



Short communication

Thermal studies of charged cathode material (Li_xCoO_2) with temperature-programmed decomposition–mass spectrometry

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ABSTRACT

Thermal reactions of charged Li_xCoO_2 and electrolyte are investigated by means of temperature-programmed decomposition–mass spectrometry (TPD–MS), DSC, TGA, and XRD. The electrolyte is composed of ethylene carbonate, propylene carbonate, and dimethyl carbonate. Direct observation of gas species resulting from the reactions is beneficial in understanding the reaction mechanisms. From O_2 peaks in the TPD–MS spectra with weight loss in TGA and XRD results, it is obvious that the reduction of Li_xCoO_2 to LiCoO_2 and Co_3O_4 is triggered at 190°C and completed at 400°C . The initial stages of electrolyte combustion and decomposition are confirmed by H_2O and CO_2 peaks in the TPD–MS spectra along with exothermic peaks in DSC plots. The reaction of electrolyte with O_2 released from the reduction of Li_xCoO_2 begins at 240°C ; the decomposition starts at 290°C .

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1. Introduction

Lithium-ion batteries have been used widely as power sources for various mobile electronics due to their high cell voltage and high specific energy [1]. In the last decade, however, more than 10 million lithium-ion batteries have been recalled because of safety issues, such as burning and explosion. Most of the safety concerns are associated with the instability of cathode materials in charged batteries. When the batteries are fully charged, x in Li_xCoO_2 is close to 0.5. Most commercial lithium-ion batteries use Li metal oxides, such as LiCoO_2 , for the cathode materials. At high temperatures, charged Li_xCoO_2 decomposes to LiCoO_2 , CoO , and Co_3O_4 with the evolution of O_2 . Electrolytes in batteries react with the evolved O_2 with the release of a large amount of heat than can result in thermal runaway [2–8]. In order to understand the thermal runaway mechanism, many research groups have studied the reaction of Li_xCoO_2 and electrolyte by using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and/or accelerating rate calorimetry (ARC) [2,3,8,9]. Exothermic peaks in DSC and ARC can be related to thermal reactions at different temperatures. Gas species of O_2 , CO_2 , and H_2O have been reported to be produced by the thermal reactions, such as the reduction of Li_xCoO_2 and the combustion of electrolytes [1–3]. Thus monitoring the gas species during the thermal reactions

could be very useful in understanding the reaction mechanisms. To the best of our knowledge, there are no reports where the gas products have been directly identified. In this regard, temperature-programmed decomposition–mass spectrometry (TPD–MS) is a useful tool in identifying evolved gas species from thermal reactions [10].

In the present study, TPD–MS results for thermal reactions between charged Li_xCoO_2 and electrolyte are interpreted together with thermogravimetric analysis (TGA), DSC, and XRD results.

2. Experimental

Fully charged cathode materials were obtained from LG 18650 cylindrical batteries. The cathode materials were composed of 2 wt.% acetylene black (Denka Black, Denki Kagaku Kogyo Kabushiki Kaisha, Japan), polyvinylidene fluoride (PVdF, 2 wt%) and LiCoO_2 (96 wt%). Anode materials consisted of Denka black, styrenebutadiene rubber (SBR), and mesocarbon micro-beads (MCMB). The electrolyte solution was lithium hexafluoro phosphate (LiPF_6 , 1.0 M) dissolved in a mixture of ethylene carbonate (EC, 30 vol%), propylene carbonate (PC, 5 vol%), and dimethyl carbonate (DMC, 65 vol%). The batteries were charged to 4.2 V and disassembled in a dry room.

For TPD–MS analysis, cathode materials of 3–5 mg were heated from 50 to 700°C at a heating rate of 10°C per min. The heating process was conducted under flowing helium by using a double-shot pyrolyzer (2020iD, Frontier Lab). The gases evolved from the pyrolyzer were transferred to a mass spectrometer (5973N, Agilent) from which thermograms of O_2 , H_2O and CO_2 were obtained

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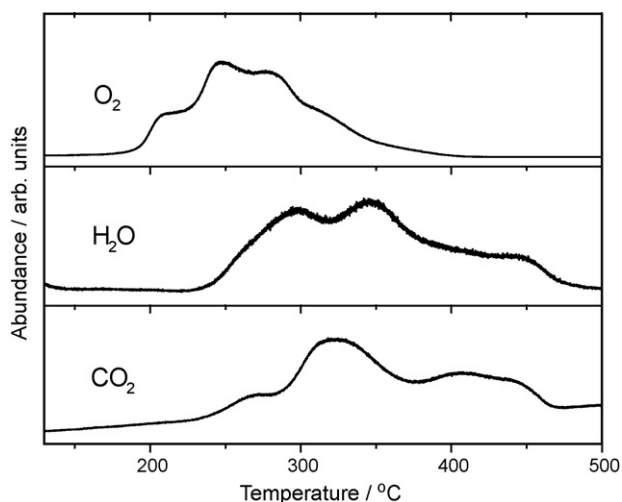


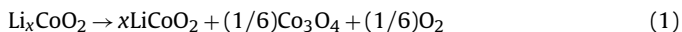
Fig. 1. TPD-MS curves of O₂, H₂O, and CO₂ for cathode materials.

by following 18, 32 and 44 *m/z* from the MS data. DSC was performed by using a Mettler-Toledo 823e-DSC over a temperature range from 25 to 400 °C at a heating rate of 10 °C per min. For DSC experiments, samples were placed in gold-plated crucibles (ME-51140405, Mettler-Toledo) and sealed hermetically. To obtain the DSC curve, cathode materials were wetted with electrolyte; 4 μl of electrolyte of the same composition as the commercial cylindrical batteries was added to 4 mg of cathode materials in the crucible before hermitical sealing. TGA experiments were performed with a Mettler-Toledo 851e-TGA.

Powder X-ray diffraction (XRD) data were collected at room temperature on a Bragg-Brentano diffractometer (Bruker-AXS Endeavor D4) with a Fe X-ray tube, a variable divergence slit of 6 mm, and a position sensitive Lynxeye detector with a 3.7° slit. Data acquisition covered the angular range 20° ≤ 2θ ≤ 95° at a step width of 0.025° and a total measurement time of 1 h. For XRD measurements, cathode materials were heated to final temperatures of 200, 250, 300, 350, and 400 °C in TGA tests at a heating rate of 10 °C per min.

3. Result and discussion

When cathode materials are heated to 700 °C at a heating rate of 10 °C per min, gases from the materials are detected only above 190 °C (TPD-MS). With increasing temperature, O₂ is produced, followed by both H₂O and CO₂ (Fig. 1). In the TPD-MS curve for O₂, the first peak starts near 190 °C and is accompanied by three more peaks at around 240, 280 and 320 °C. The O₂ peaks are related to the reduction of Li_xCoO₂, since the reduction process of Li_xCoO₂ is the only known process to produce O₂ [11], i.e.,



O₂ is observed until 400 °C, which implies that the reduction of Li_xCoO₂ is almost completed by 400 °C. A number of research groups reported that the reduction of Li_xCoO₂ starts at around 200 °C (DSC and XRD studies) [2–8] and this finding is similar to the present observation that the first O₂ peak appears near 190 °C.

The evolution of H₂O and CO₂ is observed only above 240 °C (Fig. 1) and is associated with combustion of the electrolyte. The electrolyte reacts with O₂ evolved from the reduction of Li_xCoO₂ [2,3] to produce H₂O and CO₂ according to the following reactions:

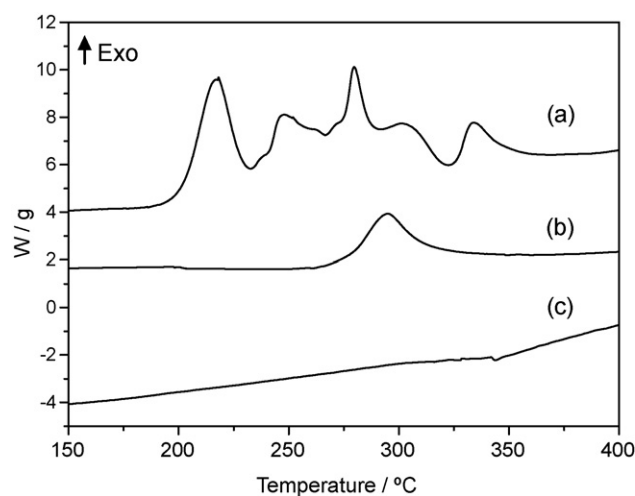
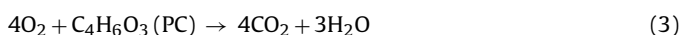
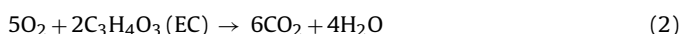
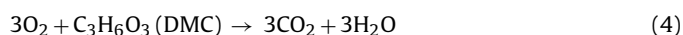
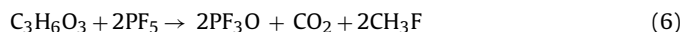


Fig. 2. DSC curves of (a) cathode materials wetted with electrolyte, (b) electrolyte alone, and (c) cathode materials without electrolyte.



From DSC profiles and high-temperature XRD analysis of Li_{0.49}CoO₂ and the electrolyte mixture, Yamaki et al. [5] suggested that the electrolyte combustion is triggered at 230 °C. The observation of peaks for H₂O and CO₂ starting at 240 °C strongly supports this suggestion.

Above 290 °C, the amount of CO₂ increases dramatically, which appears to be associated with decomposition of the electrolyte. The CO₂ is one of the products from the decomposition, and the DSC curve of electrolyte shows an exothermic peak at 295 °C (Fig. 2). The following reaction processes have been proposed [12–17] for the decomposition.



where PEO is the polyethylene oxide and PPO is the polypropylene oxide. The amount of electrolyte involved in the combustion process is only a small portion of the total amount. The quantity of residual electrolyte can be estimated by using Eqs. (1)–(4). The maximum amount of O₂ released from the reduction of 4 mg Li_xCoO₂ is about 0.011 mmol (=0.004 × 3/(12 × 94.5)) from Eq. (1), which is only 8% of the amount of O₂ required for the combustion of 4 mg of EC/PC/DMC electrolyte (0.13 mmol = 0.004 × 0.3 × 2.5/88 + 0.004 × 0.05 × 4/102 + 0.004 × 0.65 × 3/90). Therefore, only 8% of the total electrolyte is involved in the combustion process, and 92% remains after the combustion. Decomposition of the residual electrolyte may produce more CO₂ than combustion of the electrolyte.

The DSC curves between 150 and 400 °C for dry cathode materials without electrolyte, electrolyte alone and cathode materials wetted with electrolyte are presented in Fig. 2. The DSC results for dry cathode materials or electrolyte are very different from that for cathode materials wetted with electrolyte. The DSC curve for dry cathode materials does not reveal any sharp exothermic peak over the examined temperature range; DSC measurements for dry cathode materials are reproducible. Considering the reduction of Li_xCoO₂ observed by TPD-MS and XRD, the enthalpy change in the reduction appears to be small. Only one exothermic peak is found over the temperature range of the DSC curve for the electrolyte alone. This is related to the decomposition of electrolyte, as men-

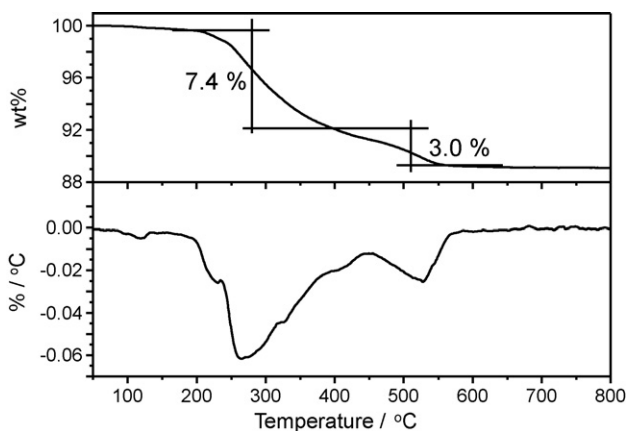


Fig. 3. TG and first-derivative curves of cathode materials.

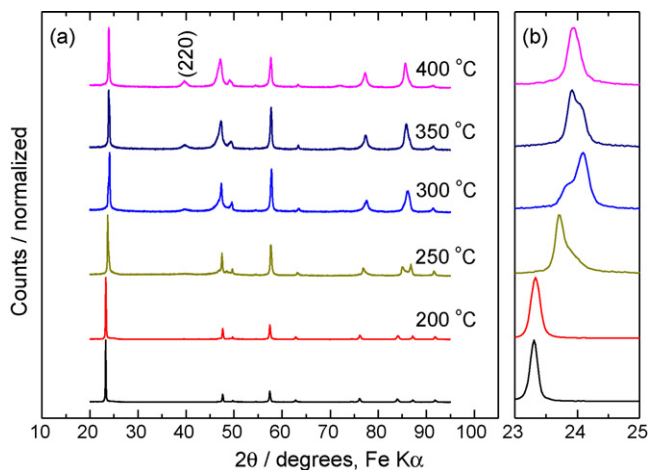


Fig. 4. (a) XRD patterns of cathode materials before heating, and heated to 200, 250, 300, 350 and 400 °C with Fe K α radiation. (b) XRD patterns in 2θ range of 23–25° in detail.

tioned before [15]. By contrast, the DSC curve of cathode materials wetted with electrolyte reveals several exothermic peaks (Fig. 2). The first of these peaks starts at 200 °C, which is similar to the observation in the O₂ TPD–MS curve. The origin of this peak in the DSC is not evident, however, because an exothermic peak is not observed at 200 °C in the DSC curves for the dry cathode materials. Yamaki et al. [5] suggested that the first peak starting near 190 °C in the DSC of Li_{0.49}CoO₂ with electrolyte is ascribed to the decomposition of solvents due to an active cathode surface caused by the reduction of Li_{0.49}CoO₂. To understand the decomposition of solvent, ongoing studies are being carried out with GC–MS. The second exothermic peak starting near 240 °C is due to electrolyte combustion caused by O₂ released from the reduction of Li_xCoO₂ since H₂O and CO₂ are observed from 240 °C with TPD–MS. One or both of the other peaks in the DSC curve may be related to the decomposition of the remaining electrolyte from the electrolyte combustion.

The TGA curve for cathode materials in the temperature range of 70–800 °C is given in Fig. 3. Weight loss starts near 200 °C, which is in good agreement with the observation of O₂ in the TPD–MS and an

exothermic peak in the DSC. The total weight loss amounts to 7.4% at 400 °C and this includes the weight loss due to the decomposition of PVdF (1.0 wt%). The weight loss from only Li_xCoO₂ in this step is 6.4%. The estimated weight loss due to the reduction of Li_xCoO₂ is calculated to be 5.4% from Eq. (1).

XRD patterns of cathode materials heated to 200, 250, 300, 350 and 400 °C are presented in Fig. 4, together with that of cathode materials before heating (or pristine cathode materials). Data in the 2θ range of 23–25° are shown in detail in Fig. 4(b) and reveal clearly a gradual change in the structure with increasing temperature. The XRD pattern of the cathode materials heated to 200 °C is very similar to that of pristine cathode materials except the increase in diffraction peak widths. The diffraction peak of Co₃O₄ (2 2 0) near 39.63° is very weak in the XRD pattern for the cathode materials heated to 250 °C. The peak becomes more prominent with increasing temperature. The Li_xCoO₂ (0 0 3) peak of pristine cathode materials shifts towards a high angle with a shoulder on the high-angle side when heated to 250 °C. This indicates partial reduction of charged Li_xCoO₂. Two Li_xCoO₂ (0 0 3) peaks are observed for samples heated to 300 and 350 °C. The two peaks merge into one when the sample is heated at 400 °C and this agrees with the completion of the reduction of Li_xCoO₂ observed in TPD–MS.

4. Conclusions

The TPD–MS technique has been adopted to investigate thermal reactions between charged Li_xCoO₂ and the electrolyte. Direct observations of O₂, H₂O and CO₂ evolved from the reactions assist in understanding the reaction mechanisms. The O₂ peak in TPD–MS, the weight loss in TGA and the structural change in XRD clearly show that the reduction of Li_xCoO₂ is triggered at 190 °C, and completed at 400 °C. Electrolyte combustion is observed to begin at 240 °C, which is supported by the occurrence of H₂O and CO₂ peaks in TPD–MS curves along with an exothermic peak in DSC. The dramatic increase in CO₂ amount at 290 °C indicates that decomposition of electrolyte takes place at this temperature.

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