FORMATION OF LITHIATED NIO AND LiNiO₂ IN MOLten CARBONATE

Satoshi INOU, Naobumi MOTOHIRA, Nobuyuki KAMIYA,
and Ken-ichiro OTA

Department of Energy & engineering, Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan

ABSTRACT

The formations of lithiated NiO and LiNiO₂ in molten carbonate have been studied in CO₂ - O₂ atmosphere from 761K to 1123K by TGA, color change and XRD. After 24h immersion the lithiation reaction of NiO was confirmed by both XRD and the color change of a specimen. The rate of lithiation was very slow, especially in CO₂ rich atmosphere. LiNiO₂ was better formed in O₂ atmosphere at higher temperature. The temperature of LiNiO₂ formation in Li/K carbonate was higher than that in Li₂CO₃. Oxygen in the atmosphere would have an important role for the formation of LiNiO₂ as well as the applied temperature.

INTRODUCTION

Lithiated NiO (LiₓNi₁₋ₓO) and lithium nickelate (LiNiO₂) are well known compounds in Li-Ni-O system 1-3). LiₓNi₁₋ₓO was formed by doping lithium to nickel oxide (NiO). It is a metal deficit p-type semiconductor and can be used as an electrode material of the high temperature electrochemical system ⁴). LiₓNi₁₋ₓO is utilized for the cathode of a molten carbonate fuel cell ⁵, ⁶). In LiNiO₂ the valency of the nickel atom is 3⁺. LiNiO₂ is a possible candidate for the cathode material of a secondary lithium battery of future generation ⁷-⁹). LiₓNi₁₋ₓO and LiNiO₂ could be formed by the reaction between NiO and lithium containing molten carbonate at high temperature ¹⁰-¹²). However, the reaction conditions for the formation of these compounds are not clear. In this study, NiO has been put in Li₂CO₃ and 62 m/o Li₂CO₃ - 38 m/o K₂CO₃ eutectic melt (Li/K carbonate) at the temperature range from 761K to 1173K in CO₂ - O₂ atmosphere and the conditions for the formations of these compounds was made clear.

EXPERIMENTAL

The starting material was NiO powder or Ni metal plate. The NiO powder was 99% pure material supplied by Soekawa Chemicals. The major impurities were Fe (6 ppm), Ag (3 ppm), and Si (2 ppm). The NiO powder was sintered at 1273K
in air for 24h. The NiO plate was made by oxidation of nickel metal plate in air at 1273K for 24h. The Nickel plate was 99.9% pure and made by High Purity Chemicals Co. The major impurities were Al, Co, Cu, Fe, and Si. The lattice parameter of NiO of original specimen was determined to be 4.177Å by XRD.

The immersion tests were carried out in Li$_2$CO$_3$ and Li/K carbonate. Li/K carbonate was prepared by mixing reagent grade Li$_2$CO$_3$ and K$_2$CO$_3$ in a dry box. This mixture was placed in a high purity alumina crucible and dried in vacuum for 12h at 623K. In order to remove moisture, it was melted at 923K and then CO$_2$ gas was bubbled through the melt for 24h. The NiO plate suspended by gold wire was immersed in carbonate melt. Figure 1 shows the schematic drawing of the immersion test. CO$_2$ gas was bubbled through the melt for 24h. The lithiation of NiO was observed by the color of a plate.

NiO powder and carbonates was placed in a pure gold crucible. The ratio of NiO powder/carbonate was 1/5 in weight. The mixture were intimately mixed by grinding in a agate mortar for 15 min. The amount of doped lithium was determined by measuring the weight change of the crucible utilizing a Shimadzu TGA-51 thermobalance. The weight change tests were conducted in the gas that contained CO$_2$, O$_2$ or their mixture under atmospheric pressure from 623K to 1173K, at the heating rate of 1K/min.

The reaction products were identified by X-ray diffraction (XRD) utilizing Shimadzu XRD-6000. The obtained peaks were corrected by Si standard specimen in the angular range 10 < 2θ < 150°. Lattice parameter values were obtained by the linear regression method. The valence state of nickel in NiO was analyzed by the X-ray photoelectron spectroscopy (XPS) utilizing SSI SSX - 100.

RESULTS AND DISCUSSION

NiO in Lithium Carbonate

Figure 2 shows the weight change curves of Li$_2$CO$_3$ without NiO from 623K to 1173K in three kinds of atmosphere: (a) CO$_2$, (b) CO$_2$ / O$_2$ = 1 / 1, (c) O$_2$. No decomposition of Li$_2$CO$_3$ (melting point = 999K) was detected up to 1123K in CO$_2$ containing atmosphere. The amount of weight loss at the end point (1100K) was about 1 wt %. On the other hand, the sharp weight decrease was started with Li$_2$CO$_3$ at 999K in O$_2$ atmosphere. This weight decrease would be caused by the decomposition of the carbonate and the CO$_2$ liberation. The amount of weight loss at the end point (1100K) was 5 times larger than that in CO$_2$ containing atmosphere. Above 999K Li$_2$O would be formed in the mixture in the carbonate melt. If all of the weight loss was equal to the CO$_2$ liberation, the amount of Li$_2$O in the melt would be 5 mol % at the end point (1100K).
Figure 3 shows the weight changes of NiO with Li$_2$CO$_3$ from 623K to 1173K in O$_2$ atmosphere. There was a small difference in weight between with and without NiO. The maximum weight difference was 0.5 wt % at 1100K, that means that 0.5 mol % lithium was doped into NiO.

The color of the products and the lattice parameters after NiO immersion into Li$_2$CO$_3$ are summarized in Table I. When NiO was immersed in Li$_2$CO$_3$ in CO$_2$, containing atmosphere, the color of NiO (originally green) didn’t change after immersion. LiNiO$_2$ was not found by XRD after immersion. The lattice parameter of the products was 4.176Å. While that of the original NiO was 4.177Å. Taking into accounts of the change of the lattice parameter and the color, the amount of lithiation of NiO was expected to be very small, and the lithium content x in Li$_x$Ni$_{1-x}$O was estimated less than 0.01.

In Table I, the lattice parameter of the reaction products was 4.175Å in O$_2$ atmosphere at 1073K. The color of NiO changed from green to black in oxygen atmosphere. The formation of lithiated NiO was confirmed by this change of lattice parameter and the color of the product in oxygen atmosphere. The x value was estimated about 0.05 under this condition. LiNiO$_2$ was found by XRD after the reaction in Li$_2$CO$_3$ in O$_2$ atmosphere above 1073K. LiNiO$_2$ was reported to be formed by the reaction of NiO with Li$_2$O that was made by the decomposition of Li$_2$CO$_3$ \(^{10}\). However, an oxidant is necessary to form LiNiO$_2$ from NiO. Oxygen might have an important role for the LiNiO$_2$ formation in the melt.

| Temp. | Gas Comp. | CO$_2$ | CO$_2$ / O$_2$ | O$_2$ |
|-------|-----------|--------|----------------|------|
| 1023K | (green)   | 4.176  | 4.176          | 4.175|
| 1073K | (green)   | 4.176  | 4.176          | 4.175|
| 1123K | (green)   | 4.176  | 4.176          | 4.124|

Figure 4 shows the XPS spectrum of NiO before and after immersion into Li$_2$CO$_3$. In this study, the valence state of nickel was estimated by observing Ni 2p spectrum. Figure 6 (a) shows the results of the wave form analysis of Ni 2p spectrum immersed into Li$_2$CO$_3$. Figure 6 (b) shows results of the wave form analysis of Ni 2p spectrum before immersion. Two peaks were observed at 856 and 862 eV, when immersed into Li$_2$CO$_3$. These peaks corresponded to Ni 2p and Ni 2p
satellite peak, respectively. The energy gap ($\Delta E$) between Ni 2p and Ni 2p satellite peak was about 5.7-5.9 eV. Since Kung has reported that $\Delta E$ value of Ni$_2$O$_3$ was 5.9 eV $^{13)}$, the existence of Ni$^{3+}$ was also confirmed by XPS.

$\text{NiO in Li/K Carbonate}$

Figure 5 shows the weight change curves of Li / K carbonate from 623K to 1173K in the three kinds of atmosphere: (a) CO$_2$, (b) CO$_2$ / O$_2$ = 1 / 1, (c) O$_2$. No decomposition of Li / K carbonate (melting point = 726 K) was detected up to 1123K in CO$_2$ containing atmosphere. The slow weight decrease of Li/K carbonate was observed from 726K in oxygen atmosphere. The rate of decomposition of Li/K carbonate slightly increased above 1000K. The decomposition rate of Li/K carbonate was smaller than that of Li$_2$CO$_3$, namely, Li/K carbonate eutectic was more thermally stable than Li$_2$CO$_3$.

Figure 6 shows the weight change curves of NiO with Li/K carbonate from 623K to 1173K in O$_2$ atmosphere. Although the trends are complicated, the weight loss of the melt that contained NiO is larger than that without NiO in Li/K carbonate. The color of products and lattice parameter of NiO after immersion into Li/K carbonate are shown in Table II. The color of NiO changed from green to black under oxygen atmosphere. The lattice parameter of the reaction products was about 4.175 Å at 1023K. The formation of lithiated NiO was confirmed again by this change of lattice parameter and the color. The lattice parameter was smaller than that in Li$_2$CO$_3$. This might be caused by the lower activity of Li ion in the melt.

| Temp  | CO$_2$ | CO$_2$ / O$_2$ | O$_2$  |
|-------|--------|----------------|--------|
| 1023K | 4.176  | 4.176          | 4.176  |
|       | (green)| (green)        | (black)|
| 1073K | 4.176  | 4.176          | 4.176  |
|       | (green)| (green)        | (black)|
| 1123K | 4.176  | 4.176          | 4.125  |
|       | (green)| (green)        | (black)|

LiNiO$_2$ was also found by XRD after the reaction in Li/K carbonate in oxygen atmosphere above 1123K. The formation temperature of LiNiO$_2$ in Li/K carbonate was higher than that in Li$_2$CO$_3$. The formation of LiNiO$_2$ in Li/K carbonate might be
more difficult than that in Li$_2$CO$_3$.

CONCLUSIONS

The reactions of NiO in Li$_2$CO$_3$ and Li/K eutectic carbonate have been studied thermochemically. Doping of Li into NiO was confirmed by the change of color and XRD.
1. In CO$_2$ containing atmosphere the rate of Li doping was very small even at 1123K.
2. LiNiO$_2$ was formed above 1073K in Li$_2$CO$_3$ and above 1123K in Li/K carbonate, that corresponded to the stability of the carbonate melts.
3. In either case the nickel ion is oxidized from Ni$^{2+}$ to Ni$^{3+}$. Further study is necessary to confirm the oxidant or the role of oxygen in the atmosphere.

REFERENCES

1. R. J. More, and J. White, J. Mater. Sci., 9, 1401 (1974).
2. A. Hirano, R. Kanno, Y. Kawamoto, Y. Takeda, K. Yamaura, M. Takeno, K. Ohyama, M. Ohashi, and Y. Yamaguchi, Solid State Ionics, 78, 123 (1995).
3. R. Kanno, H. Kudo, F. Izumi, Y. Takada, and M. Takano, J. Solid State Chem., 110, 216 (1994).
4. E. Iguchi and K. Akashi, J. Phys. Soc. Japan, 61, 3385 (1992).
5. O. Bohme, F. U. Leidich, H. J. Salge, and H. Wendt, Int. J. Hydrogen Energy, 19, 349 (1994).
6. Charles E. Baumgartner and Kenneth P. Zarnoch, Am. Ceram. Soc. Bull., 64, 593 (1985).
7. S. Lee, J. Lee, D. Kim, H. Baik and S. Lee, J. Electrochem. Soc., 143, L268 (1996).
8. J. R. Dahn, U. V. Sacken, M. W. Juzkow, and H. Al-Janaby, J. Electrochem. Soc., 138, 2207 (1992).
9. T. Ohtuku, A. Ueda, and M. Nagayama, J. Electrochem. Soc., 140, 1862 (1993).
10. J. B. Goodenough, Wickham, and W. J. Croft, J. Phys. Chem. Solids, 5, 107 (1958).
11. A. Rougier, P. Gravereau, and C. Delmas, J. Electrochem. Soc., 143, 1168 (1996).
12. C. B. Azzoni, A. Paleari, V. Massarotti, M. Bini, and D. Capsoni, Phys. Rev. B, 53, 703 (1996).
13. Kung T. Ng and David M. Hercules, J. Phys. Chem., 80, 2094 (1976).
Fig. 1 Schematic drawing of immersion test.

Fig. 2 TGA curves of Li$_2$CO$_3$ in (a) CO$_2$, (b) CO$_2$ / O$_2$ = 1 / 1, (c) O$_2$

Fig. 3 TGA curves of Li$_2$CO$_3$ with and without NiO.
Fig. 4 XPS spectrum of NiO (a) before and (b) after immersion in Li$_2$CO$_3$. 

Fig. 5 TGA curves of Li/K carbonate in (a) CO$_2$, (b) CO$_2$/O$_2$ = 1/1, (c) O$_2$ in oxygen atmosphere, 1K/min.

Fig. 6 TGA of Li/K carbonate with and without NiO in oxygen atmosphere, 1K/min.