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Formation of Li-Doped NiO and $LiNiO_2$ in Molten Carbonate

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The formations of Li-doped NiO and $LiNiO_2$ in molten carbonate have been studied in CO_2–O_2 atmospheres from 761 to 1173 K by TGA, color change and XRD. After 24 h of immersion into a Li_2CO_3 or $(Li_{0.62}K_{0.38})_2CO_3$ melt, the lithiation reaction of NiO was confirmed by both XRD and the color change of a specimen. The rate of the lithiation reaction was very slow, especially in a CO_2-rich atmosphere. $LiNiO_2$ was formed in an O_2 atmosphere at higher temperatures. The temperature of $LiNiO_2$ formation in Li/K carbonate was higher than that in Li_2CO_3. Oxygen in the atmosphere would have an important role for the formation of $LiNiO_2$ as well as the reaction temperature.

Li–Ni–O compounds show both structural and compositional varieties, depending on their synthesis conditions.[1)] Li-doped NiO ($Li_xNi_{1-x}O$) and lithium nickel dioxide ($LiNiO_2$) are well-known compounds in the Li–Ni–O system.[1—3)] Li-doped NiO ($Li_xNi_{1-x}O$) is formed by doping lithium to nickel oxide (NiO), where Li^+ ions substitute the Ni^{2+} lattice, and in order to achieve charge neutrality Ni^{3+} ions are created. Normally, x (the amount of Li in NiO) is less than 0.3.[4)] $Li_xNi_{1-x}O$ is a metal-deficit p-type semiconductor, and the electrical resistivity of the system drops from 10^7 Ω cm to about 1 Ω cm upon the Li-doping of $x = 0.1$.[2)] The high electrical conductivity, even at low lithium-content phases, has led to the use of $Li_xNi_{1-x}O$ as an electrode material for high-temperature electrochemical systems.[5)] For example, $Li_xNi_{1-x}O$ has been utilized for the cathode of a molten carbonate fuel cell.[6,7)]

Layered nickel oxide $LiNiO_2$ is a possible candidate for the cathode material of a secondary lithium battery of future generation.[8—10)] In $LiNiO_2$, Li and Ni form layered structures and occupy the octahedral sites of a cubic close packing of oxide ions, making up a rhombohedral sites structure with a R3m space group. $LiNiO_2$ is not easy to obtain, because the formation of $LiNiO_2$ requires a high-temperature treatment.

$LiNiO_2$ and $Li_xNi_{1-x}O$ could be formed by the reaction between NiO and lithium containing molten carbonate at high temperature.[11—13)] $LiNiO_2$ was reported to be formed owing to the decomposition of Li_2CO_3 above 1073 K.[11)] However, the reaction conditions for the formation of these compounds are not clear. Usually, a metal ion of some lower valent ion is thermochemically more stable than that of a higher valent ion at lower temperature.[3)] The reaction rate might be a point for $LiNiO_2$ formation. In this study, NiO was reacted in Li_2CO_3 or 62 mol% Li_2CO_3–38 mol% K_2CO_3 eutectic melt (Li/K carbonate) at the temperature range from 761 to 1173 K in a CO_2–O_2 atmosphere in order to clarify the conditions for the formation of these compounds. The rate of lithiation (Li-doping or $LiNiO_2$ formation) of NiO in Li/K carbonate was also measured.

Experimental

Material. A NiO powder sample used for thermogravimetric analysis (TGA) had 99.99% purity, and was obtained from Soekawa Chemicals. The major impurities were Fe (6 ppm), Ag (3 ppm), Si (2 ppm), Ca (1 ppm), Cu (1 ppm), and Mg (1 ppm). The NiO powder was sintered at 1273 K in air for 24 h before conducting weight-change measurements. The lattice constant of the NiO powder was determined to be 4.177 Å by the X-ray diffraction method (XRD) after sintering. The NiO plates used for immersion tests were made by the oxidation of Ni metal plates in air at 1273 K for 24 h. The original Ni plate was 99.9% pure, and was obtained from High Purity Chemicals Co. The major impurities of the original Ni plate were Al, Co, Cu, Fe, and Si. After oxidation, the thickness of NiO on a metal was 30 μm and the lattice constant of the NiO plate was determined to be 4.177 Å by XRD.

A TG analysis and immersion tests were carried out with Li_2CO_3 and Li/K carbonate melts. Li/K carbonate was prepared by mixing reagent-grade Li_2CO_3 and K_2CO_3 in a dry box. This mixture was placed in a high-purity alumina crucible and dried in a vacuum for 12 h at 623 K. In order to remove any moisture, it was melted at 923 K, and then CO_2 gas was bubbled through the melt for 24 h before the test.

Weight Changes. NiO powder and carbonates were thoroughly mixed by grinding in a agate mortar for 15 min. The molar ratio of NiO powder (2.678×10^{-4} mol)/carbonate (1.339×10^{-3} mol) was 1/5. The mixture was placed in a pure-gold crucible. The amount of doped lithium was determined by measuring the weight difference (ΔW) between with and without carbonate and XRD. The TG analyses were carried out using a Shimadzu TGA-51 thermobalance. The weight-change tests were conducted in a gas containing CO_2, O_2 or their mixture under atmospheric pressure from 623 to 1173 K. The heating rate for TGA was normally 1 K min^{-1}. The background runs were conducted with nothing in a pure-gold crucible in each different gas mixture as a function of the temperature in order to determine the apparent weight changes due to the effects of buoyancy and gas viscosity.

Immersion Test. A NiO plate made by the oxidation of a Ni plate was suspended by gold wire and immersed in a carbonate melt.

Figure 1 shows a schematic drawing of the immersion test. The tests were carried out in a gas containing CO_2, O_2 or their mixture under atmospheric pressure for 24 h from 873 to 1173 K. During the test gas was bubbled through the melt. The lithiation of NiO was observed by the color change of a plate. Pure NiO that contains no Li has a green color. When lithium is doped in the lattice, the NiO is known to be a semiconductor,[2)] and the color changes to black. The lattice constant decreases slightly with increasing lithium content, owing to the difference in the ionic radius of Ni^{2+} and Ni^{3+} ions. Based on the change in the lattice constant, the amount of Li-doping in NiO was estimated. The reaction products after immersion were analyzed by XRD (Shimadzu XRD-6000) with a Cu target. The obtained peaks were corrected by a Si standard specimen in the angular range $10 < 2\theta < 150°$. The lattice-constant values were obtained by a linear-regression method. The valence state of nickel in NiO was also analyzed by X-ray photoelectron spectroscopy (XPS) utilizing a SSI SSX-100.

Results and Discussion

NiO in Lithium Carbonate. Molten carbonates decompose at high temperature in a low-CO_2 atmosphere. The decomposition of carbonates can be expressed as

$$Li_2CO_3 \longrightarrow Li_2O + CO_2 \uparrow . \qquad (1)$$

Owing to the decomposition reaction, the weight loss would be detected due to the release of CO_2 gas. Figure 2 shows TGA curves of Li_2CO_3 without NiO from 623 to 1173 K in four kinds of atmosphere: (a) CO_2, (b) $CO_2/O_2 = 1/1$, (c) O_2 and (d) Ar. The heating rate for these measurements was 1 K min^{-1}. No decomposition of Li_2CO_3 (melting point = 999 K) was detected up to 1173 K in a CO_2-containing atmosphere. The amount of weight loss at the end point (1173 K) was about 1 wt%. On the other hand, a sharp weight decrease of Li_2CO_3 started at 999 K in an O_2 or Ar atmosphere, where no CO_2 existed. This weight decrease would be caused by decomposition of the carbonate and CO_2 liberation. The amount of weight loss at the end point (1173 K) was 5-times larger than that in a CO_2-containing atmosphere. Above 999 K, Li_2O would be formed, due to CO_2 liberation in the carbonate melt. If all of the weight loss was due to CO_2 liberation, the amount of Li_2O in the melt could be calculated to be 2.3×10^{-4} mol at the end point (1173 K).

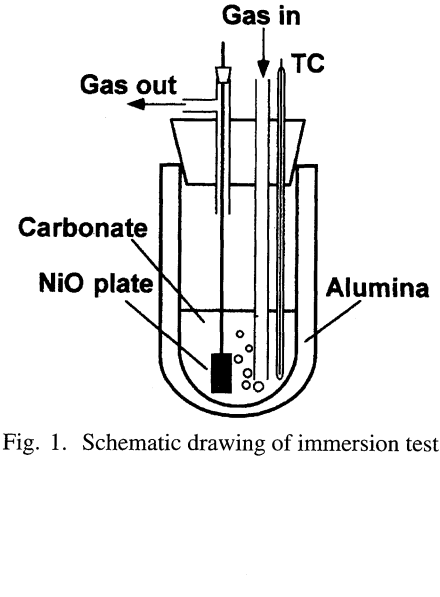

Fig. 1. Schematic drawing of immersion test.

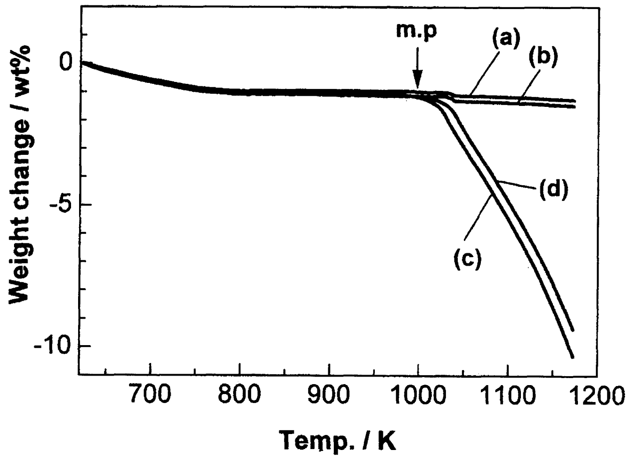

Fig. 2. TGA curves of Li_2CO_3 in (a) CO_2, (b) CO_2–O_2, (c) O_2, and (d) Ar atmosphere.

Figure 3 shows the weight changes of Li_2CO_3 with and without NiO from 623 to 1173 K in an O_2 atmosphere. There was a small difference in weight between with and without NiO. The maximum weight difference was 0.81 wt% compared to the initial weight at 1100 K. If all of the Li_2O was consumed for the lithiation of NiO, the total reaction can be expressed as follows:

$$(x/2)Li_2CO_3 + (1-x)NiO + (x/4)O_2 \longrightarrow Li_x^{+}Ni_{1-2x}^{2+}Ni_x^{3+}O + (x/2)CO_2 . \qquad (2)$$

The incorporation of Li_2O into NiO causes the oxidation of Ni^{2+} to Ni^{3+}. If the reaction proceeded as Eq. 2, the amount of Li-doping into NiO could be calculated to be 0.10 ($Li_{0.10}Ni_{0.90}O$) based on the weight difference between with and without NiO.

The lithiation of NiO can be detected by the color of a specimen and the lattice constant. The observed color of the products and the lattice constant after an immersion test in Li_2CO_3 for 24 h are summarized in Table 1. The X-ray diffraction pattern of NiO after immersion indicated a single phase having the same structure as the initial NiO, but

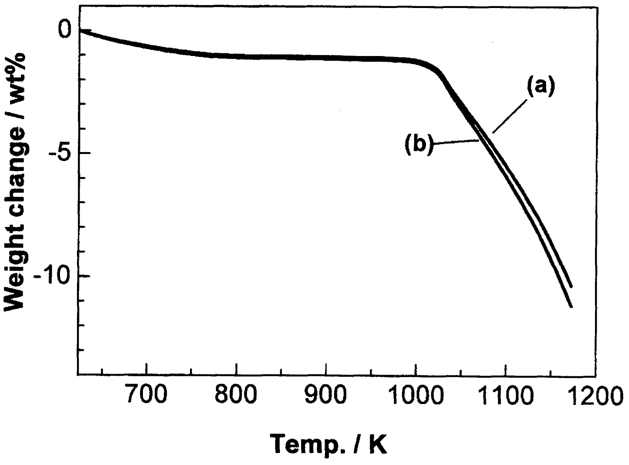

Fig. 3. TGA of Li_2CO_3 (a) without and (b) with NiO in O_2 atmosphere, at the heating rate of 1 K min^{-1}.

Table 1. Lattice Constant and Color of NiO in Li_2CO_3 for 24 h[a)]

Gas comp. / Temp	CO_2	CO_2/O_2	O_2
1023 K	4.1764±0.00026 (Green)	4.1763±0.00032 (Green)	4.1751±0.00023 (Black)
1073 K	4.1762±0.00024 (Green)	4.1762±0.00043 (Green)	4.1719±0.00039[b)] (Black)
1123 K	4.1760±0.00038 (Green)	4.1759±0.00026 (Green)	4.1254±0.00042[b)] (Black)

a) Original NiO = 4.1774±0.00023. b) $LiNiO_2$ and $Li_xNi_{1-x}O$ were formed.

with a smaller lattice constant. When NiO was immersed in Li_2CO_3 in a CO_2-containing atmosphere, the color of NiO (originally green) did not change after immersion. $LiNiO_2$ was not detected by XRD after immersion tests in a CO_2-containing atmosphere. The lattice constant of the products was 4.176 Å, while that of the original NiO was 4.177 Å. Taking into account the change in the lattice constant and the color, the amount of lithiation of NiO was expected to be very small in a CO_2-containing atmosphere, and the lithium content (x) in $Li_xNi_{1-x}O$ was estimated to be less than 0.01.

As shown in Table 1, the lattice constant of NiO changed to 4.175 Å in an O_2 atmosphere at 1073 K. The color of NiO changed from green to black in an O_2 atmosphere. The formation of lithiated NiO in an O_2 atmosphere was confirmed by both this change in the lattice constant and the color of the product. The x value was estimated to be about 0.05 under this condition based on the lattice constant measured by XRD.[13)]

Figure 4 shows the X-ray diffraction pattern of the specimens before and after being immersed in Li_2CO_3 at various temperatures in O_2 atmosphere. $LiNiO_2$ was found by XRD after a reaction in Li_2CO_3 in an O_2 atmosphere above 1073 K. $LiNiO_2$ was reported to be formed by the reaction of NiO with Li_2O, which was made by the decomposition of Li_2CO_3.[11)] However, an oxidant is necessary to form $LiNiO_2$ from NiO. The color of NiO did not change up to 1073 K in an Ar atmosphere. The color of NiO changed slightly to black at 1073 K in an Ar atmosphere; the lithium content (x) in $Li_xNi_{1-x}O$ was estimated to be less than 0.01. $LiNiO_2$ was not detected by XRD after immersion tests in an Ar atmosphere at 1073 K. Oxygen would have an important role for $LiNiO_2$ formation in the melt.

Figure 5 shows the XPS spectra of NiO before and after immersion into Li_2CO_3 in an O_2 atmosphere at 1123 K. Under this condition, $LiNiO_2$ was detected by XRD. In this study, the valence state of nickel in NiO was estimated by observing the Ni 2p spectrum. Figure 5a shows the results of an analysis of the Ni 2p spectrum before immersion. Figure 5b shows the results of a wave form analysis of the Ni 2p

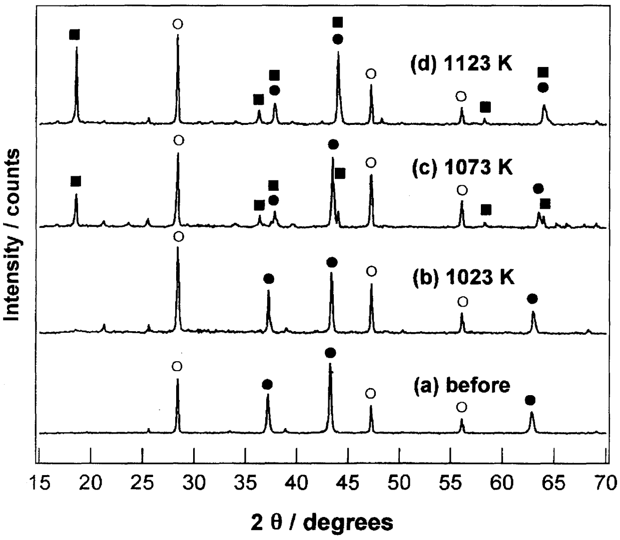

Fig. 4. X-Ray diffraction pattern of the specimens before and after immersed in Li_2CO_3 at various temperatures in O_2 atmosphere. (■): $LiNiO_2$, (●): NiO, (○): Si.

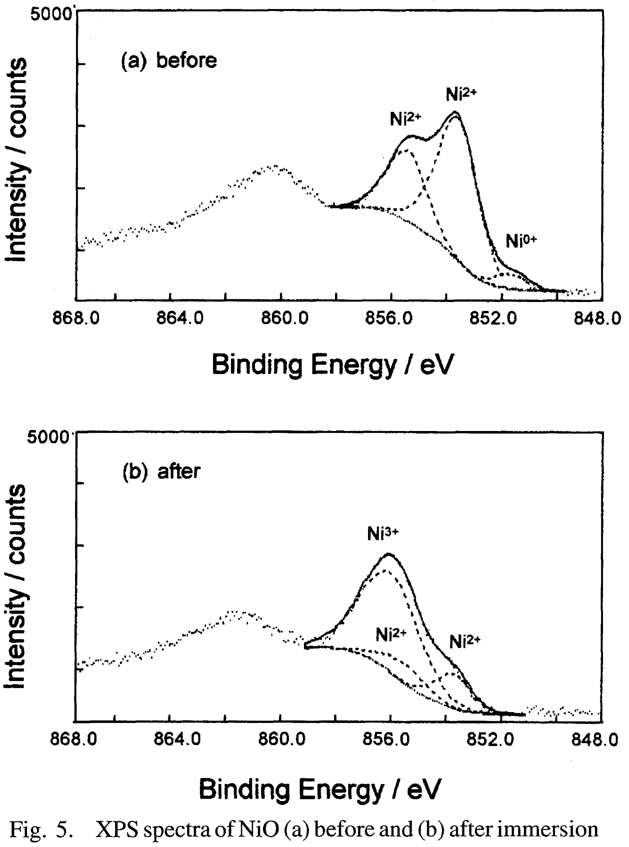

Fig. 5. XPS spectra of NiO (a) before and (b) after immersion in Li_2CO_3.

spectrum after being immersed into Li_2CO_3 for 24 h. Two peaks were observed at 856 and 862 eV when immersed into Li_2CO_3. These peaks correspond to the Ni 2p peak and the Ni 2p satellite peak, respectively. The energy gap (ΔE) between the Ni 2p peak and the Ni 2p satellite peak was about 5.7—5.9 eV. Since Kung has reported that the ΔE value of Ni_2O_3 is 5.9 eV,(14) the existence of Ni^{3+} in NiO was also confirmed by XPS.

NiO in Li/K Carbonate. Figure 6 shows TGA curves of Li/K carbonate from 623 to 1173 K in four kinds of atmospheres: (a) CO_2, (b) $CO_2/O_2 = 1/1$, (c) Ar, (d) O_2. The heating rate for these measurements was 1 $K\,min^{-1}$. No decomposition of Li/K carbonate (melting point = 726 K) was detected up to 1173 K in a CO_2-containing atmosphere. The amount of weight loss at the end point (1173 K) was less than 1 wt% in a CO_2-containing atmosphere. A slow weight decrease of Li/K carbonate was observed from 726 K in the absence of CO_2 gas. This weight decrease would be caused by the decomposition of the carbonate and CO_2 liberation. Li_2O would be formed due to CO_2 liberation in the carbonate melt. The amount of Li_2O in the melt was calculated to be 1.6×10^{-5} mol at the end point.

The decomposition rate of Li/K carbonate slightly increased above 800 K in an Ar or O_2 atmosphere. Above the melting point, the decomposition rate of Li/K carbonate was smaller than that of Li_2CO_3. In other words, Li/K carbonate eutectic was more thermally stable than Li_2CO_3. Generally, the increase in the boiling point and the decrease in the melting point occur upon mixing a second compound, which means that the stability of the liquid phase increases. In this study, the increase in the stability of Li_2CO_3 by adding K_2CO_3 was also confirmed dynamically.

Figure 7 shows TGA curves of Li/K carbonate with and without NiO from 623 to 1173 K in an O_2 atmosphere. Although the difference is very small, the weight loss of the carbonate that contained NiO is larger than that without NiO in Li/K carbonate. The maximum weight difference was 0.55 wt% at 1100 K. This value is smaller than that in Li_2CO_3. The low concentration of Li_2CO_3 in Li/K carbonate might be one reason for this low Li-doping content.

The observed color of the products and the lattice constant of NiO after immersion into Li/K carbonate for 24 h are given in Table 2. The Li-doping content of NiO was expected to be very small in a CO_2-containing atmosphere as well as NiO in Li_2CO_3.

The color change of NiO was not clear in the presence of an Ar atmosphere. $LiNiO_2$ was not detected by XRD after the immersion tests in an Ar atmosphere, even at 1123 K. Since the weight change of Li/K carbonate in an Ar atmosphere was almost the same as that in an O_2 atmosphere, the formation of $LiNiO_2$ cannot be explained only by the decomposition of carbonate. The presence of O_2 in the atmosphere might have an important role on the formation of $LiNiO_2$. In order to form Ni^{3+} ($LiNiO_2$) from Ni^{2+} (NiO), an oxidant is needed.

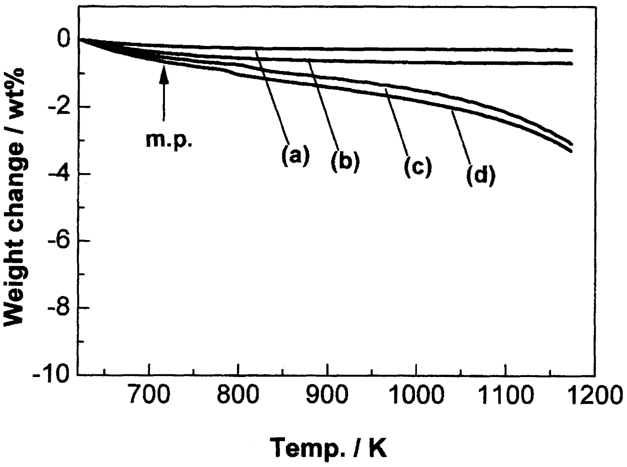

Fig. 6. TGA curves of Li/K carbonate in (a) CO_2, (b) CO_2–O_2, (c) Ar and O_2 atmosphere.

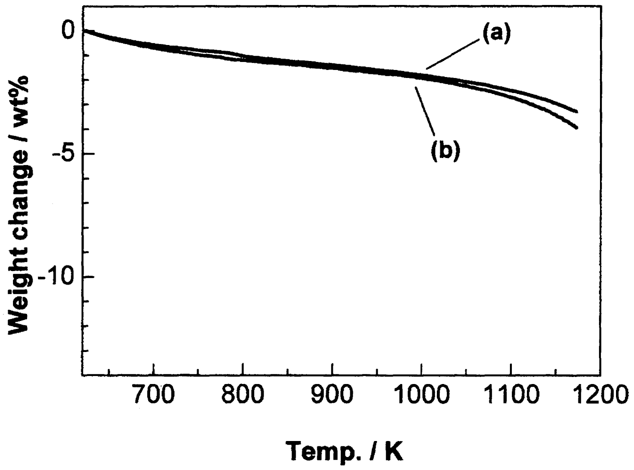

Fig. 7. TGA of Li/K carbonate (a) without and (b) with NiO in O_2 atmosphere, at the heating rate of 1 $K\,min^{-1}$.

Table 2. Lattice Constant and Color of NiO in Li/K Carbonate for 24 h[a)]

Gas comp. / Temp	CO_2	CO_2/O_2	O_2	Ar
1023 K	4.1763±0.00026 (Green)	4.1764±0.00022 (Green)	4.1753±0.00024 (Black)	4.1762±0.00046 (Green)
1073 K	4.1762±0.00048 (Green)	4.1764±0.00026 (Green)	4.1752±0.00025 (Black)	4.1760±0.00026 (Green)
1123 K	4.1762±0.00038 (Green)	4.1760±0.00024 (Green)	4.1254±0.00036[b)] (Black)	4.1758±0.00022 (Dark green)

a) Original NiO = 4.1774±0.00023. b) $LiNiO_2$ and $Li_xNi_{1-x}O$ were formed.

O_2 is a more effective oxidant for the formation of $LiNiO_2$ than CO_2 (or CO_3^{2-}). The color of NiO changed from green to black under an O_2 atmosphere. The lattice constant of the reaction products was about 4.162 Å at 1023 K. The formation of lithiated NiO was again confirmed by these changes in the lattice constant and color. The lattice constant of lithiated NiO in Li/K carbonate was larger than that in Li_2CO_3. In another words, the amount of Li in NiO into Li/K carbonate was smaller than that in Li_2CO_3. This might have been caused by the lower activity of the Li^+ ion in Li/K carbonate than in Li_2CO_3.

$LiNiO_2$ was also found by XRD after a reaction in Li/K carbonate in an oxygen atmosphere above 1123 K. The formation temperature of $LiNiO_2$ in Li/K carbonate was slightly higher than that in Li_2CO_3 (1073 K). The formation of $LiNiO_2$ in Li/K carbonate would be more difficult than in Li_2CO_3.

Figure 8 shows the weight change of Li/K carbonates in an O_2 atmosphere at a fixed temperature from 873 to 1173 K. A weight change of Li/K carbonates was not detected at 873 K. At 973 K, a slight weight decrease of Li/K carbonates appeared, and the reaction proceeded very slowly. The weight decrease would be caused by decomposition of the carbonate. At 1073 and 1173 K decomposition could be easily detected from the beginning of the measurement.

Figure 9 shows weight-change curves of Li/K carbonate with and without NiO at 973 K for 20 h in an O_2 atmosphere. If the difference (ΔW) was due to the lithiation,

$$(x/2)Li_2CO_3 + (1-x)NiO + (x/4)O_2 \longrightarrow Li^{+}_{x}Ni^{2+}_{1-2x}Ni^{3+}_{x}O + (x/2)CO_2 \quad (3)$$

$$\text{Li-doping content } x = M_{O_2}/2 - M_{CO_2}/4 = \Delta W \quad (4)$$

The Li-doping content (x) is due to the difference in the absorption of O_2 into the NiO lattice (M_{O_2}) and CO_2 liberation (M_{CO_2}) for the lithiation reaction. In Fig. 9, ΔW is 4.99×10^{-5} mol at 5 h. From this value, the Li-doping content (x) was estimated to be 0.08. By a XRD study, the Li content (x) in $Li_xNi_{1-x}O$ was determined to be $x \fallingdotseq 0.08$.

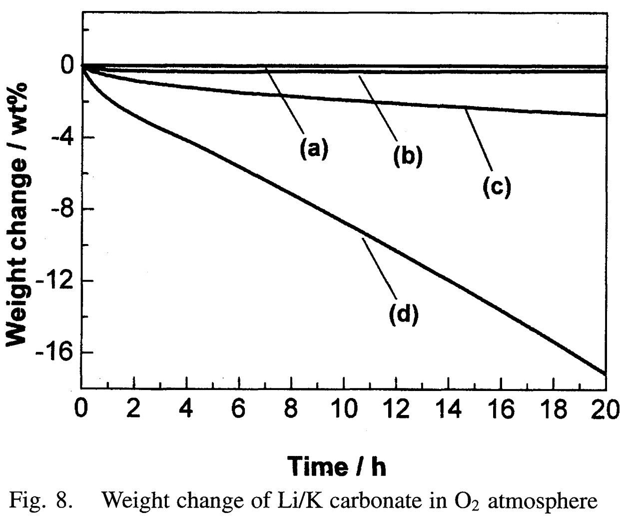

Fig. 8. Weight change of Li/K carbonate in O_2 atmosphere (a) 873 K, (b) 973 K, (c) 1073 K, and (d) 1173 K.

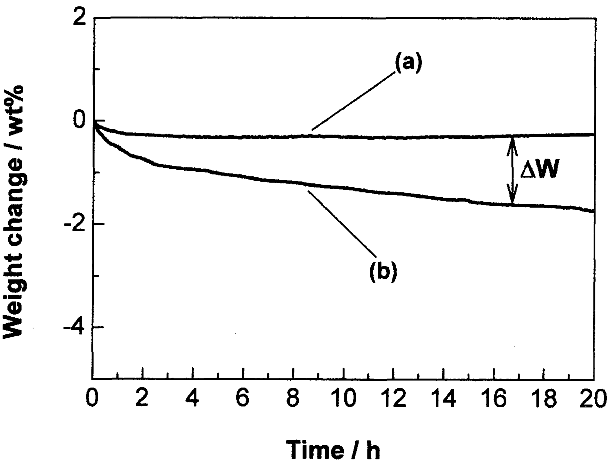

Fig. 9. Weight change of Li/K carbonate (a) without and (b) with NiO at 973 K in O_2 atmosphere.

The amount of Li content (x) from ΔW was almost equal to that from XRD. The maximum weight difference was 1.05×10^{-4} mol for 20 h; the Li-doping content (x) was estimated to be 0.19. This value is almost equal to that from XRD at 20 h.

Figure 10 shows the amount of Li in NiO in Li/K carbonates at 873, 973, 1073, and 1173 K under an O_2 atmosphere. This value was calculated from Eqs. 3 and 4, and expressed as moles of Li doped in 1 mol NiO (mol Li/mol NiO). The difference increases with time, and is considered to correspond to the amount of Li in NiO. A linear increase was observed during the first 5 h of each reaction. During the period, $Li_xNi_{1-x}O$ was only one product, and $LiNiO_2$ was not found. The amount of Li content (x) calculated from ΔW was almost equal to that from the XRD results. The reaction rate became higher at higher temperatures. Figure 11 shows Arrhenius plots of the reaction rate (k) of Li absorption in NiO in Li/K carbonates from 873 to 1173 K. The rate was obtained at the initial period of the reaction ($<$ 5 h). The activation energy for the Li absorption reaction was calculated to be 68.43 kJ mol^{-1}.

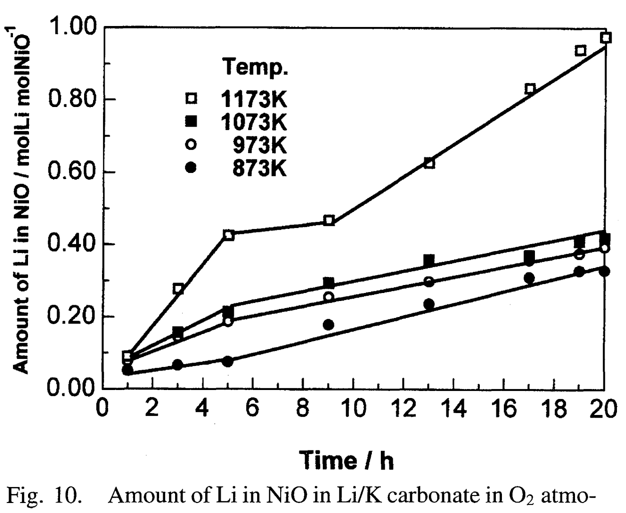

Fig. 10. Amount of Li in NiO in Li/K carbonate in O_2 atmosphere.

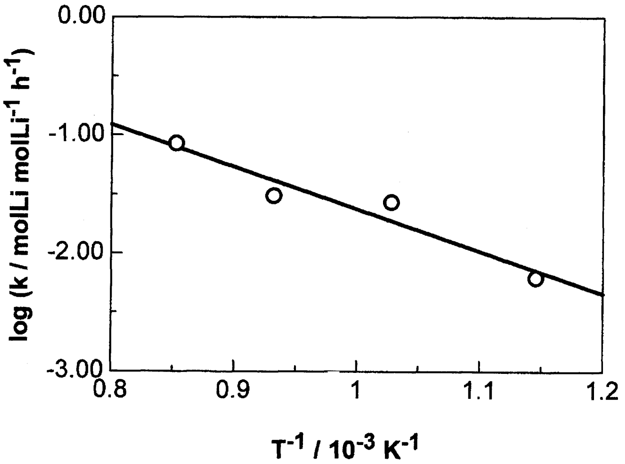

Fig. 11. Arrhenius plot of lithiation rate (*k*) of NiO in Li/K carbonate at the initial period (< 5 h).

After 5 h, the curves in Fig. 10 become complicated. Below 1073 K, $Li_xNi_{1-x}O$ was the only product of NiO, and $LiNiO_2$ was not found by XRD after 20 h. The gradual increase in the difference after 5 h would correspond to a growth in the Li content (x) in $Li_xNi_{1-x}O$.

At 1173 K, both $Li_xNi_{1-x}O$ and $LiNiO_2$ were obtained simultaneously after 20 h of reaction. The weight difference significantly increased after 10 h at 1173 K. Since $LiNiO_2$ was not formed before 5 h, and was found at 20 h, the large increase in the Li content after 10 h would correspond to $LiNiO_2$ formation. The formation rate was 4.8×10^{-2} [mol Li/mol NiO/h]. The lithiation reaction proceeded first by the formation of Li-doped NiO ($Li_xNi_{1-x}O$), followed by $LiNiO_2$ formation. Considering the result at 1173 K (Fig. 10), $LiNiO_2$ formation started with an x value of 0.3.[4] $LiNiO_2$ formation might need a critical Li content. Since the Li content could not attain a critical value below 1073 K, $LiNiO_2$ was not formed.

In conclusion, the reaction of NiO in Li_2CO_3 and Li/K eutectic carbonate has been studied thermochemically from 873 to 1173 K in a CO_2/O_2 atmosphere, and the following result were obtained:

1. Doping of Li into NiO and $Li_xNi_{1-x}O$ formation were confirmed by the color change and lattice constant of NiO.
2. In a CO_2-containing atmosphere, the rate of Li doping was very slow, even at 1123 K.
3. $LiNiO_2$ was formed above 1073 K in Li_2CO_3 and 1123 K in Li/K carbonate, which corresponded to the stability of the carbonate melts.
4. The lithiation reaction was significantly affected by the existence of O_2 in the atmosphere.

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