

Effects of CO₂ in air on Li deintercalation from LiNi_{1-x-y}Co_xAl_yO₂

Kazutoshi Matsumoto^{a,*}, Ryuichi Kuzuo^a, Kaname Takeya^b, Atsushi Yamanaka^b

^a Central Research Laboratories, Sumitomo Metal Mining, 18-5, Nakakokubun 3-chome, Ichikawa-shi, Chiba 272, Japan

^b Niihama Research Laboratories, Sumitomo Metal Mining, 17-5, Isoura-cho, Niihama-shi, Ehime 792, Japan

Abstract

The reaction of CO₂ and practical high-performance cathode materials LiNi_{1-x-y}Co_xAl_yO₂ was examined with XRD at RT and high temperature, TGA, IR, and chemical analysis. Even at room temperature, Li deintercalation took place and formed Li₂CO₃ on the mother surface. The conversion to Li₂CO₃ in air at 55% RH at 25°C was in proportion to the square root of exposure time. It was 8% after being left for 500 h. Using high-temperature XRD at 25–800°C, the Li₂CO₃ phase formation was confirmed from about 500°C, and the conversion exceeded 70% under atmospheric CO₂ at 675°C. The activation energy of the reaction of deintercalated Li and CO₂ was estimated by Ozawa's method. The activation energy obtained using Ozawa's method was 130 kJ/mol for CO₂ diffusing through the Li₂CO₃ layer which formed on the surface during the reaction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium secondary batteries; Lithium nickel oxide; Reaction with CO₂; Activation energy

1. Introduction

LiNiO₂ is a very important material and a promising candidate as a cathode active material for lithium secondary batteries. This material is also a strong potential candidate to replace the actually commercialized LiCoO₂ because of its low cost and high specific capacity. However, the main difficulties with this material are low reproducibility, short life, and low stability at high temperature. In order to overcome these problems, the substitution of Co and/or Al for Ni has been investigated [1–3]. Another problem with this material is that its basicity is higher than that of LiCoO₂. Therefore, degradation by atmospheric CO₂ during storage is a concern.

In this study, the reaction of CO₂ and practical high-performance cathode materials, LiNi_{1-x}Co_xAl_yO₂, was examined at RT and high temperature, and the activation energy of the reaction obtained from TG data.

2. Experimental

LiNi_{0.81}Co_{0.16}Al_{0.03}O₂ used as a practical sample was prepared using spherical high-density (Ni, Co, Al) (OH)₂ and LiOH·H₂O as starting materials. A 1:1.01 mixture of

(Ni, Co, Al) (OH)₂ and LiOH·H₂O was dehydrated at 250°C, then heated at 300°C/h to 700°C and kept at this temperature for 20 h under a flow of oxygen. The resultant powder was subject to XRD (M18XHF MAC-science) with Cu-Kα radiation. There were trace peaks except for the layered hexagonal structure. The Rietvelt refinement (RIETAN-94) [4] revealed that the Li ions occupancy at the 3a sites was over 99%. The mean particles size (*D*₅₀) and specific surface area were 10.01 μm and 0.86 m²/g, respectively.

The effect of atmospheric CO₂ on the sample powder was tested as follows: For 0–500 h, the powder was placed in a chamber maintained at 25°C, 55% RH and air were circulated. In comparison to the climate of the Japanese rainy season, this condition is mild. Using IR spectroscopy, Li₂CO₃ was detected on the powder surface after the exposure test. After testing, the powder was dissolved in acid, and the generated CO₂ gas was quantified by coulometric titration.

High-temperature X-ray diffraction (RINT1400/PTC-10C, RIGAKU) patterns of the sample were collected with graphite monochromated Cu-Kα radiation on a Pt heating strip, in air. The sample was heated at 5°C/min from 25°C to 800°C and held at every 25°C for 10 min prior to data collection. XRD patterns were recorded at a scan rate of 6°C/min between 10 to 90° (2θ).

The apparent activation energy of the reaction of the sample and CO₂ was determined by Ozawa's method [5].

* Corresponding author. Tel.: +81-47-374-1192; Fax.: +81-47-375-0241; E-mail: kazutoshi_matsumoto@ni.smm.co.jp

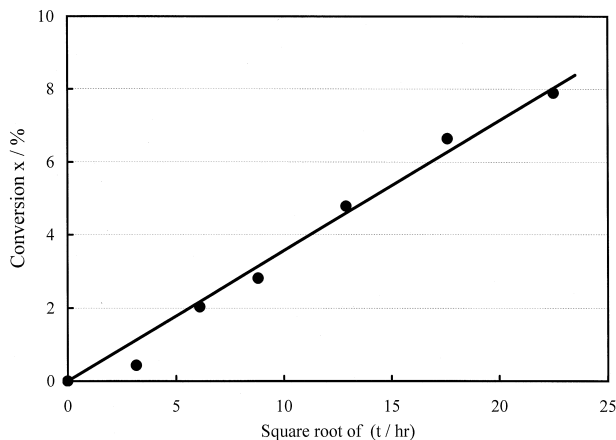


Fig. 1. Conversion, x , versus square root of exposure time t . Samples were maintained at 25°C in 55% RH under flow of air.

The activation energy, E_a , is represented by the following equation with a certain constant heating rate, r_H , of thermogravimetric analysis (TGA) and absolute temperature, T , at which a given weight change occurs:

$$\log r_H + 0.4567E_a/RT = \text{const.} \quad (1)$$

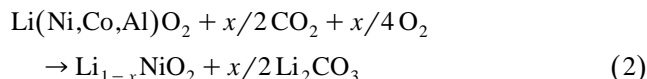
Thus, the plots of $\log r_H$ versus the reciprocal T for more than three various constant heating rates must give a straight line, whose slope gives the activation energy.

Thermogravimetric (TG-DTA2200S, MAC-science) data were collected under CO_2 content gas flow. To accelerate the reaction, higher partial pressures of CO_2 than in atmospheric air were used. Sample powder was heated at four constant rates: 2, 4, 8, and 16°C/min from 400 to 800°C. The CO_2 contents were 100% (gas 1), 10% (gas 2), and 1% (gas 3). Gas 3 and gas 2 contained 20% O_2 . All gases were dried. In addition, 100% CO_2 with 100% RH at 25°C gas (gas 4) was also used to examine the effect of moisture on the sample. Considerable amount of Li_2CO_3 was detected for every sample after testing by XRD.

3. Results and discussion

3.1. Exposure test at room temperature

IR detected Li_2CO_3 for all samples after the exposure test. The following reaction might occur with atmospheric CO_2 :



to simplify the sample is transcribed into $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ here.

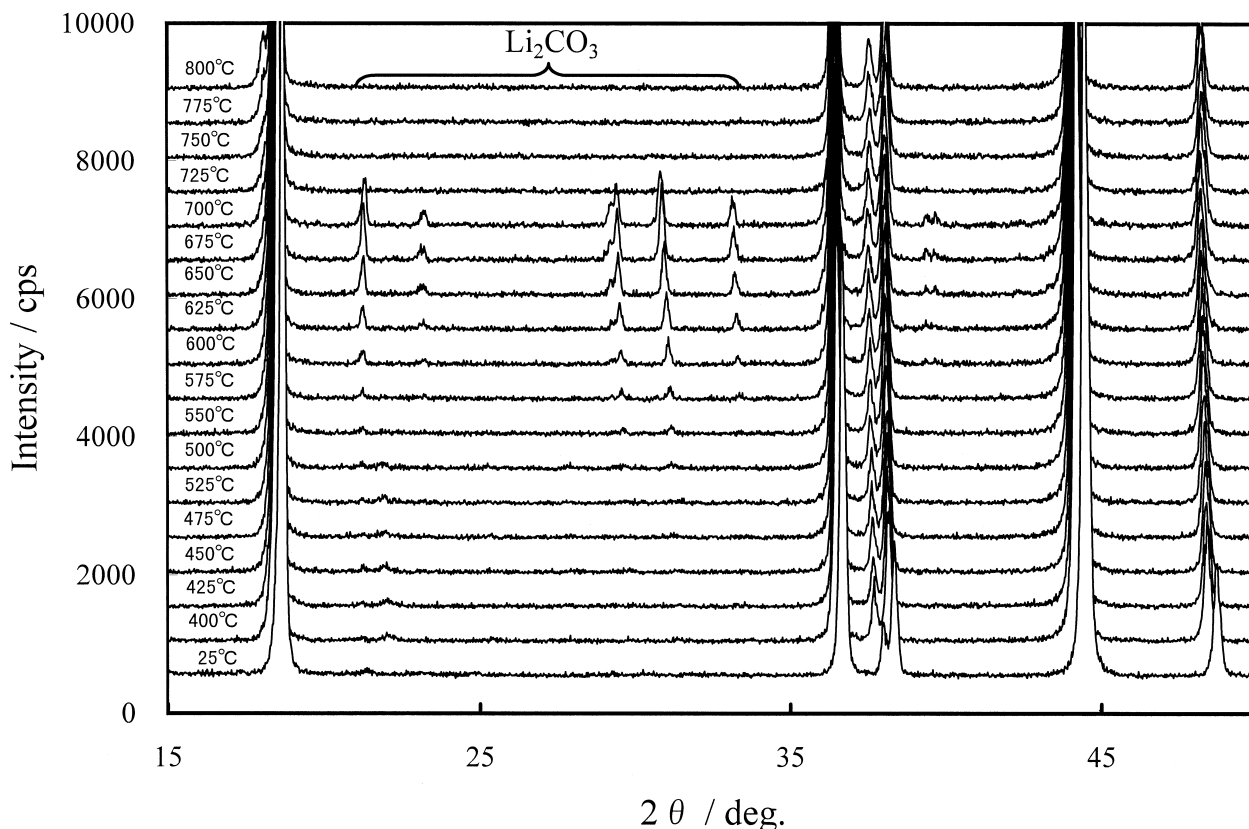


Fig. 2. XRD patterns of $\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.03}\text{O}_2$ recorded in situ, from temperature 25 to 800°C. The sample heated under flow of air. Characteristic peaks between 20 to 35° belonged to Li_2CO_3 .

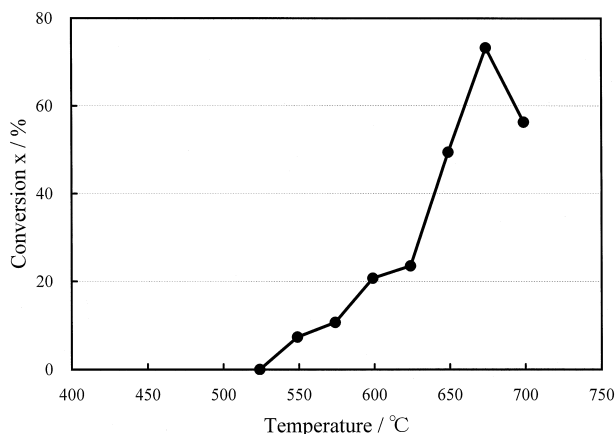


Fig. 3. Conversion, x , versus temperature. The x was obtained from the intensities of Li_2CO_3 in Fig. 2.

Conversion quantities, x , in Eq. (2) were calculated from the quantified CO_2 values. The value was corrected by the 0.88% contained in the starting sample. The dependency between exposure time, t , and x is shown in Fig. 1. Conversion quantities, x , was in proportion to the square root of the exposure time, t , and following the equation: x (%) = $0.36(t/h)^{1/2}$. The reaction is thought to be diffusion controlled. The conversion after 500 h was approximately 8%. On the other hand, LiCoO_2 was also subjected to the atmospheric exposure test, but the detection of CO_2 was within measurement error.

3.2. High-temperature XRD

The XRD patterns of the sample heated from 400 to 800°C are shown in Fig. 2. The formation of Li_2CO_3 was recognized from the 525°C vicinity and increased with temperature. The intensity of Li_2CO_3 reached maximum at 675°C and then became extinct over 725°C. Because the

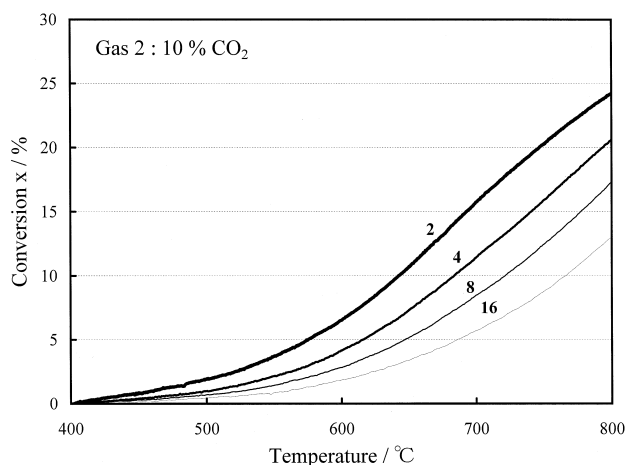


Fig. 4. Conversion, x , versus temperature at various heating rates under flow of gas 2 (10% CO_2). The number indicates heating rate in $^\circ\text{C}/\text{min}$ of thermogravimetry.

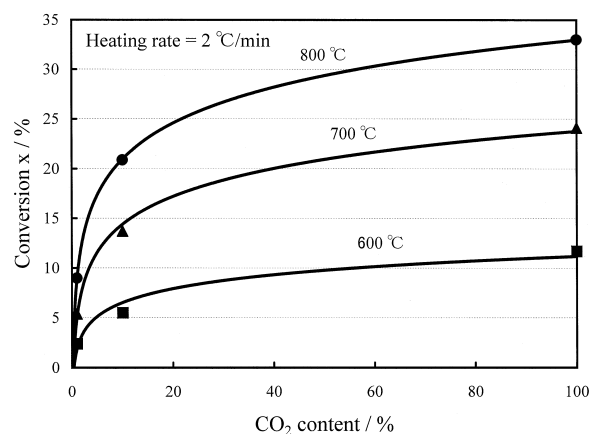


Fig. 5. Conversion, x , at 600, 700, and 800°C versus CO_2 content in thermogravimetry at a heating rate of $2^\circ\text{C}/\text{min}$. The curves are logarithmic regression.

melting of Li_2CO_3 occurred at this temperature, the peaks of Li_2CO_3 could not be detected with XRD.

The conversion quantities, x , were obtained from the intensities of Li_2CO_3 using the calibration curve for XRD of the mixtures of $\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.03}\text{O}_2$ and Li_2CO_3 plotted in Fig. 3. More than 70% of the Li came out from the mother structure at 675°C.

3.3. Activation energy for the reaction

Assuming that the weight change by TGA obeyed Eq. (2) entirely, x versus the temperature curves is plotted in Fig. 4 for the case of gas 2. The x increased with temperature at each rate, but for extensive conversion, for example in the case of rate 2 over 700°C, the curves became less steep. It is thought that the Li_2CO_3 that formed by the reaction melted and covered the surface of the sample. Similar behavior observed under other CO_2 pressures.

Fig. 5 shows the dependence of x at 600, 700, and 800°C on the CO_2 pressure at a heating rate of $2^\circ\text{C}/\text{min}$.

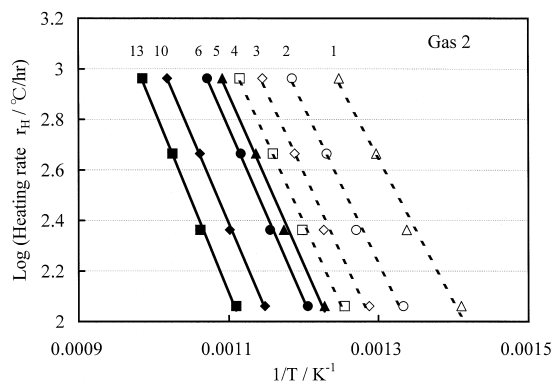


Fig. 6. Logarithm of heating rate r_H versus reciprocal absolute temperature. The numbers indicate conversion, x , during thermogravimetric testing under the flow of gas 2.

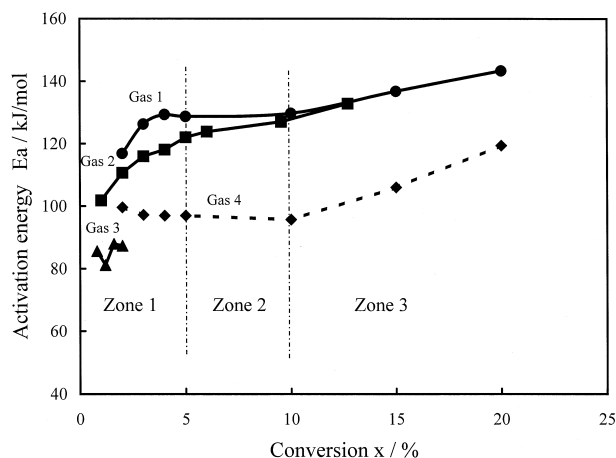


Fig. 7. Apparent activation energy E_a obtained by Ozawa's method versus conversion, x , under flow of gas 1, gas 2, gas 3, and gas 4.

The curves fitted with the regression curves of the log of the CO_2 content. Similar tendencies were shown at other heating rates.

The log of each rate in Fig. 4 and the reciprocal absolute temperature for the indicated conversions are plotted in Fig. 6.

The apparent activation energy of the reaction calculated from the slope of a straight line of each log rate– $1/T$ plot using Eq. (1) is plotted in Fig. 7 for each gas. The dependency of the activation energy on x is divided into three zones. In the first zone, the activation energy increased with conversion quantities less than 5%. In the second zone, the activation energy remained constant from $x = 5$ to 10%. Finally, the activation energy increased again for x over 10%. For low CO_2 content, zone 2 shifted to larger values of x .

Considering these results, the mechanism of the reaction is proposed as follows. The sample and CO_2 was readily reacted to form a little Li_2CO_3 but not enough to cover the surface of the sample and the activation energy

of the reaction was small. Then from conversion quantities of around 5%, the spreading Li_2CO_3 entirely covered the surface, and the activation energy was approximately 130 kJ/mol, which would be equivalent to that of the CO_2 gas diffusing through the Li_2CO_3 layer. For further conversion, a temperature greater than the Li_2CO_3 melting point was necessary as in the case of a high heating rate. Therefore, a higher energy might be required to diffuse into the fused Li_2CO_3 layer.

The activation energy for gas 4 is also plotted in Fig. 7. The profile resembled that for gas 1, but the values were low. The TG curves for gas 1 and gas 4 were overlapped at higher temperature, which indicated that moisture promoted the carbonation reaction at low temperature.

4. Conclusions

$\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.03}\text{O}_2$ reacted with atmospheric CO_2 even at room temperature. The conversion quantity, x , was proportional to the square root exposure time and followed the equation: $x (\%) = 0.36(t/h)^{1/2}$ under these test conditions. High-temperature XRD revealed that more than 70% of Li in the mother structure was deintercalated and reacted with CO_2 to form Li_2CO_3 at 675°C. The activation energy obtained by Ozawa's method was 130 kJ/mol for CO_2 diffusing through the Li_2CO_3 layer which formed on the surface during the reaction.

References

- [1] T. Ohzuku, H. Komori, K. Sawai, T. Hirai, Chem. Express 5 (1990) 733.
- [2] C. Delmas, I. Saadoune, Solid State Ionics 53–56 (1992) 370.
- [3] T. Ohzuku, A. Ueda, M. Kouguchi, J. Electrochem. Soc. 143 (1996) 1168.
- [4] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method, Chap. 13, Oxford Univ. Press, Oxford, 1993.
- [5] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.