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Short communication

Thermal stability and kinetics of delithiated $LiCoO_2$

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ABSTRACT

The thermal stability of the materials that comprise the battery has been one of the important issues. By using temperature programmed desorption-mass spectrometry (TPD-MS) and XRD, the thermal decomposition reaction of delithiated Li_xCoO_2 ($x = 1, 0.81, 0.65$) was quantitatively analyzed. Delithiated Li_xCoO_2 samples were metastable and liberated oxygen at a temperature of above 250 °C. Liberated oxygen gas was quantified by TPD-MS. Structural changes of the samples were confirmed by XRD. We identified the stoichiometry of the thermal decomposition reaction of Li_xCoO_2. Furthermore, to analyze the heating rate dependence of the oxygen generation, we calculated the activation energy (E_a) of the thermal decomposition reaction. The average E_a through the reaction of $Li_{0.81}CoO_2$ is 130 kJ mol^{-1}, and that of $Li_{0.65}CoO_2$ is 97 kJ mol^{-1}. The Li content decreased as the activation energy increased.

1. Introduction

Lithium-ion batteries are in great demand commercially because of their advantages of high energy density and long shelf life for cyclic use. The thermal stability of the materials that comprise the battery has been one of the important issues. The thermal properties of the general cathode material $LiCoO_2$ have been investigated since the early 1990s [1–9]. When the batteries are charged electrochemically, $LiCoO_2$ releases Li ions and becomes partially delithiated Li_xCoO_2 (x is usually $0.5 < x < 1$). These delithiated samples can also be prepared using a chemical method [8,9].

Yamaki et al. confirmed that the DSC chart of chemically delithiated $Li_{0.49}CoO_2$ agreed well with the profile obtained from an electrochemically charged battery [4]. Moreover, the lattice constants and structural parameters of the chemically delithiated $Li_{0.52}CoO_2$ are in good agreement with those of the electrochemically delithiated $Li_{0.48}CoO_2$ [5].

The DSC study revealed that delithiated Li_xCoO_2 ($x = 0.49–0.9$) undergoes an exothermic reaction above 200–350 °C. As the Li content decreases, the exothermic heat increases and the exothermic peak shifts toward the lower temperature side [6].

The electron density of a single-crystal delithiated $LiCoO_2$ was analyzed by performing XRD measurements. No bonding is found to occur around the Li atoms, and the electron density at the Li site gradually decreases upon delithiation [5]. The formation of $LiCoO_2$ ($x = 1$) is attributed to the $R\bar{3}m$ space group, which consists of a hexagonal unit cell (H1). When the value of x decreases below 0.9, another large-sized hexagonal unit cell (H2) starts to generate, and a state is reached where the two phases coexist. The H1 phase reduces in proportion to the delithiation degree. When x is below 0.75, only the H2 phase exists. A monoclinic structure (M) appears when x is nearly 0.5. However, the M region disappears above 60 °C (333 K) [7]. The structure of $Li_{0.49}CoO_2$ from room temperature to 200 °C is identified as a hexagonal ($R\bar{3}m$) structure. Above 300 °C, a mixture of hexagonal unit cell $LiCoO_2$ ($R\bar{3}m$) and a nonstoichiometric spinel Co_3O_4 structure ($Fd\bar{3}m$) appears [1,2,6].

From the TG-MS (thermogravimetry-mass spectrometry) and XRD on heating process, O_2, $LiCoO_2$ and Co_3O_4 are formed during the reaction [1,2,3].

$$Li_xCoO_2 \rightarrow (1-x)/3Co_3O_4 + xLiCoO_2 + (1-x)/3O_2$$

However, as of today, the weight loss observed is substantially less than that predicted by the above equation. Therefore, a precise stoichiometrical analysis is required. It is necessary to carry out a detailed research of the thermal decomposition of Li_xCoO_2 [1–3].

Wang et al. [10] reported the activation energy of $LiCoO_2$ charges to 4.2 V is 148.87 kJ mol^{-1} from TG or 88.87 kJ mol^{-1} from C80. However, their activation energy is not reliable since they used a positive-electrode obtained from a battery with solvents and binders. Their calculation was based on the TG curve with several steps including decomposition or evaporation of solvents and binders. Therefore, their TG curve shows five steps through the degradation. We guess their calculated activation energy consist of several reactions. For example, thermal decomposition reaction of Li_xCoO_2 cathode, oxidization of the PVDF binder by the oxygen generated from above reaction and so on.

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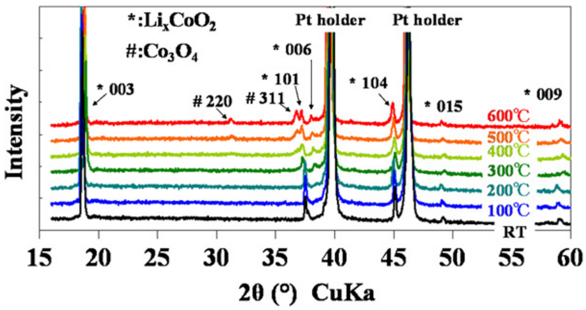

Fig. 1. Temperature-dependent XRD patterns of chemically delithiated $Li_{0.65}CoO_2$.

The purpose of this paper is to determine the stoichiometry and calculate the activation energy (E_a) of the decomposition reaction. We quantified the O_2 gas volume from the TPD-MS measurement to discuss the decomposition reaction stoichiometrically. Furthermore, we discussed the kinetics of the reaction by performing TPD-MS measurement for different heating rates. We propose to use the activation energy as an index to evaluate the battery stability, which is directly linked to the thermal stability.

2. Experimental

A powdered sample of $LiCoO_2$ was obtained from the Aldrich Co. Chemical delithiation was carried out by stirring 300 mg of $LiCoO_2$ in 50 mL of 1.25 M H_2SO_4 for 30–90 min [8,9]. The Li content of Li_xCoO_2 was determined by using atomic absorption spectroscopy (SII, SPS4000), and the Co content was determined by using ICP (inductively coupled plasma) emission spectroscopy (HITACHI, Z2300). From the ratio of these contents, the chemical formulae for $Li_{0.81}CoO_2$ and $Li_{0.65}CoO_2$ were obtained.

A temperature programmed desorption-mass spectrometer consists of a temperature-controlled furnace with a mass spectrometer (Shimazu GC/MS, QP5050A(7)). The heating rate was 10 °C min^{-1}; the sample weight of approximately 5 mg. The carrier gas was helium and its flow rate was controlled by 50 mL min^{-1} at ambient pressure. The furnace and mass spectrometer was connected by capillary column heated at 250 °C. The TPD-MS was used to count the mass number of desorption gas when the sample was heated. In this study, we used the mass number 32 (oxygen gas). The calibration was prepared by the linear fitting of controlled oxygen concentration vs. ion strength of MS plots. Using the calibration line, we quantified the concentration of the released oxygen gas from the samples. In addition, the kinetics of thermal decomposition reaction was studied by analyzing the heating rate dependence (5, 10, 20 °C min^{-1}) of the TPD-MS measurement.

Powder XRD patterns were obtained with a Brucker D8 ADVANCE equipment using CuKα radiation from 15° to 60° (2θ) with a step size of 0.0171° and a dwell time of 1 s. In the high-temperature XRD measurement, the sample was set on the heating stage (Anton Paar HTK16). The samples exposed to the atmosphere during the high temperature XRD measurement.

3. Results

The in situ XRD patterns of $Li_{0.65}CoO_2$ at high temperatures are illustrated in Fig. 1. At room temperature, 0 0 3, 1 0 1, 1 0 4, 0 1 5 and 0 0 9 were indexed, which is defined by a $LiCoO_2$ hexagonal unit cell [7]. At temperatures higher than 200 °C, 2 2 0 pattern of Co_3O_4 structure was observed in the delithiated samples [6].

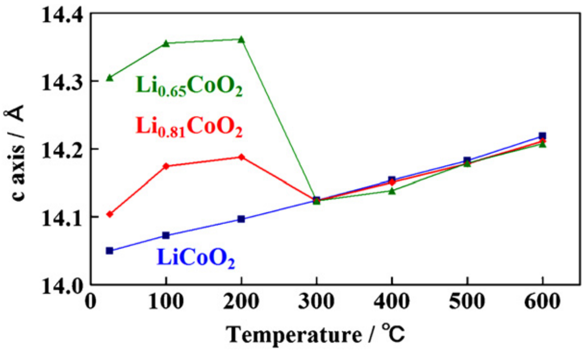

Fig. 2. Temperature dependence of c-axis length.

Fig. 2 shows the temperature dependence of the c-axis length. The length of the c-axis was calculated for a hexagonal cell. The c-axis length of $LiCoO_2$ gradually increases with the temperature. This is because of the thermal expansion of the lattice parameter. On the other hand, for delithiated $LiCoO_2$, the c-axis length decreases dramatically at temperatures between 200 and 300 °C. Above 300 °C, the lattice parameter of these three samples shows almost the same value. In contrast, from the room temperature to 600 °C, the a-axis length shows nearly constant values.

Fig. 3 shows the temperature dependence of the oxygen evolution rate of Li_xCoO_2. Even if $LiCoO_2$ is heated up to 600 °C, oxygen is not generated. On the other hand, delithiated samples liberated oxygen above 250 °C. The amount of liberated oxygen increases gradually and the peak temperature decreases as the delithiation ratio increases. We found the temperature range of the oxygen evaluation is in good agreement with exothermic behavior and mass loss behavior at previous studies [1–4]. In this study, we calculated the total amount of liberated oxygen by time integration for the oxygen evolution rate. The result of $Li_{0.81}CoO_2$ is 1.79 wt.%, and that of $Li_{0.65}CoO_2$ is 3.56 wt.%.

4. Discussion

The thermal decomposition reaction is expressed by the following expression.

$$Li_xCoO_2 \rightarrow xLiCoO_2 + (1-x)/3Co_3O_4 + (1-x)/3O_2$$

The chemical composition of the compounds was determined by substituting the amount of the generated gas in the above expression. The result obtained is $Li_{0.84}CoO_2$ and $Li_{0.68}CoO_2$. The chemical composition of the samples calculated from the TPD-MS measurement corresponded to the chemical composition calculated using atomic absorption spectroscopy and ICP emission spectroscopy. The difference of the composition value (x) requested by two methods was about 4%. We confirmed the thermal decomposition reaction stoichiometrically from the TPD-MS and XRD measurements.

The previous TG measurements [1] were carried out with electrochemically charged Li_xCoO_2 which contained not only $LiCoO_2$

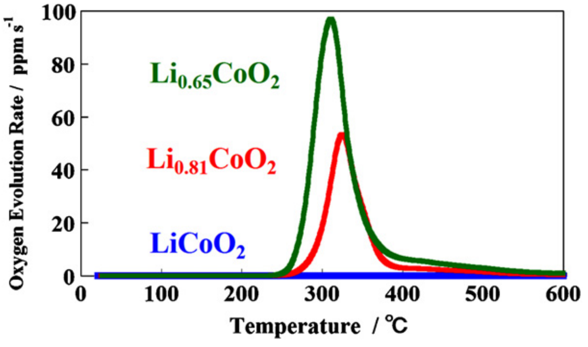

Fig. 3. Temperature dependence of oxygen evolution rate of Li_xCoO_2.

but also polymer binders and electrolytes. TG curves should be adversely affected by thermal decomposition of such impurities. Additionally, the thermal conductivity of the polymeric materials is generally low, so that linear heating rate TG experiments have serious problems of pressure gradient and temperature distribution within the samples [11]. The shape of TG curves is likely to be dependent on sample weights.

On the other hand, we used unmixed Li_xCoO_2 to prevent other reactions. Moreover, quantitative measurement of the amount of oxygen enables to assess the precise reaction rate at a certain temperature since other reactions caused by impurities may not have oxygen generation. Furthermore, to avoid pressure gradient of desorption gas in all experimental temperature range, flow rate of the mass spectrometer's carrier gas (He) was controlled at 50 mL min^{-1}. Given these deliberate attempts, determination of more precise activation energy can be expected.

5. Kinetics

The results of a nonisothermal kinetic analysis are described in this section. The model free iso-conversional method (Friedman–Ozawa plot) estimating the reliable activation energy of chemical reactions by using both the conversion and the rate in the thermoanalytical data. This method is based on a hypothesis that the activation energy is constant through a reaction. In other words, the reaction follows a single elementary process [12,13].

In general, the rate of the thermal decomposition reaction of solid state materials can be described as

$$\frac{d\alpha}{dt} = \left(B\frac{d\alpha}{dT}\right) = k(T)f(\alpha)$$

where t is the time, α, the reaction rate representing the extent of reaction, B, a constant heating rate, $f(\alpha)$, a function called the reaction model, and $k(T)$, the temperature dependence rate constant, which is described by the Arrhenius equation.

$$k(T) = A\exp\left(\frac{-E_a}{RT}\right)$$

where A is the pre-exponential factor, E_a, the activation energy, and R, the gas constant.

Thus, by using the above equations, the reaction rate can be described as

$$\frac{d\alpha}{dt} = \left(B\frac{d\alpha}{dT}\right) = \exp\left(\frac{-E_a}{RT}\right)Af(a)$$

At the same α value, $d\alpha/dt$ is proportional to $\exp(-E_a/RT)$.

In this study, we also measured different heating rate dependence (5, 10, 20 °C min^{-1}) of TPD-MS measurements to obtain $d\alpha/dt$ for the same α values. Here, the total amount of evolution oxygen below 600 °C (time integration of Fig. 3) was normalized at $\alpha = 100\%$. Then, $\ln(d\alpha/dt)$ plotted against $1/T$ gives a straight line with a slope $-E_a/R$.

Fig. 4 shows Friedman–Ozawa plots for the thermal decomposition reaction. The results of reaction rate of 30–70% are shown in the figure. The activation energy for each reaction rate was calculated from the inclination of the straight line approximation. All correlation factors (R^2 values) of the fitting lines were more than 0.98.

Fig. 5 shows the variation in activation energy as a function of the conversion degree. E_a is approximately constant in the conversion range of 5–70% for the $Li_{0.65}CoO_2$. This implies that the decomposition reaction of $Li_{0.65}CoO_2$ can be expected to be a single reaction. The behavior is basically the same in $Li_{0.81}CoO_2$. However in the reaction rate of 20–55%, E_a is lower than 5–15% and 60–70% regions. It is not clear the origin of this behavior. We guess it may derive from the crystal structure of $Li_{0.81}CoO_2$. Reimers and Dahn [7] reported two different hexagonal phases coexist in the $0.75 < x < 0.93$ region (where x is delithiated ratio).

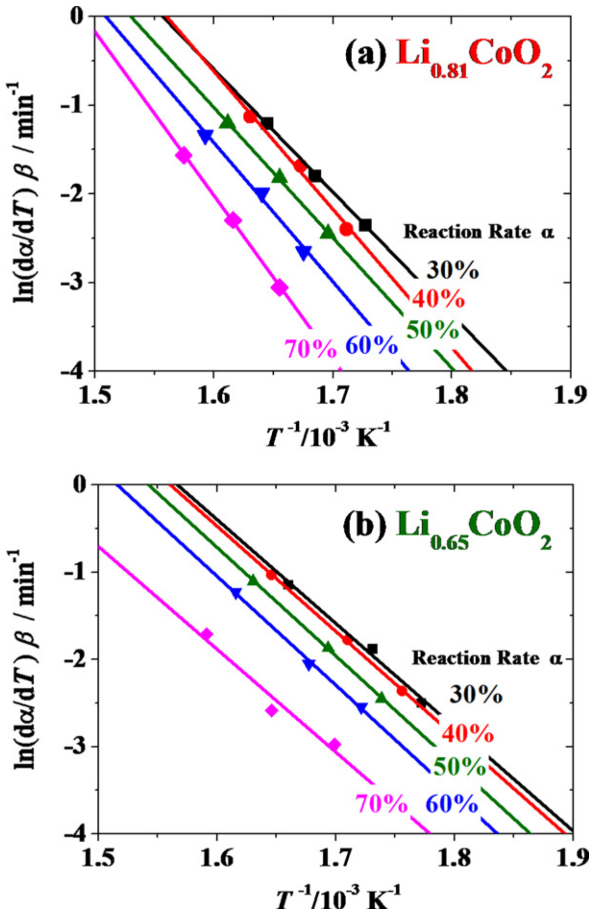

Fig. 4. Friedman–Ozawa plots for thermal decomposition of (a) $Li_{0.81}CoO_2$ (b) $Li_{0.65}CoO_2$ powder in helium flow.

The average (5–70%) E_a of $Li_{0.81}CoO_2$ is 130 kJ mol^{-1}, and that of $Li_{0.65}CoO_2$ is 97 kJ mol^{-1}. The Li content decreases as the activation energy increases. We succeeded in establishing the activation energy as a parameter to evaluate the battery stability.

The activation energy of Wang's paper [10] was not a pure thermal decomposition reaction of Li_xCoO_2. On the other hand, our samples were made from pure $LiCoO_2$ by chemical treatment. Our TPD-MS data (Fig. 3) shows single peak and the reaction rate dependence of the activation energy shows almost constant values. These results revealed that only thermal decomposition reaction of Li_xCoO_2 proceeded in our sample.

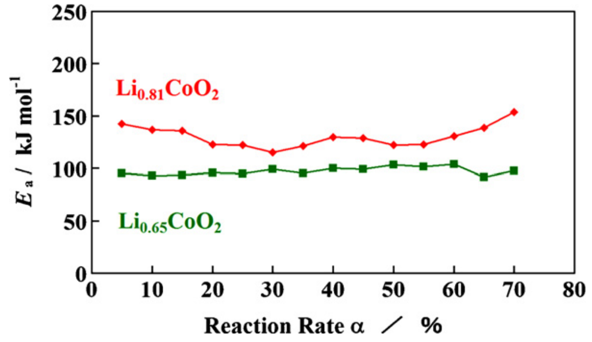

Fig. 5. Dependence of activation energy on extent of conversion during Li_xCoO_2 thermal decomposition.

6. Conclusion

In this study, we performed the quantitative O_2 gas measurement using TPD-MS to determine the stoichiometric thermal decomposition reaction of Li_xCoO_2. In addition, we derived the reaction-ratio-dependent activation energy of the reaction by carrying out TPD-MS measurements at different heating rates. The results show that the decomposition reaction of Li_xCoO_2 can be expected to be a single reaction. The average (5–70%) E_a of $Li_{0.81}CoO_2$ is 130 kJ mol^{-1}, and that of $Li_{0.65}CoO_2$ is 97 kJ mol^{-1}. As the Li content decreased the activation energy increased. The thermal stability of different cathode materials can be discussed quantitatively by the activation energy.

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