

# Thermal stability of electrolytes with $\text{Li}_x\text{CoO}_2$ cathode or lithiated carbon anode

Jun-ichi Yamaki<sup>\*</sup>, Yasunori Baba, Noriko Katayama, Hideyasu Takatsuji,  
Minato Egashira, Shigeto Okada

*Institute of Advanced Material Study, Kyushu University, Kasuga Koen 6-1, Kasuga 816-8580, Japan*

## Abstract

The thermal stability of electrolytes with  $\text{Li}_x\text{CoO}_2$  cathode or lithiated carbon anode was reviewed including our recent results. From our experiments, it was found that  $\text{Li}_x\text{CoO}_2$ , delithiated by a chemical method using  $\text{H}_2\text{SO}_4$  showed two exothermic peaks, one beginning at 190 °C and the other beginning at 290 °C. From high-temperature XRD, it was found that the first peak, from 190 °C, was the phase transition from a monoclinic ( $R\text{-}3m$ ) to a spinel structure ( $Fd\bar{3}m$ ). The spinel structure  $\text{Li}_x\text{CoO}_2$  showed a very small cycling capacity. Probably, cation mixing was induced by the heat treatment. The DSC measurements of  $\text{Li}_{0.49}\text{CoO}_2$  with 1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$  showed two exothermic peaks. The peak starting at 190 °C probably resulted from the decomposition of solvent due to an active cathode surface, and the peak starting at 230 °C was electrolyte oxidation caused by released oxygen from  $\text{Li}_{0.49}\text{CoO}_2$ . From DSC profiles of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  and 1 M PC electrolytes with various Li salts, it was found that the inhibition effect of the surface reaction starting at 190 °C was large when  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ , and  $\text{LiClO}_4$  were used.

The thermal stability of electrochemically lithiated graphite with 1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$  and PVdF-binder has been investigated. DSC revealed a mild heat generation starting from 130 °C with a small peak at 140 °C. The mild heat generation continued until a sharp exothermic peak appeared at 280 °C. The lithiated graphite with the electrolyte without PVdF-binder did not show the small peak at 140 °C. The peak at 140 °C seems to be caused by the reaction (the solid electrolyte interphase (SEI) formation) of the electrolyte and lithiated graphite, which surface is covered by poly(vinylidene fluoride) (PVdF)-binder without formation of SEI at a lower temperature.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Li-ion batteries; Chemical delithiation;  $\text{Li}_x\text{CoO}_2$ ; Lithiated graphite; 1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$ ; Thermal stability

## 1. Introduction

Recently, demand for Li-ion batteries has increased enormously as a power source for portable devices, due to their excellent characteristics of high voltage, high energy density, and light weight. Large Li-ion batteries are expected to be used in EV and similar applications in the future. However, the larger batteries have a serious safety problem: the risk of explosion resulting from either shorting or an external temperature increase [1–6]. Therefore, safety improvements to the large batteries are indispensable for their practical application. It is generally believed that the “thermal runaway” of Li cells occurs if the heat output exceeds the thermal diffusion [2,5]. Therefore, it is difficult to design large cells that can pass a safety-test criteria.

The thermal stability or the thermal behavior of Li-ion cells has been investigated extensively by DSC or accel-

erating rate calorimetry (ARC) [7–11] in order to reduce the heat output. The thermal behavior of lithium nickel oxide [4,12–16,18], lithium manganese oxide [4,12,18,20], and lithium cobalt oxide [4,12,17–21], as the cathode materials of the Li-ion batteries, has been investigated.  $\text{Li}_x\text{CoO}_2$  is a widely used cathode material for Li-ion cells. However, the thermal behavior of  $\text{Li}_x\text{CoO}_2$  is not clear. MacNeil et al. reported that the first reaction that occurs when  $\text{Li}_x\text{CoO}_2$  is heated in electrolyte can be modeled using a simple kinetic model that describes an auto-catalytic reaction [19], though they did not attempt to identify the chemical reaction. Recently, they found that the reaction of  $\text{Li}_{0.5}\text{CoO}_2$  with EC + DEC solvent initiates at temperatures as low as 130 °C, which is much lower than the decomposition temperature of  $\text{Li}_{0.5}\text{CoO}_2$  itself [21]. Oxygen loss from the material according to the reaction  $\text{Li}_{0.5}\text{CoO}_2 \rightarrow 0.5\text{LiCoO}_2 + (1/6)\text{Co}_3\text{O}_4 + (1/6)\text{O}_2$  occurs at temperatures above 200 °C [18]. MacNeil et al. also reported that the amount of reaction heat generated by the reaction of  $\text{Li}_x\text{CoO}_2$  with electrolyte is independent of the

<sup>\*</sup> Corresponding author. Fax: +81-92-583-7790.

E-mail address: [yamaki@cm.kyushu-u.ac.jp](mailto:yamaki@cm.kyushu-u.ac.jp) (J.-i. Yamaki).

electrode/electrolyte mass ratio [20], though their experiment is a rough estimation because they cannot remove the electrolyte, carbon black, and PVdF from the electrode when they measured the weight of the electrode.

The thermal stability of carbon anodes in an electrolyte is controlled by a solid electrolyte interphase (SEI) formed on the lithiated carbon anode. Edstrom et al. [22] reported that thermal breakdown of the SEI when using  $\text{LiBF}_4$  electrolytes starts at  $58^\circ\text{C}$  (Graphite,  $\text{LiBF}_4/\text{EC} + \text{DMC}$ ) [23], while use of  $\text{LiPF}_6$  shifts the breakdown temperature to  $102^\circ\text{C}$  [7,8]. However, Zhang et al. [12] suggested that the exothermic reaction (MCMB,  $\text{LiPF}_6/\text{EC} + \text{DMC}$ ) at around  $130^\circ\text{C}$  is related to the surface passivation of the lithiated carbon materials. von Sacken et al. [8] also proposed a reaction model based on a simple heterogeneous reaction between the electrolyte solvent and the lithiated carbon, where the reaction produces a passivating film on the carbon surface. Richard and Dahn [7] reported that the initial form of the self-heating rate profile at around  $100^\circ\text{C}$  (MCMB,  $\text{LiPF}_6/\text{EC} + \text{DEC}$ ) was a result of the conversion of metastable solid electrolyte interphase (SEI) components to stable SEI components. The question thus arises as to what is the real reason of the exothermic reaction at around  $100^\circ\text{C}$ .

In this paper, we would like to introduce our recent study on thermal stability of electrolytes with  $\text{Li}_x\text{CoO}_2$  cathode [24,25] or lithiated carbon anode [26].

## 2. Experimental

$\text{LiCoO}_2$  was prepared by firing a mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$  at  $850^\circ\text{C}$  for 24 h following firing at  $500^\circ\text{C}$  for 5 h in air [27]. Chemical delithiation of  $\text{LiCoO}_2$  was carried out by stirring a suspension of 5 g of  $\text{LiCoO}_2$  in 250 ml of 0.5 M  $\text{H}_2\text{SO}_4$  from 1 to 24 h [27,28]. The product was filtered and washed several times with acetone, and dried at  $80^\circ\text{C}$  in a vacuum. The Li content of  $\text{Li}_x\text{CoO}_2$  was analyzed by atomic absorption spectroscopy (HITACHI, Z-5000). The electrochemical property of delithiated  $\text{Li}_x\text{CoO}_2$  was tested by measuring the quasi-open circuit voltage (QOCV). The QOCV was measured after the cell had been standing for about 1 h at zero current flow for every 0.025 Li/mol at a discharge current of  $0.2\text{ mA/cm}^2$ . The cathode disk contained 70 wt.%  $\text{Li}_{0.49}\text{CoO}_2$ , 25 wt.% acetyleneblack (Denki Kagaku Co. Ltd.), and 5 wt.% polytetrafluoroethylene (Polyflon TFE F-103, Daikin Industry Ltd.). The  $\text{Li}_{0.49}\text{CoO}_2$  was characterized by high-temperature X-ray diffraction with  $\text{Cu K}\alpha$  radiation (Rigaku, RINT-2500).

A coin cell with a graphite anode and a counter electrode of Li metal sheet was used in all experiments. Anode electrode used in this study were prepared by mixing 95 wt.% of natural graphite (LF-18D from Chuestu Graphite) with 5 wt.% of poly(vinylidene fluoride) (PVdF)-binder (KF#9100 from Kureha Chemical) dissolved in 1-methyl-2-pyrrolidinone (NMP). The slurry was coated

onto a 0.1 mm thick copper current collector. The electrodes were then dried for 12 h at  $70^\circ\text{C}$  in a vacuum oven. Graphite anodes without PVdF-binder were fabricated by compressing the graphite powder onto the copper current collector using an oil hydraulic press at about 3 t.

The cells were cycled between 0.01 and 1.5 V with a relaxation period of 60 min at the end of charge, at a constant current of  $0.2\text{ mA/cm}^2$ . After two cycling in this condition, the cells were charged to 0 V with the time limit of 372 mAh/g to obtain a full charged anode.

The thermal stability of those cathode and anodes with or without 1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$  (1:1 (v/v)) electrolyte was monitored by a TG-DSC apparatus (Rigaku Thermo plus TG8110, Rigaku, Japan). Each sample for TG-DSC measurement was packed in the stainless steel pan. All of the DSC experiments were carried out at a heating rate of  $5^\circ\text{C/min}$ .

## 3. Result and discussion

### 3.1. Chemically delithiated $\text{Li}_x\text{CoO}_2$

The Li content of chemically delithiated  $\text{Li}_x\text{CoO}_2$  decreased as reaction time increased. The minimum  $x$  value in  $\text{Li}_x\text{CoO}_2$  was 0.49 at a reaction time of 24 h. QOCV profiles of chemically and electrochemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  during the first discharge was similar in both cases. The difference was probably a result of proton intercalation into the chemically delithiated  $\text{Li}_x\text{CoO}_2$  during the treatment with  $\text{H}_2\text{SO}_4$  [27,28]. The thermal behavior (DSC) of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  with acetyleneblack and polytetrafluoroethylene was almost the same as the DSC profile obtained from electrochemical delithiated  $\text{Li}_{0.49}\text{CoO}_2$  (Fig. 1).

DSC measurements of chemically delithiated  $\text{Li}_x\text{CoO}_2$  ( $x = 0.49, 0.57, 0.64, 0.75, 0.84, \text{ and } 0.94$ ) alone, without any other components were performed. The profiles show gradual exothermal heat between  $190$  and  $400^\circ\text{C}$ . The temperature of the exothermic reaction shifted to the low side, and heat flow increased as Li content decreased.  $\text{Li}_{0.49}\text{CoO}_2$  showed two main peaks at  $230$  and  $320^\circ\text{C}$ , corresponding self-heating temperatures of electrochemically delithiated  $\text{Li}_{0.5}\text{CoO}_2$  from ARC at  $140$  and  $240^\circ\text{C}$  reported by MacNeil and Dahn [21]. The exothermic heats of  $\text{Li}_{0.49}\text{CoO}_2$  at the first peak and the second peak are about 50 and 10 J/g based on cathode weight, respectively. The exothermic heats of  $\text{Li}_x\text{CoO}_2$  at  $x = 0.53, 0.64, 0.75, 0.84, \text{ and } 0.94$  were about 40, 30, 20, 20, 10 J/g, respectively.

From TG measurement of chemically delithiated  $\text{Li}_x\text{CoO}_2$  alone, the derivative,  $dM/dT$ , of  $\text{Li}_{0.49}\text{CoO}_2$  showed sudden weight loss at  $230^\circ\text{C}$ , which is a similar tendency to that of electrochemically delithiated  $\text{Li}_{0.4}\text{CoO}_2$  with carbon black reported by Dahn et al. [18]. Oxygen loss from the material according to the reaction  $\text{Li}_{0.5}\text{CoO}_2 \rightarrow 0.5\text{LiCoO}_2 + (1/6)\text{Co}_3\text{O}_4 + (1/6)\text{O}_2$  occurs at temperatures

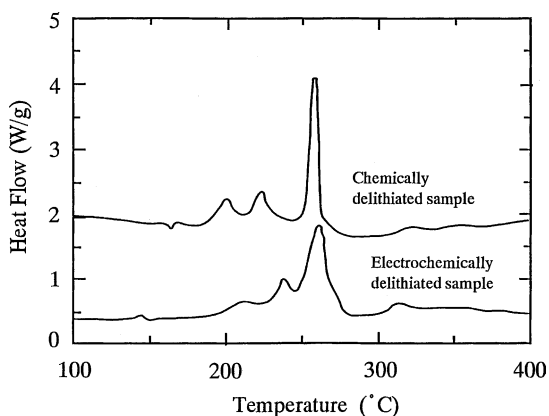


Fig. 1. Thermal behavior of chemically delithiated and electrochemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  with acetyleneblack, polytetrafluoroethylene and electrolyte (1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$ ).

above 200 °C [18]. The exothermic reactions occurred at the same temperature as the onset temperature of weight loss measured by TG, except for the case of  $\text{Li}_{0.49}\text{CoO}_2$ . Therefore, the exothermic reaction of  $\text{Li}_{0.49}\text{CoO}_2$  starting at 190 °C can be another reaction or phase transition, without cathode weight change.

High-temperature XRD profiles of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  was undertaken. The structure at room temperature was identified as a monoclinic ( $R-3m$ ) structure, which is the same structure of electrochemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  [18,29]. The X-ray pattern of  $\text{Li}_{0.49}\text{CoO}_2$  at 220 °C shows a spinel structure ( $Fd3m$ ). These experimental results suggest that the exothermic reaction starting at 190 °C was probably caused by the phase transition from the layered rocksalt to the spinel structure. The result at 350 °C is consistent with the result of electrochemically delithiated  $\text{Li}_{0.4}\text{CoO}_2$  [18].

As shown in Fig. 2, the spinel like  $\text{Li}_{0.49}\text{CoO}_2$  could not insert and de-insert Li ions. Therefore, the material is probably cation mixed spinel.

DSC measurements of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  and 3  $\mu\text{l}$  electrolyte (1 M  $\text{LiPF}_6/\text{EC}/\text{DMC}$ ) were performed (Fig. 3). The cathode weight was altered from 0 to 3.9 mg. There were mainly two peaks, one starting at 190 °C and the other starting at 230 °C. The peak starting at 190 °C probably resulted from the decomposition of solvent due to an active cathode surface, and the peak starting at 230 °C was electrolyte oxidation caused by released oxygen from  $\text{Li}_{0.49}\text{CoO}_2$ .

The exothermic heat from 190 to 230 °C based on cathode weight was  $420 \pm 120$  J/g, and that from 230 to 300 °C was  $1000 \pm 250$  J/g. The exothermic reaction of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  with EC/DMC without  $\text{LiPF}_6$  started at 170 °C and reached a broad peak at 220 °C. In this case, the exothermic heat based on cathode weight was about 1000 J/g, which is larger than the exothermic heat of electrolyte (with Li salt;  $420 \pm 120$  J/g). MacNeil et al. concluded that the reaction is inhibited in the presence of

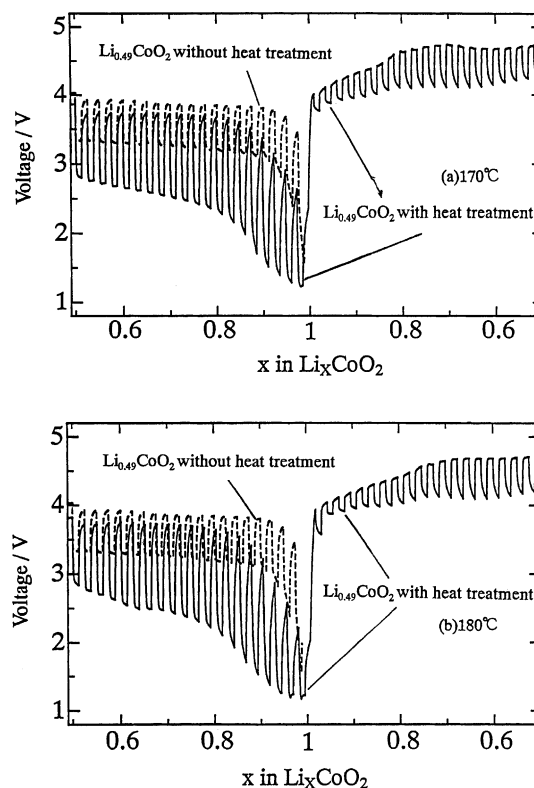


Fig. 2. QOCV profiles of delithiated  $\text{Li}_{0.49}\text{CoO}_2$  after heating to (a) 170 °C and (b) 180 °C.

electrolyte because of a coating of the electrode particles by salt decomposition products [21].

Fig. 4 shows DSC profiles of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  and 1 M PC electrolytes with various Li salts (1  $\mu\text{l}$ ). The inhibition effect of the surface reaction was large when  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ , and  $\text{LiClO}_4$  were used.

### 3.2. Lithiated graphite

Graphite anodes with and without containing PVdF-binder were made. The third discharge capacity of those

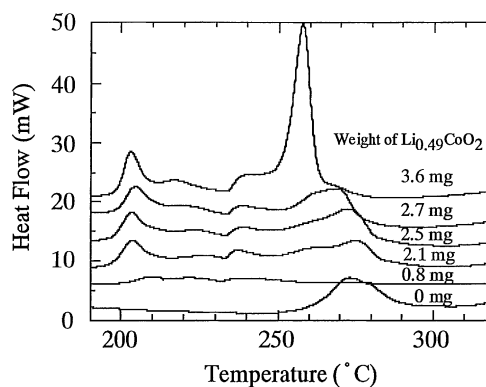


Fig. 3. DSC profiles of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  with electrolyte for various cathode weight in 3  $\mu\text{l}$  electrolyte [24].

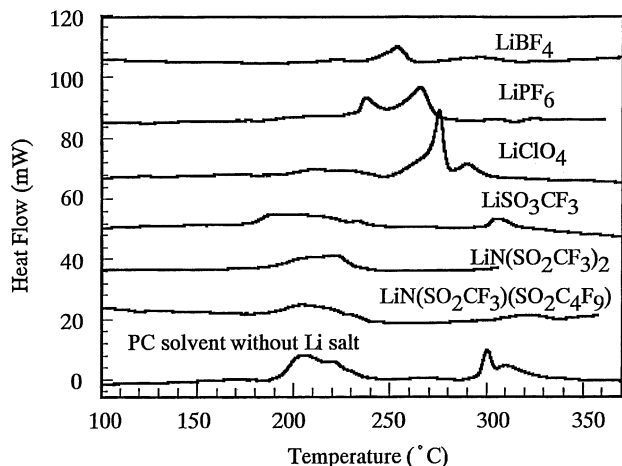


Fig. 4. DSC profiles of chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  and 1 M Li salt PC electrolyte [25].

graphite anodes are nearly 300 mAh/g. Thus, the lithiated PVdF free anode is used for DSC measurement.

Fig. 5 shows DSC curves. The washing/vacuum-drying procedure for sample (d) is performed to remove the electrolyte. The heat flow is based on the total weight of the sample. The sample (a) shows a mild heat generation started

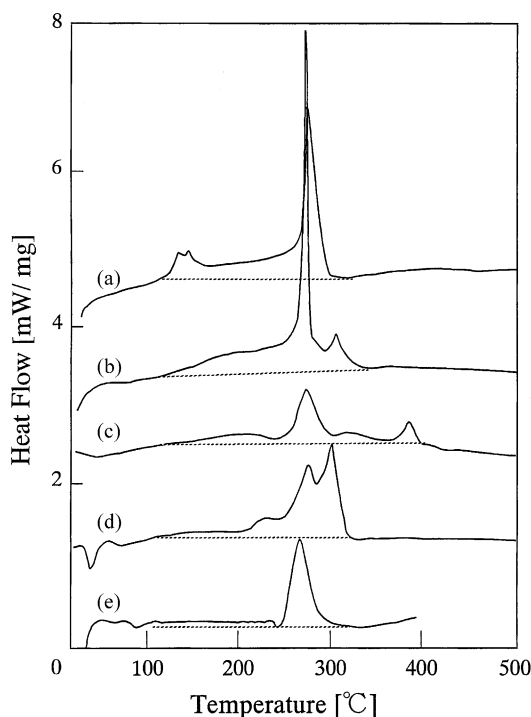


Fig. 5. DSC curves of (a) the fully lithiated graphite with the electrolyte and PVdF (the usual graphite anode); (b) the fully lithiated graphite with the electrolyte (the anode made using an oil hydraulic press); (c) the fully delithiated graphite with the electrolyte and PVdF (the usual graphite anode); (d) the fully lithiated graphite with PVdF (the usual graphite anode) with a washing/vacuum-drying procedure; and (e) the electrolyte (1 M  $\text{LiPF}_6/\text{EC} + \text{DMC}$ ) [26].

from 130 °C with a small peak at 140 °C. The mild heat generation continued until a sharp exothermic peak appeared at 280 °C. The lithiated graphite with the electrolyte without PVdF-binder (the sample (b)) did not show the small peak at 140 °C. Also, the sample (c) and (d) did not show the small peak at 140 °C. Therefore, three components of PVdF-binder, the lithiated graphite, and the electrolyte are necessary to appear the small peak at 140 °C. The small peak at 140 °C seems to be caused by the reaction (SEI formation) of the electrolyte and lithiated graphite, which surface is covered by PVdF-binder without formation of SEI at a lower temperature. PVdF-binder covers some surface area of graphite when the anode is fabricated. After charging, graphite particles are lithiated and SEI is formed on the surface of the graphite particles. However, covered area of the graphite particles by PVdF-binder do not form SEI because PVdF-binder protect the contact of the lithiated graphite particles and the electrolyte at room temperature. The protection effect of PVdF-binder changes to be not sufficient at elevated temperature. Probably, swelling of PVdF-binder by the electrolyte occurs at elevated temperature. Okamoto et al. [30] reported that the small peak at 140 °C disappears after aging graphite anode (with PVdF) with  $\text{LiPF}_6/\text{EC} + \text{DMC} + \text{diethyl carbonate (DEC)}$  electrolyte. A similar experimental result was obtained using our materials. Then SEI is formed at the covered area of the graphite particles by PVdF-binder during the aging.

DSC measurements were carried out for PVdF and PVdF with Li metal. PVdF begins to decompose at 400 °C. PVdF with Li metal shows exothermic reaction from 290 °C. Therefore, a peak at 390 °C in Fig. 5c is decomposition of PVdF. A peak at 300 °C in Fig. 5d is reaction of PVdF with the lithiated graphite.

A mild heat generation continued from 130 °C until a sharp exothermic peak appeared at 280 °C for the samples (a) and (b) in Fig. 5. As postulated by von Sacken et al. [8], this mild heat generation is caused by a simple heterogeneous reaction between the electrolyte solvent and the lithiated carbon, where the reaction produces a passivating film on the carbon surface. In other words, the mild heat generation arises from the reaction of lithiated carbon with the electrolyte to form a new SEI. The lithiated graphite and electrolyte can react if the electrolyte permeates the SEI to reach the lithiated graphite surface. Therefore, the samples (c) (delithiated graphite) and (d) (without the electrolyte) in Fig. 5 show very small heat generation in this region compared with the DSC curves of the samples (a) and (b). The very small heat generation may be caused by reactions of components in SEI.

#### 4. Conclusion

Chemically delithiated  $\text{Li}_{0.49}\text{CoO}_2$  exhibited an exothermic reaction beginning at 190 °C, at which temperature oxygen evolution does not occur. From high-temperature

XRD, it was found that the exothermic peak from 190 °C is caused by the structural change from layered *R-3m* to spinel (*Fd3m*).

The reaction of  $\text{Li}_{0.49}\text{CoO}_2$  with the electrolyte mainly exhibited two exothermic peaks. The peak starting at 190 °C probably reflected the decomposition of solvent due to an active cathode surface, and the peak starting at 230 °C was electrolyte oxidation caused by oxygen released from  $\text{Li}_{0.49}\text{CoO}_2$ .

The lithiated graphite with electrolyte showed several exothermic peaks. The small peak at 140 °C is caused by the reaction (SEI formation) of the electrolyte and lithiated graphite, which surface is covered by PVdF-binder without formation of SEI at a lower temperature. A mild heat generation continued from 130 °C until a sharp exothermic peak appeared at 280 °C comes from the reaction of lithiated carbon with the electrolyte to form new SEI. A sharp exothermic peak at 280 °C is a direct reaction of the lithiated graphite and electrolyte caused by a break down of SEI.

## References

- [1] S. Tobishima, Y. Sakurai, J. Yamaki, J. Power Sources 68 (1997) 455.
- [2] S. Tobishima, J. Yamaki, J. Power Sources 81–82 (1999) 882.
- [3] K. Kitoh, H. Nemoto, J. Power Sources 81–82 (1999) 887.
- [4] Ph. Biensan, B. Simon, J.P. Peres, A. de Guibert, M. Broussely, J.M. Bodet, F. Pertont, J. Power Sources 81–82 (1999) 906.
- [5] S. Tobishima, K. Takei, Y. Sakurai, J. Yamaki, J. Power Sources 90 (2000) 188.
- [6] S. Passerini, F. Coustier, B.B. Owens, J. Power Sources 90 (2000) 144.
- [7] M.N. Richard, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 2068.
- [8] U. von Sacken, E. Nodwell, A. Sundher, J.R. Dahn, J. Power Sources 54 (1995) 240.
- [9] U. von Sacken, J.R. Dahn, Solid State Ionics 69 (1995) 284.
- [10] B.M. Way, U. von Sacken, Abstract 830, p. 1020, The Electrochem. Soc. Meeting Abstracts, vol. 96, no. 2, San Antonio, TX, 6–11 October 1996.
- [11] H. Maleki, G. Deng, A. Anani, J. Howard, J. Electrochem. Soc. 146 (1999) 3224.
- [12] Z. Zhang, D. Fouchard, J.R. Rea, J. Power Sources 70 (1998) 16.
- [13] J. Cho, H. Jung, Y.C. Park, G. Kim, H.S. Lim, J. Electrochem. Soc. 147 (2000) 15.
- [14] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, Solid State Ionics 109 (1998) 295.
- [15] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, J. Electrochem. Soc. 144 (1997) 3117.
- [16] W. Li, J.C. Currie, J. Wolstenholme, J. Power Sources 68 (1997) 565.
- [17] Y. Sato, K. Kanari, K. Takano, T. Masuda, Thermochim. Acta 296 (1997) 75.
- [18] J.R. Dahn, E.W. Fuller, M. Obrovac, U. von Sacken, Solid State Ionics 69 (1994) 265.
- [19] D.D. MacNeil, L. Christensen, J. Landucci, J.M. Paulsen, J.R. Dahn, J. Electrochem. Soc. 147 (2000) 970.
- [20] D.D. MacNeil, T.D. Hatchard, J.R. Dahn, J. Electrochem. Soc. 148 (2001) A663.
- [21] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 148 (2001) A1205.
- [22] K. Edstrom, A.M. Andersson, A. Bishop, L. Fransson, J. Lindgren, A. Hussenius, J. Power Sources 97–98 (2001) 87.
- [23] Y. Baba, S. Okada, J. Yamaki, Solid State Ionics 148 (2002) 311–316.
- [24] N. Katayama, T. Kawamura, Y. Baba, J. Yamaki, J. Power Sources 109 (2002) 321.
- [25] J. Yamaki, H. Takatsuji, T. Kawamura, M. Egashira, Solid State Ionics 148 (2002) 241.
- [26] A.M. Andersson, K. Edstrom, J.O. Thomas, J. Power Sources 81–82 (1999) 8.
- [27] R. Gupta, A. Manthiram, J. Solid State Chem. 121 (1996) 483.
- [28] E. Zhecheva, R. Stoyanova, J. Solid State Chem. 109 (1994) 47.
- [29] G.G. Amatucci, J.M. Tarascon, L.C. Klein, J. Electrochem. Soc. 143 (1996) 1114.
- [30] A. Okamoto, T. Sasaki, S. Komatsu, K. Nakamitsu, H. Tsukamoto, M. Mizutani, GS News Tech. Rep. 56 (1999) 18.