

# Thermal and Structural Stabilities of $\text{Li}_x\text{CoO}_2$ Cathode for Li Secondary Battery Studied by a Temperature Programmed Reduction

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## Abstract

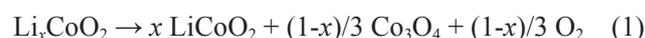
Temperature programmed reduction (TPR) method was introduced to analyze the structural change and thermal stability of  $\text{Li}_x\text{CoO}_2$  (LCO) cathode material. The reduction peaks of delithiated LCO clearly represented the different phases of LCO. The reduction peak at a temperature below 250 °C can be attributed to the transformation of  $\text{CoO}_2$ -like to  $\text{Co}_3\text{O}_4$ -like phase which is similar reduction patterns of  $\text{CoO}_2$  phase resulting from delithiation of LCO structure. The 2<sup>nd</sup> reduction peak at 300~375 °C corresponds to the reduction of  $\text{Co}_3\text{O}_4$ -like phase to  $\text{CoO}$ -like phase. TPR results indicate the thermal instability of delithiated LCO driven by  $\text{CoO}_2$ -like phase on the surface of the delithiated LCO. In the TPR kinetics, the activation energies ( $E_a$ ) obtained for as-synthesized LCO were 105.6 and 82.7 kJ mol<sup>-1</sup> for  $T_{m,H1}$  and  $T_{m,H2}$ , respectively, whereas  $E_a$  for the delithiated LCO were 93.2, 124.1 and 216.3 kJ mol<sup>-1</sup> for  $T_{m,L1}$ ,  $T_{m,L2}$  and  $T_{m,L3}$ , respectively. As a result, the TPR method enables to identify the structural changes and thermal stability of each phase and effectively characterize the distinctive thermal behavior between as-synthesized and delithiated LCO.

## 1. Introduction

Lithium-ion batteries (LIB) have been used in various fields from mobile devices to automobiles/energy storage devices due to numerous advantages such as light in weight, high energy density, high power density and long cycle life [1–7]. However, the battery safety is an essential issue to overcome, as the battery are required higher power density and larger capacity.

Many efforts have been conducted to improve the safety of LIB in the active material processing, as well as the cell battery manufacturing and management technology [7–12]. Especially, the thermal stability of LCO has been intensively investigated compared with those of other cathode materials to predict the thermal behaviors of lithium-ion cell. Various methods were introduced to investigate the thermal behaviors. Generally, the decomposition of LCO was measured using the weight loss

with the increase of temperature by thermogravimetry (TG). Moreover, their gases evolved were analyzed in-situ by thermogravimetry-mass spectrometry (TG-MS). Dahn et al. proposed the reaction mechanism of LCO decomposition from the weight loss and the  $\text{O}_2$  evolution of  $\text{Li}_{0.4}\text{CoO}_2$  at 220 °C, which occurred as the following equation [1, 7].



The exothermic behavior of LCO was also measured by differential scanning calorimetry (DSC). Using the DSC study, Baba et al. reported that the decomposition temperature of LCO in the presence of an electrolyte (~200 °C) was lower than that of chemically delithiated LCO (230 °C) due to solvent decomposition on the LCO surface. This phenomenon is explained by the reducing power of the solvent, which is identified by oxidation of electrolyte solvent [7]. The research on the self-heating characteristics of LCO active material was also studied by accelerating rate calorimetry (ARC).

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Although these methods provide very useful information on the thermal behavior and safety of the LCO, it is difficult to explain the nature of LCO alone. Since the information is resulted from complex electrochemical reactions influenced by various factors, including electrode consisting materials such as conducting agents, binders, electrolyte solvents and salts, as well as their composition in the battery cell. To obtain the decomposition of LCO itself without other reactions involved, Furushima et al. quantified the  $\text{O}_2$  evolution rate with chemically delithiated LCO ( $\text{Li}_{0.65}\text{CoO}_2$  and  $\text{Li}_{0.81}\text{CoO}_2$ ) by using a temperature programmed desorption-mass spectrometry (TPD-MS) and determined the activation energy of the delithiated LCO decomposition kinetics [11]. Yamaki et al. also studied on the  $\text{O}_2$  evolution from delithiated LCO state [12]. The onset temperature of  $\text{O}_2$  evolution by TG-MS was shifted from 240 °C to 210 °C with micro-sized (1~5 mm) and nano-sized (200~400 nm) materials, respectively. The difference between micro- and nano-sized LCO active material was explained by the surface area due to the particle size, and the frequency factor was optimized for the nano-sized LCO. Furthermore, the chemical states of overcharged LCO surfaces and interiors were observed in the recent literature [13, 14]. They reported that LCO, delithiated by overcharging, has  $\text{Co}_3\text{O}_4$ -like and  $\text{CoO}_2$ -like phases at the surface region and lithium-rich LCO phases at the core region showing a gradient of lithium contents between the surface and the core of the delithiated LCO. They explained that the key factors affecting the degradation are nano-cracks with deficient Li-ions on the surface of LCO.

Therefore, in this study, we investigated the characteristics of LCO by a thermochemical reaction using a simple temperature programmed reduction (TPR) with  $\text{H}_2$  (reducing reagent). The thermal behavior and phase changes of LCO were examined without the electrochemical charge-discharge and those of LCO compared with the delithiated LCO (charged state) after the electrochemical activation. In addition, kinetic studies were conducted to quantify the thermal stability of as-synthesized LCO and delithiated LCO in each phase in the TPR.

## 2. Experimental

The synthesized of LCO powder was prepared by a solid-state mixing of  $\text{Li}_2\text{CO}_3$  (Umicore) and  $\text{Co}_3\text{O}_4$  (Junsei Chemical) and calcined at 875 °C for

8 h in air flow. The heat-treatment of LCO was performed at 450 °C for 3 h. The calcined sample was crushed to 1~5  $\mu\text{m}$  using ball milling and sieving.

X-ray diffractometer (Rint-2000, Rigaku) was used to identify the crystallinity of as-synthesized LCO and delithiated  $\text{Li}_x\text{CoO}_2$  state using  $\text{CuK}\alpha$  X-ray radiation. The spectra were scanned with a step size of  $0.03^\circ$  in the range of  $10\sim 90^\circ$ .

The cathode electrode was fabricated through a mixing, coating, drying and pressing process. The composition of the electrode was 96 wt% active material ( $\text{LiCoO}_2$ ), 2 wt% conducting agent (SuperP, TIMCAL) and 2 wt% polyvinylidene fluoride (PVDF, Solef) binder. A homogenous slurry mixture was made by a homogenizing mixer (2000 rpm, ARE-310, Thinky) with the electrode components in N-methyl-2-pyrrolidone (NMP) solvent and the slurry was coated on aluminum foil to be loaded 10  $\text{mg cm}^{-2}$  of  $\text{LiCoO}_2$ . The coated electrode was dried at 120 °C for 0.5 h and pressed to be the electrode density of  $3.6 \text{ g cm}^{-3}$ .

For all electrochemical tests and spectroscopic analyses, coin cells (2016 type) were assembled in an argon-filled glove box. The cells consisted of a positive electrode, Li metal as a negative electrode, a microporous separator (Celgard 2500) and an electrolyte of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 volume ratio, Panax E-Tec Co.) with a 1M  $\text{LiPF}_6$  salt. The electrochemical performances were tested in the galvanostatic mode using a battery cycler (Won A tech, WBCS 3000) in the voltage range of 3.0 and 4.3 V. For delithiated LCO, the coin cells were electrochemically activated with the same steps through an aging for 1 day, the activation with 1<sup>st</sup> charge-discharge, the capacity measurement of 2<sup>nd</sup> charge-discharge and the final charge up to a desired voltage to adjust the state of charge (SOC) or lithium contents of LCO [14].

The thermal stability of LCO materials were investigated by DSC (Mettler Toledo). For the DSC analysis, delithiated LCO which was electrochemically fully charged up to 4.3 V was taken from coin cells in an argon-filled glove box. The sample was loaded in a stainless steel high pressure pan and measured with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . The reduction behaviors of as-synthesized LCO and delithiated LCO were analyzed by TPR with  $\text{H}_2$ . The reference materials, including quartz wool,  $\text{Li}_2\text{O}$ ,  $\text{LiOH}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$ , were also measured under the same conditions. The TPR was carried out in a quartz tubular reactor equipped with a thermal conductivity detector (TCD).

TCD was used to determine the amount of  $H_2$  consumption. 10 mg of the sample was loaded in the reactor and 4%  $H_2/Ar$  was fed at a rate of  $10 \text{ ml min}^{-1}$ . The reduction of cathode material was observed in the temperature range of 100 to  $760 \text{ }^\circ\text{C}$  at different heating rates of 2, 5,  $10 \text{ }^\circ\text{C min}^{-1}$  [15–18]. For TPR analysis, electrochemically delithiated LCO was taken from the coin cell and the electrode disk was cleaned with dimethyl carbonate solvent and dried in an argon-filled glove box.

### 3. Results and discussion

#### 3.1. Electrochemical performance

The electrochemical performances of synthesized LCO are shown in Fig. 1. The initial 3 cycles were measured at a 0.1C charge/discharge rate and from the 4<sup>th</sup>–50<sup>th</sup> cycles were measured at a 0.5C charge/discharge rate. The initial discharge capacity was  $158 \text{ mAh g}^{-1}$  (0.1C charge – 0.1C discharge) with coulombic efficiency of 95.6%, and the discharge capacity after 50 cycles (0.5C charge – 0.5C discharge) was 87.4% of the initial one. The specific capacity of LCO appears a typical behavior in the charge (4.3 V) and discharge (3.0 V) process compared with previous studies [2, 5]. The cycle life indicates good stability with high capacity retention in the half coin cell. In the charge-discharge profile after 50 cycles, an increase of charge voltage and a decrease of discharge voltage were observed, which attributed to the current increase according to the C-rate increase from 0.1 to 0.5 as well as the deterioration of LCO in the progress of the cycle.

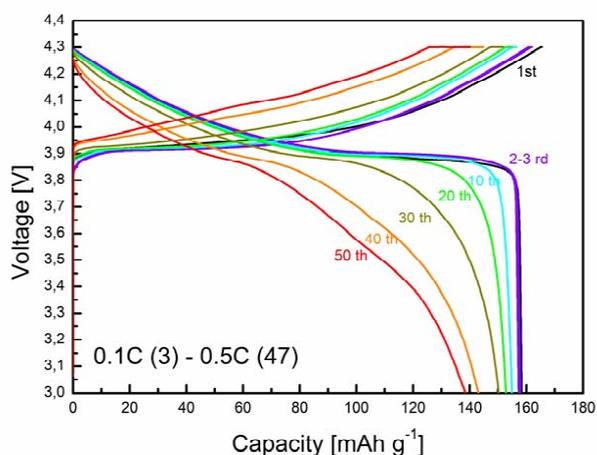


Fig. 1. Electrochemical performance of as-synthesized LCO. The 1<sup>st</sup>–3<sup>rd</sup> charge/discharge profiles were measured at 0.1C rate and 4<sup>th</sup>–50<sup>th</sup> profiles were measured at 0.5C rate.

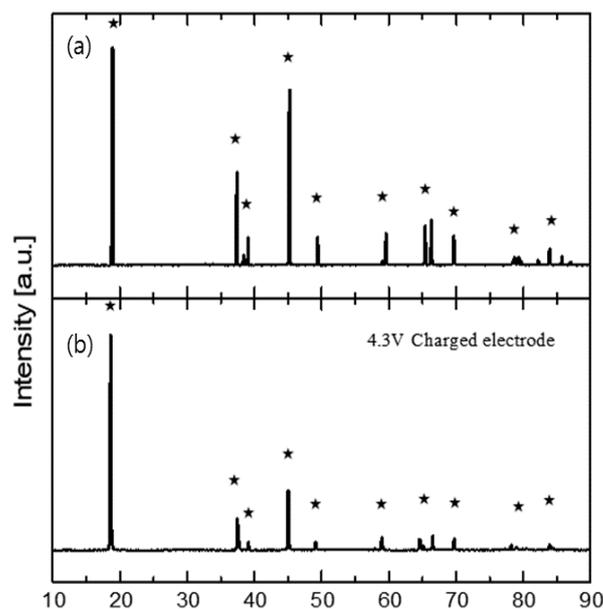


Fig. 2. XRD patterns of (a) as-synthesized LCO and (b) delithiated LCO (4.3 V charged).

Figure 2 shows XRD patterns of as-synthesized LCO and delithiated LCO (4.3 V charged state). As-synthesized LCO shows a strong (003) diffraction peak, slightly strong other (001) peaks and other relatively weak peaks. When the LCO was charged up to 4.3 V, the (003) peak decreases to a lower angle from  $18.9$  to  $18.6$  resulted from the layered structure expansion. In the previous study [6], however, the (003) peak increases with charged state above 4.5 V which was explained by a contraction of the host structure along the c-axis due to the decrease of charged oxygen ions followed by lowered electrostatic repulsion between the oxygen ions.

#### 3.2. Thermal behavior in DSC

The thermal behaviors of as-synthesized LCO and delithiated LCO (4.3 V charged) in the presence of the electrolyte (EC/EMC/DMC=1/1/1 with 1M  $LiPF_6$  salt), by DSC analysis are shown in Fig. 3. The electrolyte used in the experiment showed exothermic behaviors which have a peak temperature around  $250 \text{ }^\circ\text{C}$  and a broad area of the peak (Fig. 3(a)). In the case of as-synthesized LCO with the electrolyte (Fig. 3(b)), the exothermic peak area is significantly smaller than that of the electrolyte itself. No exothermic peaks are observed with as-synthesized LCO alone under  $400 \text{ }^\circ\text{C}$  (not shown in Fig. 3), therefore, the reduced area of the exothermic peak can be attributed to the relatively small amount of the electrolyte in the sample rather

than mixed behavior between LCO and the electrolyte. The calorific values are obtained as  $431.7 \text{ J g}^{-1}$  and  $106.6 \text{ J g}^{-1}$  for the electrolyte only and as-synthesized LCO with electrolyte, respectively. In the as-synthesized LCO with electrolyte, the amount of heat generation (1<sup>st</sup> peak) is lower than that of the expected calorific value ( $141.9 \text{ J g}^{-1}$ ) calculated from the equivalent amount of electrolyte, however, sample b shows 2<sup>nd</sup> exothermic peak at higher temperature  $\sim 290 \text{ }^\circ\text{C}$  which has  $100.5 \text{ J g}^{-1}$  due to the reaction between LCO and the electrolyte. The delithiated LCO with electrolyte (Fig. 3(c)) shows two major exothermic peaks at lower temperature ( $\sim 220 \text{ }^\circ\text{C}$ ) with relatively high calorific value of  $543.0 \text{ J g}^{-1}$ . Yamaki et al., in their TG-MS and DSC studies with  $\text{Li}_{0.49}\text{CoO}_2$ , reported that 1<sup>st</sup> peak at  $\sim 200 \text{ }^\circ\text{C}$  should be attributed to a surface reaction of  $\text{Li}_{0.49}\text{CoO}_2$  with the electrolyte without  $\text{O}_2$  evolution and 2<sup>nd</sup> peak at higher temperature is likely to be caused by oxidation of the electrolyte by the  $\text{O}_2$  evolution [10].

From DSC analysis, the thermal parameters such as the on-set and maximum temperature and the calorific value of the exothermic reactions have been obtained [8–10, 12, 19]. However, the results of as-synthesized LCO and delithiated LCO cannot be represent the active materials' characteristics since they are not only resulted from LCO itself but the reactions of LCO with the electrolyte, conducting material and the binder. Thus, two peaks observed in the delithiated LCO cannot explain clearly each reaction step with the separation of the two phases.

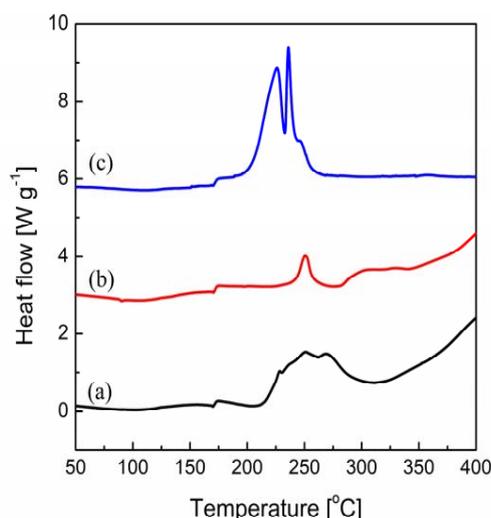
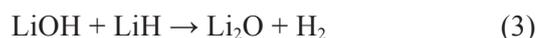


Fig. 3. DSC thermograms for (a) electrolyte 2 mg (1M  $\text{LiPF}_6$  in EC/EMC/DMC=1/1/1) (b) as-synthesized LCO 1.5 mg and electrolyte 0.75 mg and (c) delithiated LCO (4.3 V charged) 1.5 mg and electrolyte 0.75 mg.

### 3.3. Thermal behavior and reduction mechanism in TPR

To investigate clear degradation reaction mechanism of LCO, TPR characterization is employed as a complementary method which is expected to provide a structural stability of the metal oxide active material in the reduction conditions with the increase of temperature.

As shown in Fig. 4, the baseline of an empty tubular reactor with a quartz wool as a sample supporter (Fig. 4(a)) is stable without  $\text{H}_2$  consumption up to  $650 \text{ }^\circ\text{C}$ . For  $\text{LiOH}$  (Fig. 4(c)) and  $\text{Li}_2\text{CO}_3$  (Fig. 4(d)) as Li sources of LCO synthesis,  $\text{LiOH}$  is very stable below  $400 \text{ }^\circ\text{C}$ , but  $\text{H}_2$  outgassing is observed at  $450 \text{ }^\circ\text{C}$ . Similar reactions from  $\text{LiH}/\text{Li}_2\text{O}/\text{LiOH}$  system on  $\text{H}_2$  outgassing were reported as below [20].



Generally,  $\text{Li}_2\text{CO}_3$  is thermally decomposed without  $\text{H}_2$  reduction at high temperature in the range of  $730\text{--}1270 \text{ }^\circ\text{C}$  [21]. In the TPR experimental temperature range ( $<650 \text{ }^\circ\text{C}$ ),  $\text{Li}_2\text{CO}_3$  shows a stable behavior (Fig. 4(d)).



However, in the case of metal oxide,  $\text{Co}_3\text{O}_4$  is reduced via typical two step reaction mechanisms ( $\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$ ) [16, 17]. Two peaks according to the two step reaction are observed in the TPR analysis for  $\text{Co}_3\text{O}_4$  (Fig. 4(e)).



As-synthesized LCO is reduced at a higher temperature compared to those of  $\text{Co}_3\text{O}_4$ , and shows a similar two-step reduction (Fig. 4(f)). A possible mechanism of LCO reduction is the reaction of Eqs. (7) and (6).



$\text{Li}_2\text{O}$  decomposed from LCO reduction can be reacted with  $\text{H}_2\text{O}$  and has an equilibrium with  $\text{LiOH}$  compound as below Eq. (8) [22]. The  $\text{Li}_2\text{O}$  shows relatively stable behavior compared with that of  $\text{LiOH}$  in TPR analysis (Fig. 4(b)).



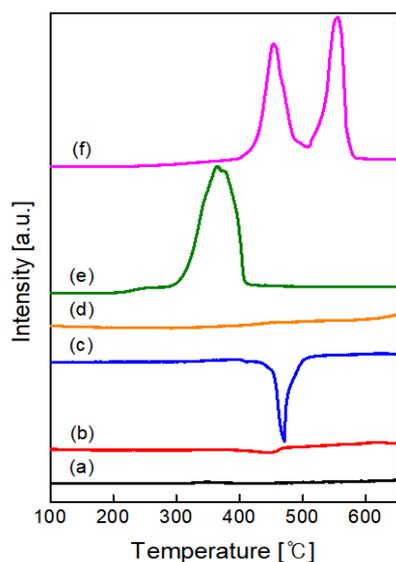


Fig. 4. TPR profiles of as-synthesized LCO and raw materials, (a) quartz wool, (b)  $\text{Li}_2\text{O}$ , (c)  $\text{LiOH}$ , (d)  $\text{Li}_2\text{CO}_3$ , (e)  $\text{Co}_3\text{O}_4$ , and (f) as-synthesized LCO with heating rate of  $5\text{ }^\circ\text{C min}^{-1}$ .

Above TPR results of as-synthesized LCO show clear structural change with the increase of temperature unlike DSC thermograms. Thus, it is considered that TPR analysis can be applied as a suitable method to investigate the thermal behavior and related structural change of metal oxide active materials. Moreover, TPR method can simply analyze the thermal behavior of LCO itself without an effect of the electrolyte.

Based on the TPR results of as-synthesized LCO and the raw materials, TPR patterns of LCO

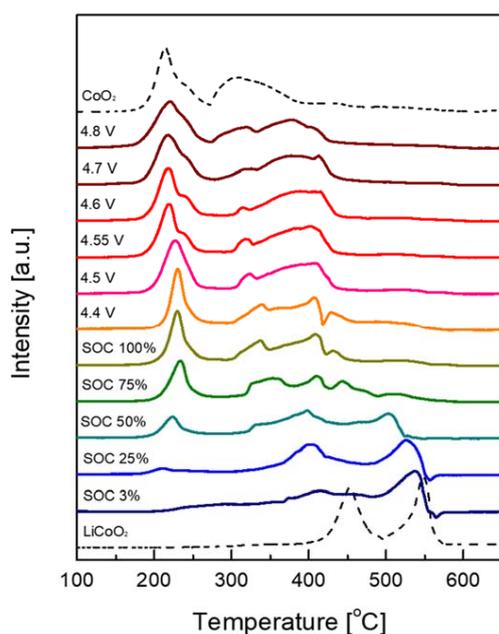


Fig. 5. TPR patterns of  $\text{Li}_x\text{CoO}_2$  with the increase of delithiation state ( $5\text{ }^\circ\text{C min}^{-1}$  heating rate).

with the increase of delithiation state were investigated as shown in Fig. 5. The delithiation state was represented by the ratio of the charge capacity to the theoretical capacity of  $274\text{ mAh g}^{-1}$  when  $x = 1$  in  $\text{Li}_x\text{CoO}_2$ . The SOC denotes the percentage ratio (%) of the charge capacity on the basis of the one of LCO up to 4.3 V with  $158\text{ mAh g}^{-1}$ . As-synthesized LCO sample shows much higher reduction temperatures than those of delithiated LCO. This can be attributed to the strong layered structure, which composed at high temperature ( $870\text{ }^\circ\text{C}$ ). As-synthesized LCO shows two reduction peaks appeared at high temperature above  $400\text{ }^\circ\text{C}$  in the TPR profile. The 1<sup>st</sup> peak mainly corresponds to the reduction of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  to  $\text{Co}^{2+}$ , and the 2<sup>nd</sup> peak to the reduction of  $\text{Co}^{2+}$  to  $\text{Co}^0$  [23]. However, in the case of delithiated LCO, the reduction peaks are observed at a much lower temperature. The reduction peaks at low temperatures below  $250\text{ }^\circ\text{C}$  may be attributed to the transformation of  $\text{CoO}_2$ -like to  $\text{Co}_3\text{O}_4$ -like phase, which appears similar reduction patterns of  $\text{CoO}_2$  phase resulting from the delithiation of LCO structure and the 2<sup>nd</sup> reduction peak at  $300\text{--}375\text{ }^\circ\text{C}$  corresponds to the reduction of  $\text{Co}_3\text{O}_4$ -like phase to  $\text{CoO}$ -like phase.

LCO of  $x = 0.98$  state (SOC 3%) after the electrochemical charge and discharge shows a broad and weak reduction peak in the temperature range of  $200\text{--}350\text{ }^\circ\text{C}$  and relatively strong two peaks at  $410$  and  $540\text{ }^\circ\text{C}$  which are lower temperatures compared with those of as-synthesized LCO ( $x = 1$ ). The former may be attributed to the lithium loss due to the irreversible contents ( $\sim 2.6\%$ ) of the initial charge and discharge process and the latter may be referred to the existence of a considerable amount of lithium-deficient phase on the surface of LCO and the residual by-product of the electrolyte on the surface of LCO in spite of DMC washing.

Two-step reduction peaks of as-synthesized LCO are observed with the increase of SOC 50% ( $x = 0.71$ ) although the intensity of peaks are reduced and shifted to a lower temperature. However, TPR pattern of the SOC 75% ( $x = 0.56$ ) state revealed drastic change with the occurrence of the strong reduction peak around  $220\text{ }^\circ\text{C}$  and the disappearance of 2<sup>nd</sup> peak in the two-step reduction of as-synthesized LCO above  $500\text{ }^\circ\text{C}$ . These changes of TPR can be comparable to the structural phase transitions of LCO charge-discharge curves [6] corresponding to the metal-insulator transition around 3.9 V charged ( $x = \sim 0.7$ ) and the order-disorder transitions between 4.05 V and 4.20 V charged ( $x = \sim 0.5$ ).

The intensity of reduction peak at 220 °C increases with the increase of the delithiation state in the range from  $x = 0.42$  (4.3 V charged) to  $x = 0.36$  (4.4 V charged). As the delithiation further progresses to the state of  $x = 0.29$  (4.5 V charged), the main peak becomes broader and the on-set temperature decreases to the temperature lower than 200 °C. The result indicates that the thermal stability of LCO is deteriorated significantly as increase of the delithiation in the LCO structure.

On the other hand, the reduction peak of  $x = 0.2$  (4.55 V charged) shows a clear phase change with the separated reduction peak at 200 °C. Also, at a charge of 4.7 V or more ( $x = 0.15$ ), the peak at 200 °C was observed as a main peak and the peak at 220 °C was diminished gradually. The result corresponds to the transition from the O3 phase to H1-3 phase and from the H1-3 phase to O1 phase in the results of  $dQ/dV$  curve which have two transition peaks at 4.55 V and 4.62 V [6].

In order to elucidate the phase at 200 °C, a fully delithiated  $\text{CoO}_2$  phase was prepared by charge up to 5.0 V (3 days continuous charge) and the reduction temperature of  $\text{CoO}_2$  phase is in good agreement with the transition peak at 200 °C. The  $\text{CoO}_2$  phase has been investigated for its existence as an end member of LCO [2, 3]. The results of the TPR, also, exactly matched in the previous differential thermogravimetry (DTG) with 5%  $\text{H}_2/\text{Ar}$  gas flow study reported by Motohashi et al. [24] and they proposed two step reductive reactions of  $\text{CoO}_2\text{-}\delta \rightarrow \text{CoO} \rightarrow \text{Co}$ . They explained that it is in the equilibrium under unstable state of oxygen deficiency with the  $(2-\delta)$  value in the range of 1.72 to 1.92. The oxygen content  $(2-\delta)$  of  $\text{CoO}_2$  depends strongly on the synthesis procedure such that the more equilibrated synthesis and/or more highly oxidizing conditions tend to suppress the formation of oxygen vacancies.

In a view of thermal stability, the exothermic behavior of LCO occurs below 200 °C which depends on the reaction between LCO and the electrolyte in the case of DSC analysis, whereas the reduction of LCO itself starts at 200 °C with all the variation of SOC and overcharge level except  $x = 1$  in the case of TPR analysis. TPR results indicate the thermal instability of delithiated LCO driven by  $\text{CoO}_2$ -like phase on the surface of the delithiated LCO. Ohzuku et al. observed a stability of monoclinic phase ( $x = 0.55$ , OCV 4.12) with XRD study, which examine the average bulk structure regardless of surface variations [2].

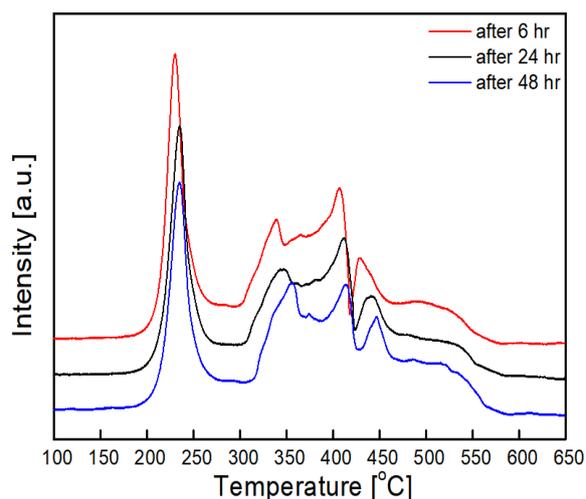


Fig. 6. TPR patterns for delithiated LCO (4.3 V charged) with different aging times at room temperature.

In this TPR study, Fig. 6 shows TPR patterns of delithiated LCO with different aging time at room temperature. Peak temperature of  $\text{CoO}_2$ -like phases at around 220 °C is shifted during an initial aging of 24 h, whereas, the peak temperature of  $\text{Co}_3\text{O}_4$ -like phases at around 340 °C is shifted sequentially after 24 h. This time lag between the peak shifts can be explained that  $\text{CoO}_2$ -like phases on the surface of  $\text{Li}_x\text{CoO}_2$  are quickly stabilized through contacting Li ions polarized in electrolyte, whereas  $\text{Co}_3\text{O}_4$ -like phases in the core of  $\text{Li}_x\text{CoO}_2$  are much slowly changed via Li ion diffusion in the solid state. This implies that TPR method can resolve surface and core effect.

### 3.4. TPR kinetics of as-synthesized LCO and delithiated LCO

TPR spectra has been analyzed not only qualitatively to compare materials but also to estimate the respective kinetic parameter as well [25]. For the TPR kinetics of as-synthesized LCO and delithiated LCO solid state materials, the Kissinger Method [26, 27] was applied, since it is a simple approach to determine the activation energies under the condition of the maximum reaction rate. In general, the rate of the non-isothermal TPR can be described as follows:

$$\frac{d\alpha}{dt} = \left( \beta \frac{d\alpha}{dT} \right) = k(T)f(\alpha) \quad (9)$$

where  $t$ ,  $\alpha$  and  $\beta$  represent the time, the rate of conversion and a constant heating rate in a function of

the reaction model  $f(\alpha)$  and the temperature dependence of rate constant,  $k(T)$  which is expressed by the Arrhenius equation.

$$\frac{d\alpha}{dt} = \left( \beta \frac{d\alpha}{dT} \right) = k(T)f(\alpha) \quad (10)$$

where  $A$ ,  $E$ ,  $T$  and  $R$  are the pre-exponential factor, the activation energy ( $\text{J mol}^{-1}$ ), the reaction temperature and the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). By using the above equations, the reaction rate can be expressed as:

$$-\frac{E_a \beta}{RT_m^2} = A f'(\alpha_m) \exp\left(\frac{-E_a}{RT_m}\right) \quad (11)$$

where  $f'(\alpha) = df(\alpha)/d\alpha$  and the subscript  $m$  denotes the value of maximum. From the logarithm rearrangements, Kissinger equation (Eq. (12)) obtained under the assumption of the reaction is the first order and the independent of heating rate.

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(-\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (12)$$

The maximum reduction temperatures are obtained with different heating rates as shown in Fig. 7. TPR patterns of as-synthesized LCO and delithiated LCO (4.3 V charged state) with different heating rates (2, 5, 10 °C min<sup>-1</sup>). As-synthesized LCO shows two reduction peaks in the TPR profile. The 1<sup>st</sup> peaks mainly correspond to the reduction of Co<sup>3+</sup> and Co<sup>4+</sup> to Co<sup>2+</sup>. They are appeared at high temperature above 400 °C with different heating rates ( $T_{m\_H1}$  421.4, 452.5 and 481.3 °C for 2, 5 and 10 °C min<sup>-1</sup> heating rate). The 2<sup>nd</sup> peaks correspond to the reduction of Co<sup>2+</sup> to Co<sup>0</sup>. The temperatures of 2<sup>nd</sup> peaks ( $T_{m\_H2}$ ) with different heating rates are 502.6, 548.2 and 596.9 °C for heating rate of 2, 5 and 10 °C min<sup>-1</sup>, respectively. However, in the case of delithiated LCO, the reduction peaks are observed at a much lower temperatures. The 1<sup>st</sup> reduction peaks at low temperatures below 250 °C (212.2, 230.3 and 245.5 °C for 2, 5 and 10 °C min<sup>-1</sup> heating rate) may be attributed to the transformation of (i) CoO<sub>2</sub>-like to Co<sub>3</sub>O<sub>4</sub>-like phase, which appears similar reduction patterns of CoO<sub>2</sub> phase resulting from the delithiation of LCO structure. The 2<sup>nd</sup> reduction peaks (325.3, 340.5 and 362.7 °C for 2, 5 and 10 °C min<sup>-1</sup> heating rate) correspond

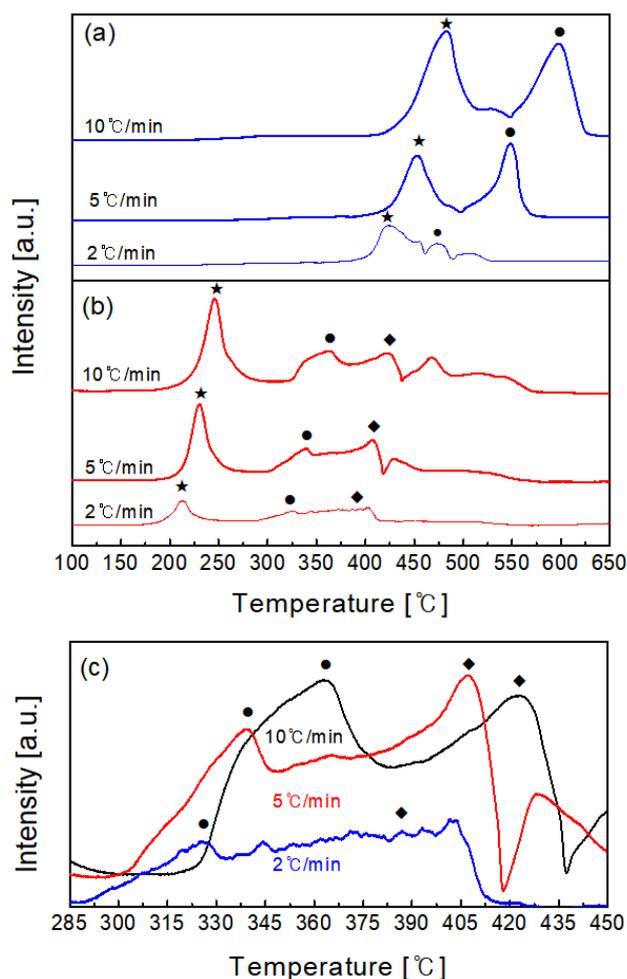


Fig. 7. TPR patterns of (a) as-synthesized LCO, (b) delithiated LCO (4.3 V charged state) and (c) magnified graph of delithiated LCO (4.3 V charged state) with different heating rates.

to the reduction of (ii) Co<sub>3</sub>O<sub>4</sub>-like phase to CoO-like phase. Finally, the 3<sup>rd</sup> reduction peaks at 386.9, 407.4 and 423.4 °C for 2, 5 and 10 °C min<sup>-1</sup> heating rate, correspond to the reduction of (iii) CoO-like phase to Co<sup>0</sup>.

From the above the maximum temperature ( $T_m$ ) of the TPR experiment with different heating rates, kinetic parameters for as-synthesized LCO and delithiated LCO (4.3 V charged) are obtained by Kissinger method as shown in Fig 8. The  $E_a$  obtained for the as-synthesized LCO was 105.6 and 82.7 kJ mol<sup>-1</sup> for  $T_{m\_H1}$  and  $T_{m\_H2}$ , respectively. This indicates that the first reduction (1<sup>st</sup> peak) of as-synthesized LCO requires high temperature (421.4~481.3 °C) and relatively large activation energy due to the highly crystallized layer-structure, then the second reduction (2<sup>nd</sup> peak) requires relatively small activation energy once the structure collapsed at the first reduction.

Whereas,  $E_a$  for delithiated LCO was 93.2 and 124.1 and 216.3  $\text{kJ mol}^{-1}$  for  $T_{m,L1}$ ,  $T_{m,L2}$  and  $T_{m,L3}$ , respectively. This represents the reduction of delithiated LCO requires low temperature (212.2~245.5  $^\circ\text{C}$ ) and relatively small activation energy with high pre-exponential factor compared with as-synthesized LCO. Generally, the activation energy of the  $\text{CoO}_2$  reduction reaction decreases as the reduction proceeds as the result of Ji et al. In this study, however, the activation energy increases as the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> reduction proceeds since the reaction at the surface, which is the  $\text{CoO}_2$ -like phase containing a negligible amount of Li ion, occurs at a high rate and then the reaction in the core region which contains more Li ion occurs at a low rate. The kinetic properties are summarized in Table and compared with those of previous studies.

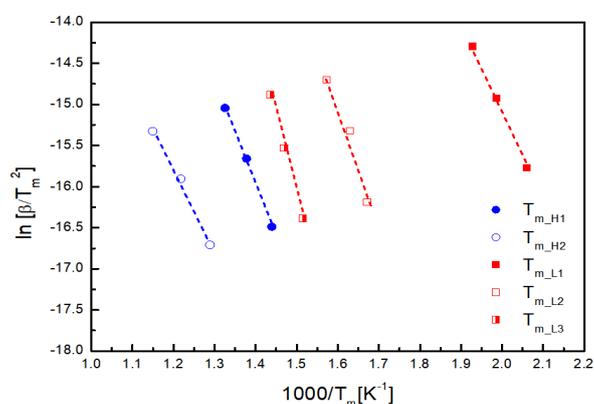


Fig. 8. Kinetics of TPR for the as-synthesized LCO and delithiated LCO (4.3 V charged).

In the previous studies for the kinetics of LCO decomposition, Wang et al. reported that  $E_a$  of the  $\text{Li}_x\text{CoO}_2$  ( $x = 0.42$ , 4.2 V charged) was obtained 88.87  $\text{kJ mol}^{-1}$  and 148.87  $\text{kJ mol}^{-1}$  by DSC (C80) and TG analysis, respectively [9]. They noted that  $E_a$  obtained by DSC is smaller than that of TG because  $E_a$  from DSC data is calculated near the onset temperature of  $\text{Li}_x\text{CoO}_2$  (~170  $^\circ\text{C}$ ) and kinetics of DSC could result in more reliable, whereas  $E_a$  from TG is obtained near the temperature of maximum mass loss (~250  $^\circ\text{C}$ ). Furushima et al., also, reported kinetic results of the thermal decomposition of chemically delithiated  $\text{Li}_x\text{CoO}_2$  with the liberated  $\text{O}_2$  gas quantified by TPD-MS [11]. They noted that the decrease of Li content in  $\text{Li}_x\text{CoO}_2$  brings about the lower  $E_a$  of thermal decomposition based on the results obtained 130  $\text{kJ mol}^{-1}$  for  $\text{Li}_{0.81}\text{CoO}_2$  and 97  $\text{kJ mol}^{-1}$  for  $\text{Li}_{0.65}\text{CoO}_2$ . On the other hand, Yamaki et al. reported relatively high value of  $E_a$  as 114  $\text{kJ mol}^{-1}$  for  $\text{Li}_{0.5}\text{CoO}_2$  which is obtained from an average value of activation energies in the range of  $a = 0.3\sim 0.7$  ( $a$  is a degree of conversion) assuming two or more reactions as a single reaction [12].

From this TPR kinetic study, it is considered that the 1<sup>st</sup> reduction reaction of delithiated LCO ( $\text{CoO}_2$ -like phase) will act as a trigger for thermal runaway and the activation energy is comparable with the one obtained from the DSC on-set temperature among the results of other previous studies.

Table

Summary of kinetic properties reported in the literature and those of present study for the  $\text{LiCoO}_2$

Authors	Experiment	Material	Temp.	$E_a$	A	n	$R^2$
Wang et al. (2008)	TG DSC	$\text{Li}_{0.52}\text{CoO}_2$	256	148.87	$1.22\text{E}+12$	1	0.946
		$\text{Li}_{0.52}\text{CoO}_2$	190	88.87	$1.87\text{E}+06$	1	0.998
Furushima et al. (2011)	TPD-MS	$\text{Li}_{0.81}\text{CoO}_2$	>250	130	-	1	>0.98
		$\text{Li}_{0.65}\text{CoO}_2$	>250	97	-	1	>0.98
Yamaki et al. (2014)	TG-MS	m- $\text{Li}_{0.5}\text{CoO}_2$	240	114	$1.88\text{E}+10$	1.62	<0.99
		n- $\text{Li}_{0.5}\text{CoO}_2$	210	114	$3.76\text{E}+10$	1.62	<0.99
Ji et al. (2009)	TPR	$\text{CoOOH}$	186	93.1	-	1	-
		$\text{Co}_3\text{O}_4$	248	80	-	1	-
		$\text{CoO}$	340	53	-	1	-
This study	TPR	$\text{LiCoO}_2$	452.5	105.6	$2.99\text{E}+01$	1	0.998
		$\text{Li-CoO}$	548.2	82.7	$3.62\text{E}-01$	1	0.993
		$\text{Li}_{0.42}\text{CoO}_2$	230.3	93.2	$1.58\text{E}+04$	1	0.999
		$\text{Co}_3\text{O}_4$ -like	340.5	123.8	$9.67\text{E}+04$	1	0.966
		$\text{CoO}$ -like	407.4	157.5	$7.27\text{E}+06$	1	-

## 4. Conclusions

We investigated the structural change and thermal stability of LCO by a thermochemical reaction using a temperature programmed reduction (TPR) with H<sub>2</sub>. As-synthesized LCO has an initial discharge capacity of 158 mAh g<sup>-1</sup> (4.3 V charged) and shows a stable cycleability, which has 87.4% discharge capacity of the initial one after 50 cycles.

In DSC thermograms, thermal behaviors of as-synthesized LCO shows the reactions with the electrolyte rather than the behaviors of LCO itself and delithiated LCO with electrolyte shows two major exothermic peaks with strong exothermic behaviors at lower temperature (~220 °C). In TPR profile, as-synthesized LCO shows two strong reduction peaks. The 1<sup>st</sup> peaks mainly correspond to the reduction of Co<sup>3+</sup>, Co<sup>4+</sup> to Co<sup>2+</sup>, and the 2<sup>nd</sup> peaks correspond to the reduction of Co<sup>2+</sup> to Co<sup>0</sup>. On the other hand, the reduction peaks of delithiated LCO are observed at a much lower temperatures. The reduction peaks at low temperatures below 250 °C may be attributed to the transformation of (i)CoO<sub>2</sub>-like to Co<sub>3</sub>O<sub>4</sub>-like phase, which appears similar reduction patterns of CoO<sub>2</sub> phase resulting from the delithiation of LCO structure. The 2<sup>nd</sup> reduction peaks at low temperatures (300 and 375 °C), correspond to the reduction of (ii) Co<sub>3</sub>O<sub>4</sub>-like phase to CoO-like phase. TPR results indicate the thermal instability of delithiated LCO driven by CoO<sub>2</sub>-like phase on the surface of the delithiated LCO.

Kinetic parameters for as-synthesized LCO and delithiated LCO (4.3 V charged) are obtained by Kissinger method. The  $E_a$  obtained for the as-synthesized LCO were 105.6 and 82.7 kJ mol<sup>-1</sup> for T<sub>m,H1</sub> and T<sub>m,H2</sub>, respectively. Whereas,  $E_a$  for delithiated LCO were 93.2 and 124.1 and 216.3 kJ mol<sup>-1</sup> for T<sub>m,L1</sub>, T<sub>m,L2</sub> and T<sub>m,L3</sub>, respectively.

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