

DSC study on the thermal stability of solid polymer electrolyte cells

C. Capiglia^{a,*}, J. Yang^b, N. Imanishi^a, A. Hirano^a, Y. Takeda^a, O. Yamamoto^c

^aDepartment of Chemistry, Mie University, Kamihama-cho, Tsu, Mie 514-8507, Japan

^bShanghai Institute of Microsystem and Information Technology, Shanghai, China

^cGenesis Research Institute, INC, Nagoya, Japan

Abstract

A novel Li-ion polymer battery (Li-IonPB) based on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as a cathode and an alternative composite anode (CA) is proposed for future application in hybrid electric vehicles (HEV). A micro-Li-ion polymer cell is prepared in situ inside the differential scanning calorimetry (DSC) sample pan, and the exothermic heat development is compared with that of the micro-lithium-solid polymer electrolyte cell. The thermal decomposition of both cells is further investigated from a qualitative point of view.

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

Keywords: Solid polymer electrolyte battery; Composite polymer electrolyte; Lithium-solid polymer battery; Composite anode; Thermal stability

1. Introduction

Li-ion batteries are widely used today as power sources for portable electronic devices. However, the cost and the presence of flammable solvent are still limiting factors, which hinder their high-power applications such as the hybrid electric vehicle (HEV) [1]. As the HEV market is expected to expand in the near future, new types of high-power batteries with high safety are needed to fit the requirement of car automakers. With this in mind we propose a novel Li-ion polymer battery (Li-IonPB) based on an alternative anode containing $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ and SnSb, and a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode. The use of polymer electrolyte in the cell presents several advantages; it allows obtaining a “plastic” battery, which can be made in any shape and size fitting the demand and requirements of automakers, and is easy to make by means of the present know-how on the processing of polymers. In addition, the new design of polymers may allow one day the control of the ion species migration and result in selective and highly Li-ion conductors (see, for example, [2,3]).

In the present work, the cell proposed is based on the common polyethylene oxide (PEO) and shows good cycling performance as well as good thermal stability (up to 300 °C). The investigation by means of differential scanning calorimetry (DSC) aims at the thermal stability of the cell and the cell components. A comparison of the exothermic heat

development between a micro-Li-ion polymer cell and a micro-lithium-solid polymer cell is performed.

2. Experimental

2.1. Electrode preparation

Composite polymer electrolyte (CPE), composite anodes (CAs) and composite cathode (CC), were prepared in a dry box.

- CPE; the proper amount of salt $\text{Li}(\text{CF}_3\text{SO}_2)_2$ [(Imide), Aldrich], and BaTiO_3 , 0.1 μm (Sakai Chemical Japan) were mixed in a mortar, then PEO (600,000 M_w from Aldrich, previously treated under vacuum for 2 h) was added and powders were mixed for about 2–5 min in order to obtain a homogeneous mixture. The powder mixture was sandwiched between two Mylar sheets, heated at 80 °C and pressed for ~1 min at 10 MPa. The resulting CPE with a composition of PEO_{18} –Imide (molar ratio of oxygen/lithium = 18/1) plus 7 wt.% of BaTiO_3 0.1 μm , was stored in a glass bottle inside the dry box.
- CA was prepared by mechanical mixing of SnSb, $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$, Ni, PEO, and polyethylene (PE, mp 144 °C), then the homogeneous powder was pressed at several MPa. The resulting CAs with a composition of CA1: 10 wt.% PE, 8 wt.% Ni, 33 wt.% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ and 49 wt.% SnSb; CA2: 9% PEO, 3% Imide, 8% PE, 10% Ni, 45.5% SnSb and 24.5% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$; CA3:

* Corresponding author. Tel.: +81-59-231-9420; fax: +81-59-231-9478.
E-mail address: capigliaaudio@yahoo.com (C. Capiglia).

15% PEO, 5% Imide, 10% PE, 15% Ni, 55% SnSb; and CA4: 82% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$, 18% PEO were stored in hermetic sealed glass bottle inside the dry box.

When CA was used for cycling test, the powder mixture was pressed on stainless steel grid of 280 mesh (used as a current collector) [4], in this case CA1 was used as composite anode. When electrodes were prepared for DSC testing the stainless steel grid was not employed. The DSC test of the micro-Li-ion polymer cell used a composite anode with composition CA1 while the DSC test of the composite anode itself employed compositions CA1, CA2, CA3 and CA4 as indicated in Table 1.

(c) CC was prepared by casting method on aluminium foil using acetonitrile as solvent. The CC film contains 52% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10% AB, 10% Imide and 28% PEO. The CC for DSC test was prepared by casting the film on a Teflon plate.

2.2. Measurements

2.2.1. Electrochemical measurements

Stainless steel cells were assembled in a dry box. Before the cycling test, they were preheated for 1 h at 80 °C in order to insure a good interface contact. The charge–discharge

Table 1
Summary of the qualitative investigation on the electrodes and the cells

Cell types and electrodes (DSC scanning speed)	Compositions	Capacity at 70 °C (mAh/g)	Peak T1 (onset 1)	Peak T2 (onset 2)	Peak T3 (onset 3)
Li-SPE ^a (5 °C min)	Cell composition (a) Cathode 52% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10% AB, 10% Imide, 28% PEO (b) Separator; PEO ₁₈ –Imide (c) Lithium Cut-off: 3.0–3.9 V, $I = 0.15 \text{ mA/cm}^2$	~130 vs. Lithium	54 (Endo) [Lithium]	174 (Endo) [Lithium]	304 (Eso)
Li-IonPB ^b (30 °C min)	Cell composition (a) Cathode 52% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10% AB, 10% Imide, 28% PEO (b) Polymer electrolyte; PEO ₁₈ –Imide (c) Anode; CA1 Cut-off: 2.2–3.7 V, $I = 0.15 \text{ mA/cm}^2$	~500 vs. lithium	64 (Endo) [PEO]	315 (Eso)	407 (Eso)
Cathode (30 °C min)	52% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, 10% AB, 10% Imide, 28% PEO Cut-off: 3.0–3.9 V, $I = 0.15 \text{ mA/cm}^2$	~130 vs. lithium	348 (Eso)		
Anode CA1 (30 °C min)	10% PE, 8% Ni, 33% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$, 49% SnSb Cut-off: 0.1–1.4 V, $I = 0.15 \text{ mA/cm}^2$	~500 vs. lithium	144 (Endo) [PE]	412 (Eso)	
Anode CA2 (30 °C min)	9% PEO, 3% Imide, 8% PE, 10% Ni, 45.5% SnSb, 24.5% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ Cut-off: 0.1–1.4 V, $I = 0.15 \text{ mA/cm}^2$	~600 vs. lithium	205 (Eso)		
Anode CA3 (30 °C min)	15% PEO, 5% IMIDE, 10% PE, 15% Ni, 55% SnSb		70 (Endo) [PEO]	144 (Endo) [PE]	439 (Eso)
Anode CA4 (30 °C min)	82% $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$, 18% PEO		69 (Endo) [PEO]	430 (Eso)	

^a The capacity is calculated on the cathode active material.

^b The capacity is calculated on the anode active material.

tests were performed at 70 °C with a current density of 0.15 mA/cm².

2.2.2. Differential scanning calorimeter

Rigaku Thermo plus 8230 was used for DSC measurements. The sample was inserted into a special designed stainless steel pan and hermetical sealed at 10 MPa pressure, which was kept in sealed glass bottle that was moved from dry box to the instrument. The selection of a stainless steel pan instead of a commonly used aluminium pan, was made in order to avoid a possible chemical reaction between lithium, when used, and aluminium.

The stainless steel sample pan was exposed to air only when transferring to the sample holder. α -Al₂O₃ was used as reference. Measurement conditions were set with scanning rate at 5 °C/min under N₂ flow 10 ml/min when the quantitative comparison between the micro-Li-ion polymer cell and the lithium-solid polymer cell was done. On the other hand, the condition for the qualitative comparison was 30 °C/min under 100 ml/min flow of N₂.

3. Results and discussion

3.1. Comparison between as-prepared Li-SPE and Li-IonPB

Fig. 1 shows the charge–discharge performance for a Li-SPE (a) and a Li-IonPB (see composition in Table 1). In case of Li-SPE the capacity is referred to the active material in the cathode while in case of Li-IonPB the capacity is referred to the active material in the anode. Both cells show good cycling performances.

For a comparison of thermal decomposition, two micro-cells with three stacked layers [CA1 (or Li)/CPE/CC] with the same compositions as the cycled cells were inserted into the DSC sample pan inside the glove box.

In order to make a similar quantitative comparison, the following rules were fixed for the DSC sample preparation:

- (1) The amount of lithium and CA were decided on basis of that capacity delivered from both anodes must be the same. The calculation was done with the assumption that 30% of lithium is utilised on practical cell when pure lithium is used as anode.
- (2) The weight ratio of anode/cathode was controlled according to the respective capacity.

The related calculations are shown in Table 2 and DSC results are displayed in Fig. 2. DSC data indicate that, for both cells, the thermal decomposition starts at about 300 °C. The Li-SPE data presents two small endothermic peaks centred at 65 and 180 °C related, respectively, to the melting of PEO and lithium, and a single exothermic peak starting at about 300 °C related to some thermal decomposition. DSC referred to Li-IonPB presents a small endothermic peak at

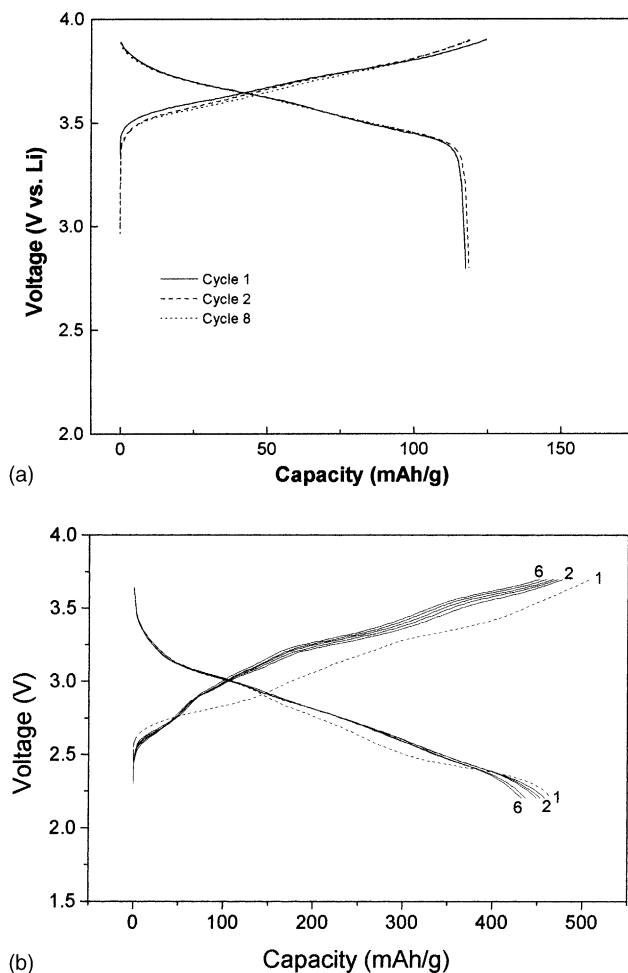


Fig. 1. (a) Charge and discharge profile for Li-SPE cell at 70 °C; (b) the first six cycle profiles for Li-IonPB cell at 70 °C.

65 °C related to PEO melting and, starting at 300 °C, a first followed by a second exothermic peak.

The heat developed during thermal decomposition was calculated from area interpolation of exothermic peaks. The ΔH for Li-SPE was 1284 J/g while for the Li-IonPB, the ΔH calculated from the two peaks interpolation was 675 J/g. The

Table 2
Calculation for the cell construction

Materials	Theoretical capacity (mAh/g)	Practical capacity (mAh/g)
LiNi _{0.8} Co _{0.2} O ₂	180	120
Li _{2.6} Co _{0.4} N + SnSb	900	580
Lithium	3862	1160 (30% ^c)
Lithium/CA	1160/(580 × 0.74 ^a) = 2.7	
CA/CC	(580 × 0.74 ^a)/(120 × 0.52 ^b) = 7	

^a 74% of active material in CA.

^b 52% of active material in CC.

^c 30% of lithium weight is effectively used for cycling of battery.

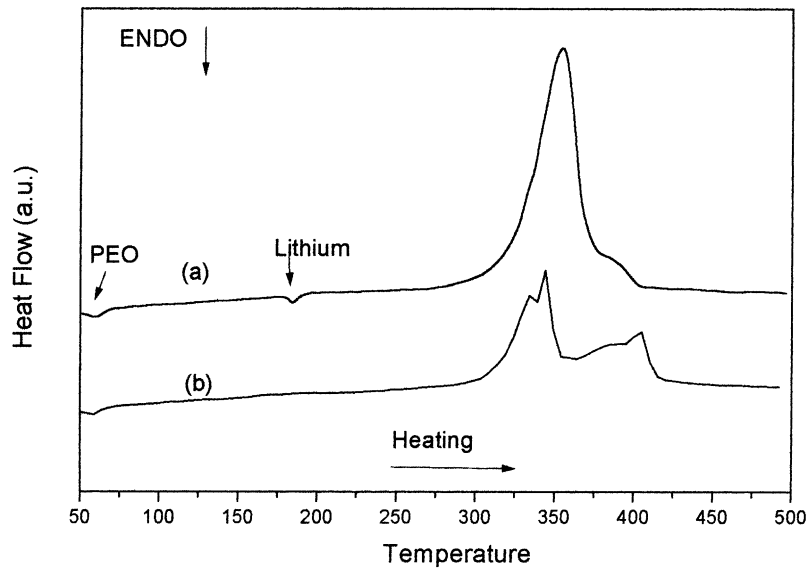


Fig. 2. DSC curves: scan rate 5 °C/min under N₂ flow 100 ml/min. (a) Li-SPE; (b) Li-IonPB.

former value is almost half of the heat developed by Li-SPE. The exothermic effect was further investigated from the qualitative point of view. The measurement fixed at 30 °C/min under 100 ml N₂/min would influence the shape of the peaks as well as the starting temperature. However, the high scanning rate reduces the possibility of the active materials to enter in contact with external atmosphere.

3.2. Thermal stability of as-prepared Li-IonPB

The Li-ion polymer cell presents one endothermic peak at about 64 °C related to melting of PEO, and two peaks

starting at 315° and 407 °C (as shown in Fig. 3a). In order to understand the origin of the first Li-IonPB exothermic peak, the DSC data of composite cathode (Fig. 3b), composite anode (Fig. 3c), and cathode powder with AB (Fig. 3d) are measured. The composite cathode shows an exothermic peak overlapping the first exothermic peak of the Li-IonPB cell, while the cathode powder with AB is stable in all temperature range. These data point out that first exothermic peak of the Li-IonPB cell is due to a reaction between the composite polymer electrolyte and the cathode material, as already reported in the literature by different authors [5]. The second Li-IonPB exothermic peak is attributed to the

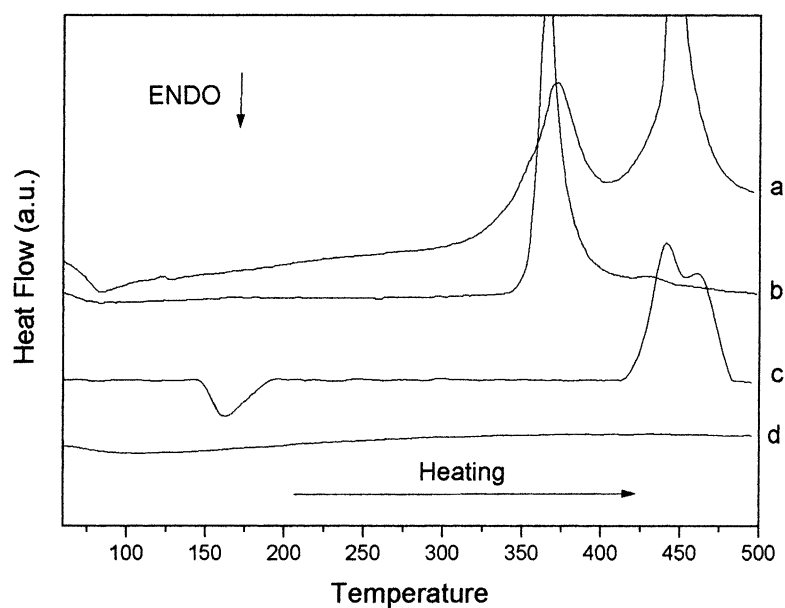


Fig. 3. DSC curves scan rate 30 °C/min under N₂ flow 100 ml/min. (a) Li-IonPB; (b) composite cathode; (c) composite anode CA1; (d) LiNi_{0.8}Co_{0.2}O₂ 90% and AB 10% powder.

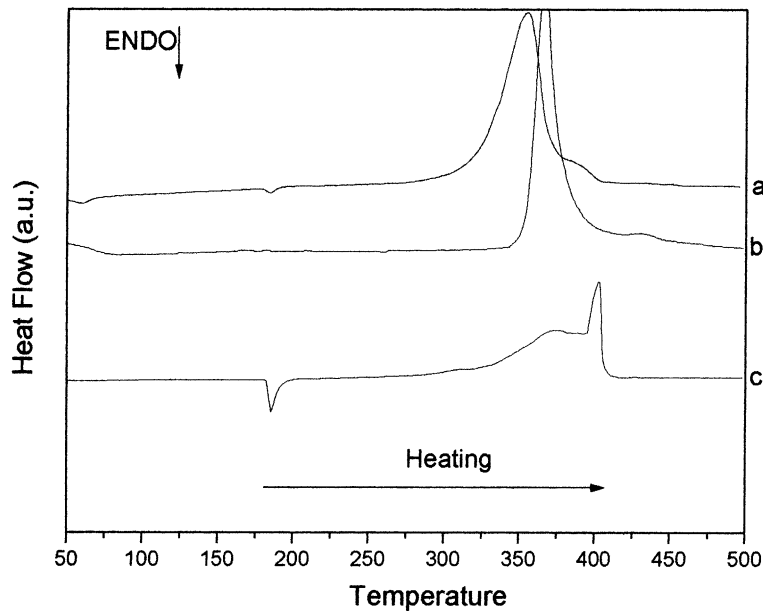


Fig. 4. DSC curves: scan rate 30 °C/min under N₂ flow 100 ml/min. (a) Li-SPE; (b) composite cathode; (c) lithium.

thermal decomposition of composite anode by, for example, a thermal decomposition reaction among the polyethylene and the anode powder (however, it cannot be ruled out that the PE might contact with external atmosphere at high temperature by, for example, DSC sample pan leakage).

This explanation is confirmed from DSC data of CA1 thermal decomposition (Fig. 3c) where an endothermic peak starting at about 144 °C related to the melting of PE and an exothermic peak starting at about 412 °C, which is about the same region of Li-IonPB second thermal decomposition peak is observed.

3.3. Thermal stability of as-prepared Li-SPE

Fig. 4 shows the DSC data for previously measured Li-SPE (a), composite cathode (b), and lithium (c). Lithium exothermic peak (c) was most likely related to DSC cell leakage at high temperature and consequent contact with N₂. In case of Li-SPE, the presence of a single exothermic peak was associated with two-step exothermic chain reactions: at first a reaction of composite polymer electrolyte with cathode, then a reaction between lithium and entered gas after leakage of the pan.

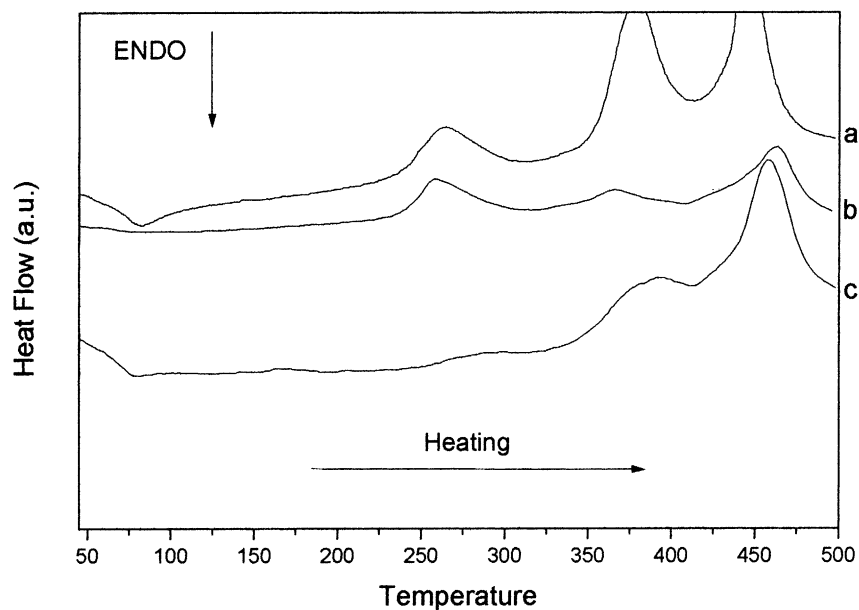


Fig. 5. DSC curves: scan rate 30 °C/min under N₂ flow 100 ml/min. (a) Li-IonPB at charged state; (b) composite cathode at charged state; (c) Li-IonPB after three cycles.

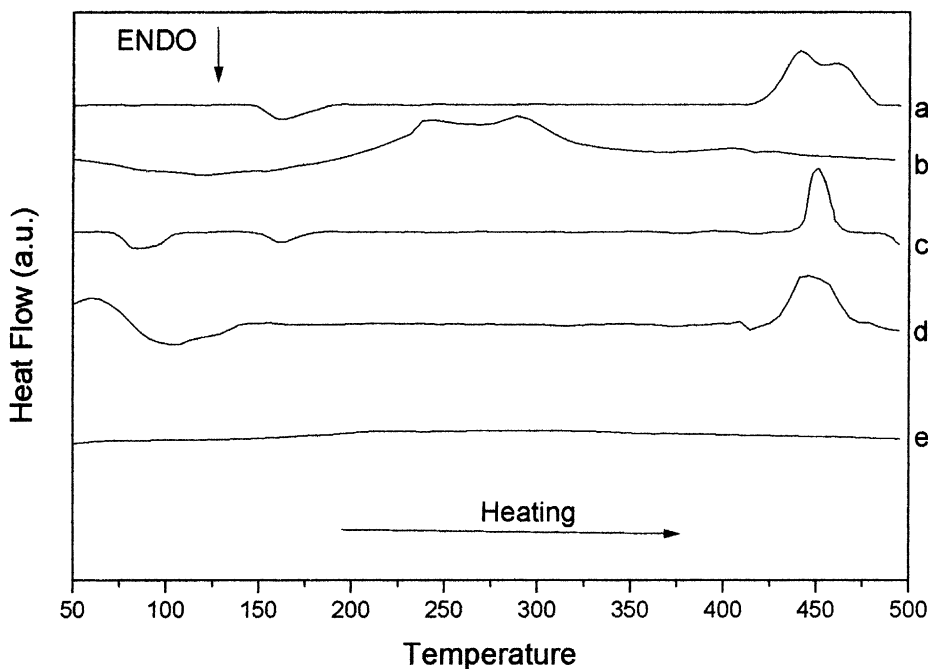


Fig. 6. DSC curves: scan rate 30 °C/min under N₂ flow 100 ml/min. (a) Composite anode CA1; (b) CA2; (c) CA3; (d) CA4; (e) 8% Ni, 38% Li_{2.6}Co_{0.4}N and 54% SnSb powder.

3.4. Thermal stability of Li-SPE at the charged state

Fig. 5 shows the thermal stability of a Li-IonPB cell after the first charging (a), the composite cathode after the first charging (b), and the cell after the third charging (c). For the DSC test the Li-IonPB cell was charged to 3.9 V ($I_c = 0.15 \text{ mA/cm}^2$), stopped and transferred into the dry box. For the full cell DSC test a part of the cell was cut and inserted into the pan. As the charged cathode was tested, the cathode layer was carefully separated from the rest of the cell.

The DSC trace of the Li-IonPB cell shows a new exothermic peak at about 250 °C. After lithium extraction from cathode, the cobalt and nickel reach a higher oxidation state [6]. This may result in higher cathode instability and reactivity to polymer electrolyte. It is notable that after three cycles (c) the peak at about 250 °C disappears and the peak related to the cathode decomposition reduces in its intensity. The exact reason for this behaviour remains unclear. It may be associated with the interface passivation and the fine-structural rearrangement of cathode material during cycling.

3.5. Thermal stability of as-prepared composite anode

Fig. 6 presents the DSC data for composite anode CA1 (a), and CA2 (b). For comparison, CA3 (prepared without Li_{2.6}Co_{0.4}N) (c), CA4 (made of PEO and Li_{2.6}Co_{0.4}N) (d), and anode components without any binder (e) are also shown. When only PE is used as binder (CA1), the composite anode is thermally stable up to 400 °C. Polyethylene

maybe responsible for the exothermic peak at about 400 °C (Fig. 6a) as previously discussed for Fig. 3c.

When PEO-Imide is used, an exothermic peak emerges at about 250 °C (Fig. 6b). This peak is attributed to some reactions between Imide salt and Li_{2.6}Co_{0.4}N. This consideration is based on the fact that CA3 (c) containing no Li_{2.6}Co_{0.4}N and CA4 (d) containing no Imide salt are thermally stable up to 400 °C.

Fig. 6c presents two endothermic peaks starting at 70° and 144 °C related, respectively, at the melting of PEO and PE and an exothermic peak starting at 439 °C which is related to a thermal decomposition reaction of polymer electrolyte and SnSb. Fig. 6d shows an endothermic peak related to PEO melting and an exothermic peak starting at 439 °C related to an exothermal decomposition of PEO and Li_{2.6}Co_{0.4}N. However, for both the exothermic peak of Fig. 6c and d it cannot be ruled out that the polymer PEO or PE might contact with external atmosphere at high temperature.

4. Conclusion

The Li-SPE and Li-IonPB were investigated in the present paper. Both cells show good cycling performance and a thermal stability up to 300 °C. The earliest thermal decomposition in the cells is associated with a reaction between the composite polymer electrolyte and the cathode material. Released heat and gas may cause cell breaking and gas entering, leading to consequent decomposition reactions.

The heat developed from a Li-SPE cell decomposition, calculated from the peak area interpolation was found twice as the heat developed from a Li-IonPB (calculated from the sum of the area of the two exothermic peaks). From the DSC comparison between the composite anode and lithium, the latter was found more reactive and therefore difficult to practical handling.

Acknowledgements

The work was carried out under a collaboration program of Mie University and Genesis Research Institute, Nagoya, Japan.

References

- [1] Robert Spotnitz, in: Walter A. van Schalkwijk, B. Scrosati (Eds.), *Advances in Lithium-Ion Batteries*, Kluwer Academic Plenum Publishers, New York, 2002, p. 437.
- [2] M.A. Metha, T. Fujinami, T. Inoue, *J. Power Sources* 81 (1999) 724.
- [3] S. Kohija, T. Kitade, Y. Ikeda, A. Hayashi, A. Matsuda, M. Tatsumisago, T. Minami, *Solid State Ionics* 154/155 (2002) 1.
- [4] J. Yang, Y. Takeda, N. Imanishi, O. Yamamoto, *J. Electrochem. Soc.* 147 (2000) 1671.
- [5] Y. Xia, T. Fujieda, K. Tatsumi, P.P. Prosini, T. Sakai, *J. Power Sources* 92 (2001) 234.
- [6] C. Delmas, M. Menetrier, L. Croguennec, I. Saadoune, A. Rougier, C. Ponillierie, G. Prado, M. Grune, L. Fournes, *Electrochim. Acta* 45 (1999) 243.