightarrow \text{Li}_x\text{Ni}_{2-x}\text{O}_2 + \frac{x}{2} \text{CO}_2 \quad (0 < x \leq 1) \quad (4)
\]

3.4 Relationship between electrochemistry and structure of LiNiO2
After preheating citrate at 350°C in O2 and air, Li2CO3,
NiO and Li$_2$CO$_3$, NiO, Ni$_2$O$_3$ were formed, respectively. Then, both powder mixtures were calcined at 800°C in O$_2$. Finally, LiNiO$_2$ were formed. The similar XRD results from these powder mixtures were obtained due to the same structure of LiNiO$_2$. The discharge capacities of these two specimens synthesized by these two routes were shown in the Fig. 11. It was observed that the discharge capacities for both specimens were about 150 mAh/g. The result indicates that the electrochemical property of LiNiO$_2$ is dependent on its crystal structure and chemical composition rather than the synthesis route.

4. Conclusions

The following conclusions are drawn based on the present work.

(1) During the synthesis of LiNiO$_2$ using Pechini process, Ni$_2$O$_3$ is found in the calcined powder. Ni$_2$O$_3$ is not present in the solid-state powder.

(2) From DTA/TG analyses, the formation of Ni$_2$O$_3$ is caused by the oxidation of nickel acetate and nickel citrate.

(3) Ni$_2$O$_3$ is essentially an unstable compound which decomposes to NiO at elevated temperatures.

(4) From the isothermal kinetics study of Pechini-processed LiNiO$_2$, it is clear that Ni$_2$O$_3$ decomposes to NiO in the beginning of the reaction. Subsequently, the decomposed NiO reacts with Li$_2$CO$_3$ and forms layer-structured LiNiO$_2$.

(5) The formation of LiNiO$_2$ using Pechini process can be described by the following reactions:

\[
\text{Citrate complex} \rightarrow \text{Li}_2\text{CO}_3 + \text{NiO} + \text{Ni}_2\text{O}_3
\]

\[
\text{Ni}_2\text{O}_3 \rightarrow 2\text{NiO} + \frac{1}{2} \text{O}_2
\]

\[
\text{Li}_2\text{CO}_3 + (2-x)\text{NiO} + \text{O}_2 \rightarrow \text{Li}_x\text{Ni}_{2-x}\text{O}_2 + \text{CO}_2 (0 < x \leq 1)
\]

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References