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Thermal and electrochemical stability of cathode materials in solid polymer electrolyte

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Abstract

Thermal stability of cathode materials, including $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, V_2O_5, V_6O_{13}, and Li_xMnO_2 in contact with poly(ethylene oxide) (PEO) based solid polymer electrolyte was systemically investigated by means of thermal analysis in combination with X-ray diffraction technique (XRD). The differential scanning calorimetry (DSC) analysis showed significant exothermic reaction of both $LiNiO_2$ and $LiCoO_2$ in contact with the polymer electrolyte. $LiMn_2O_4$ was less reactive compared with $LiNiO_2$ and $LiCoO_2$. V_2O_5, V_6O_{13}, and Li_xMnO_2 were also found less reactive, especially in their discharge states. The XRD results indicated that the thermal decomposition products of the cathode material were the low valance metal oxides, suggesting the exothermic reaction was an oxidation reaction of the polymer electrolyte with active material. The decomposition temperature is somehow dependent on the potential of the cathode active materials. Cyclic voltammetry reveals that PEO based solid polymer electrolyte is stable up to 5.0 V versus Li/Li^+ at a blocking electrode, whereas it decomposes at ca 3.8 V when contacted with a carbon composite electrode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium batteries; Polymer electrolyte; Cathode materials; Thermal stability

1. Introduction

After production of the first generation rechargeable lithium batteries, Li/MoS_2 by Moli Energy, was stopped because of an incident in 1989, most of interest both in research and industry had world-widely shifted from a metal lithium anode-based lithium battery to lithium-ion battery containing a carbon/graphite anode and a transition metal oxide cathode. Lithium-ion technology is rapidly becoming the state-of-art of secondary systems, and has been commercially used in popular portable devices such as cellular phones and note-size computers. However, such type batteries are not being rapidly developed for electric vehicle in view of the safety of devices because the use of a liquid electrolyte may result in some problems, i.e. leakage of a flammable electrolyte, production of gases upon overcharge or overdischarge, as well as thermal runaway reaction when heated to high temperatures.

The next interesting and challenging goal in the lithium battery technology is the use of metallic lithium and solid polymer electrolyte instead of carbon anode and liquid electrolyte, i.e. going from a lithium-ion battery to a solid polymer battery because of its advantages of enhanced

safety, high energy density, and flexibility. The concept was first proposed by Armand et al. in 1979 [1]. The main problem associated with such type of battery is the low ionic conductivity of the polymer electrolyte and the poor characteristics of the interface between lithium and polymer electrolyte. In the past years, many efforts have been devoted to these directions [2–8]. To date, lithium polymer battery (LPB) could work well at the elevated temperature (between 60 and 100°C). However, in a practical battery system, even if it has no risk of leakage of the liquid electrolyte compared with lithium-ion batteries, and shows the safe improvement, the most important question whether or not both cathode and anode will undergo a thermal runaway reaction with the polymer electrolyte has not yet been clarified. The present work aims to investigate the thermal stability of PEO-based polymer electrolyte with 4 V cathode materials currently commercialized in the lithium-ion batteries, as well as 3 V cathode materials suitable for lithium batteries.

2. Experimental

All 4 V cathode materials, $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ were the commercial products. V_2O_5 was purchased from Aldrich Chemical Co. V_6O_{13} was obtained from thermal decomposition of ammonia vanadate at 250°C for 5 h, then

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at 450°C for 12 h at a flow of N_2. Li_xMnO_2 was prepared by preheating a mixture of $LiNO_3$ and MnO_2 at 260°C for 5 h, followed by heating at 320°C for 12 h in air [9]. All compounds were dried at 120°C for 24 h before use. Lithium salts, $LiBF_4$, $LiClO_4$, $LiCF_3SO_3$, and $LiN(CF_3SO_2)_2$ were battery-grade, and were dried under vacuum for 24 h.

Polymer electrolyte was prepared by a hot-pressing technique originally proposed by Gray et al. [10]. It consisted of the following procedure: Poly(ethylene oxides) PEO (Aldrich Chemical Co., 4×10^6 average molecular weight) was mixed well with lithium salt at an EO/Li ratio of 20/1 in a dry room. The mixture was then placed between two Mylar sheets, followed by pressing at 9.8×10^5 Pa for 10 min at 80°C, then slowly cooled down to room temperature. Typical thickness of the polymer electrolyte film was 100 μm.

Composite electrodes were also prepared by the same procedure as that used for the polymer electrolyte. Typical weight percentage of each components in the composite electrode was: 60% active material, 8% carbon (Ketjen black), and 32% $PEO_{20}LiN(CF_3SO_2)_2$.

Thermal stability of the polymer electrolyte and the composite electrodes before and after charge or discharge, were investigated by means of thermogravimetry (TG) or differential scanning calorimetry (DSC). Experiments were conducted on a thermal analyzer system (DSC8230 and TG-DTA TG81201, Rigaku Ltd., Japan) at a heating rate of 10°C/min with a 50 ml/min Ar flow rate. About 5 mg sample was well sealed in an aluminum DSC cell in a dry room. To evaluate the thermal stability of cathode materials in their different oxidation or reduction state, the composite electrode was assembled into a Li/polymer electrolyte/cathode cell, then charged or discharged to a definite depth at a current density of 0.05 mA/cm² at 80°C, then the current was interrupted and the cell equilibrated for 12 h and cooled

to room temperature. Cells were open in the dry room. About 5 mg of composite electrode was taken and hermetically sealed in an aluminum DSC cell in a dry room.

The phase composition of the thermal decomposition products of the cathode materials was characterized by X-ray diffraction with Cu Kα radiation on a Rigaku RINT 2000 X-ray diffractometer (Rigaku Ltd., Japan).

Linear sweep voltammetry experiments were performed by using a potentio-galvanostat Model 283 (Eg & G Instruments, Princeton Applied Research) to determine the electrochemical stability of polymer electrolyte at a blocking electrode (stainless steel electrode) or a carbon composite electrode. The carbon composite was prepared by the hot-pressing technique as described above. It consisted of 60 wt.% of polymer electrolyte and 40 wt.% of carbon. The sweep rate was 50 μV/s and the operating temperature was 80°C.

3. Results and discussion

3.1. Thermal stability of the polymer electrolyte

Lithium salts mostly considered in polymer electrolyte are $LiBF_4$, $LiClO_4$, $LiCF_3SO_3$, and $LiN(CF_2SO_2)_2$. Fig. 1 shows TG curves of $PEO_{20}LiBF_4$, $PEO_{20}LiClO_4$, $PEO_{20}LiCF_3SO_3$, and $PEO_{20}LiN(CF_3SO_2)_2$ together with salt-free PEO. Salt-free PEO, either $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ salt based electrolytes are thermal stable up to 300°C; $LiClO_4$ based one is less stable and decomposes at 250°C; $LiBF_4$ based one is quite unstable and decomposition starts at 160°C. Under abusive condition, the potential exists to heat a cell beyond its thermal stability limit, producing gas and risking a safety incident. The above results clearly reveal
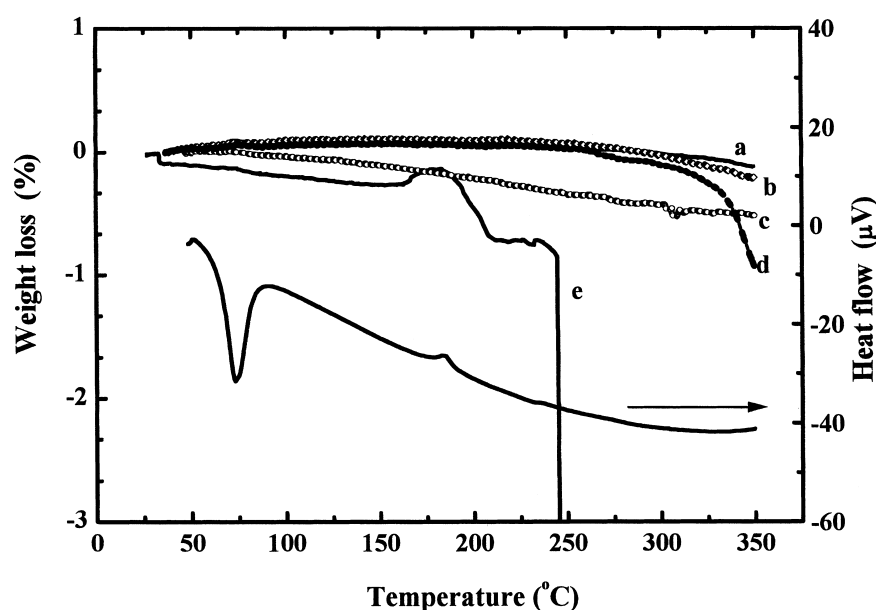

Fig. 1. TG curves for PEO polymers based on various lithium salts: (a) salt-free; (b) $LiN(CF_3SO_2)_2$; (c) $LiCF_3SO_3$; (d) $LiClO_4$, and (e) $LiBF_4$. The DTA curve for the pure PEO is also given in the figure.

Table 1
Specific energy and working voltage of cathode materials when combined with lithium anode

Cathode material	Potential (V vs. Li/Li$^+$)	Theoretical capacity (A h/kg)	Practical capacity (A h/kg)	Theoretical energy density (W h/kg)	Practical energy density (W h/kg)
LiCoO$_2$	3.8	273 (1)[a]	140	1037	532
LiNiO$_2$	3.7	274 (1)	170	1013	629
LiMn$_2$O$_4$	4.0	148 (1)	110	592	440
V$_2$O$_5$	2.7	440 (3)	200	1200	540
V$_6$O$_{13}$	2.6	420 (8)	200	1000	520
Li$_x$MnO$_2$	2.8	210 (0.7)	170	588	480

[a] The value given in the parenthesis is the maximum number of inserted/extracted lithium ion.

that all polymer electrolytes are stable in the range of the operating temperature of polymer electrolyte batteries (between 60 and 100°C). LiCF$_3$SO$_3$ and LiN(CF$_3$SO$_2$)$_2$ based electrolyte are the most promising polymer electrolytes in the view of safety problem, which are much more stable than LiPF$_6$–EC/DMC system mostly commercialized in the lithium-ion batteries. Thereby, we select PEO-LiN(CF$_3$SO$_2$)$_2$ system to investigate its thermal stability with cathode materials.

3.2. Thermal stability of the polymer electrolyte with cathode materials

One kind of cathodic materials under consideration in polymer batteries are the so-called 4 V cathode materials currently commercialized in the lithium-ion batteries, including layered structure LiCoO$_2$, LiNiO$_2$, as well as spinel-typed LiMn$_2$O$_4$. These electrodes having a very positive intercalation potential, as high as 4 V versus Li/Li$^+$, encounter some problems, e.g. high electrolyte oxidation rates and a high safety risk in some applications. The another most attractive cathode materials are the ones with the less positive intercalation potential and large capacity,

e.g. vanadium and manganese oxides. Table 1 shows average potential and energy density of these cathode materials when combined with a lithium anode. There is no major difference in the practical energy density, having practical specific energy of ca. 500 W h/kg, though they have different operating potential: LiCoO$_2$, LiNiO$_2$, and LiMn$_2$O$_4$ are at ca. 4 V, while V$_2$O$_5$, V$_6$O$_{13}$ and Li$_x$MnO$_2$ show at ca 3 V. It was reported that 4 V cathode materials, specially LiNiO$_2$ showed significant exothermic reaction with liquid electrolyte when the cell was heated to high temperature [11]. Lithium polymer batteries show improved safety because of no risk of leakage of liquid electrolyte. The question remains as to whether or not such exothermic reaction occur when these cathode materials in contact with a polymer electrolyte. To shed the light on it, we applied DSC technique to determine the decomposition temperature and the exothermic heat flow from the samples. Experiments were carried out in the sealed cell, which could exclude any effect of introduced gas since the exothermic reaction occurs via a redox reaction and it somehow depends on its oxidation environment, which will be related in the following section. Fig. 2 shows DSC traces of LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$ composite electrodes, consisting of the active material,
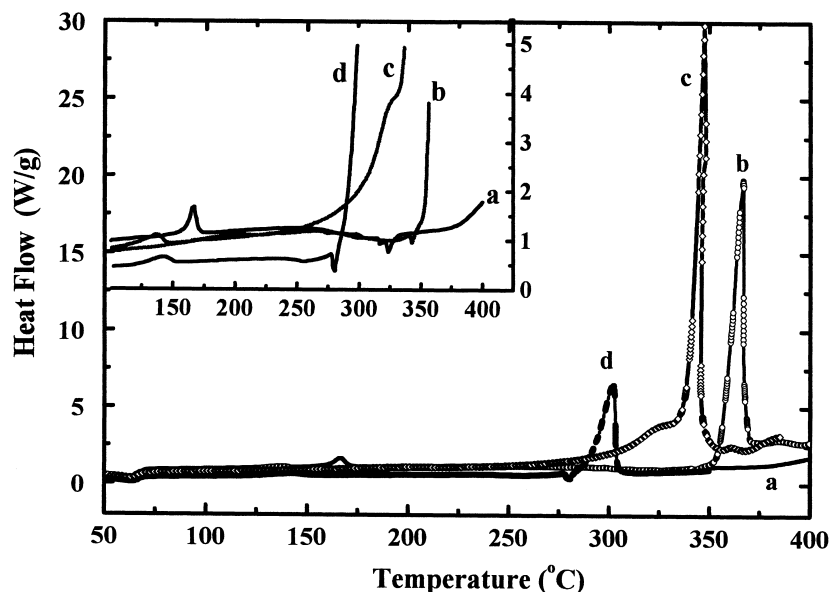

Fig. 2. DSC curves for 4 V composite electrodes: (a) carbon; (b) LiCoO$_2$; (c) LiNiO$_2$, and (d) LiMn$_2$O$_4$. Ramp rate 10°C/min. Curves a–d are enlarged.
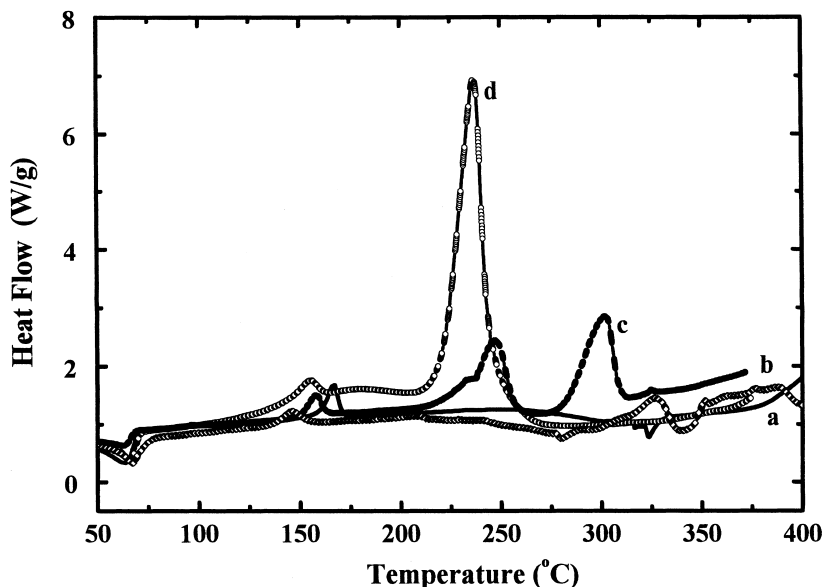
Fig. 3. DSC traces for composite electrodes: (a) carbon; (b) V_6O_{13}; (c) V_2O_5, and (d) Li_xMnO_2. Ramp rate 10°C/min.

polymer electrolyte and carbon black. Since all cathode materials were prepared above 350°C, any reaction resulting from the decomposition of cathode material themselves can be excluded before 350°C. An endothermic peak at ca. 70°C in all curves a–d of Fig. 2 is attributed to the eutectic transition of PEO. The origin of the small exothermic peak at about 170°C, which was also observed on pure PEO (DTA curves in Fig. 1), is not clear. Carbon composite was found to be stable up to 300°C. Exothermic reaction of $LiNiO_2$ with the polymer electrolyte starts at about 250°C, $LiMn_2O_4$ at 275°C, and $LiCoO_2$ at 340°C (curves b–d in Fig. 2). The exothermic peaks are 302, 348, and 367°C for $LiMn_2O_4$, $LiNiO_2$ and $LiCoO_2$, respectively. Both $LiNiO_2$ and $LiCoO_2$ exhibit significant exothermic reaction peaks, while $LiMn_2O_4$ shows much smaller one. $LiNiO_2$ and $LiCoO_2$ in presence of liquid electrolyte were reported to be fairly stable up to 400°C [11], and it was probable that the liquid electrolyte evaporated at ca. 250°C lower than its thermal decomposition temperature (ca. 300°C). DSC traces for the 3 V cathodes, V_2O_5, V_6O_{13} and Li_xMnO_2, are given in Fig. 3. A large exothermic peak was observed at 240°C for the Li_xMnO_2 composite electrode, corresponding to the decomposition of Li_xMnO_2 and electrolyte. V_2O_5 exhibited two broad exothermic peaks at 247 and 300°C. V_6O_{13} is much more stable with the polymer electrolyte, the exothermic reaction starts at 280°C and shows a small exothermic peak at 325°C. The overall heat generation calculated by integration of the area of the exothermic peaks is a direct indication of the reactivity between the active material and the electrolyte. It is evident that significant exothermic reaction occurs between both $LiNiO_2$ and $LiCoO_2$ with electrolyte. $LiMn_2O_4$ was less reactive. The 3 V cathodes were also found to be reactive with electrolyte, but the overall heat values were lower when compared to nickel and cobalt oxides.

Thermal stability of each cathode material in contact with polymer electrolyte in their charge or discharge state was also evaluated. The 4 V cathodes normally work from OCV to higher voltage, while the 3 V cathodes from OCV to lower voltage when assembled into a Li/polymer electrolyte/cathode cell. Fig. 4 shows typical DSC curves for $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ composite electrodes when partially charged to a capacity of 110 mA h/g, corresponding to a chemical composition of $Li_{0.6}CoO_2$, $Li_{0.6}NiO_2$, and $Li_{0.23}Mn_2O_4$. The results in Fig. 4 clearly reveal that the delithiated composite electrodes are much more unstable than the pristine electrodes. The decomposition temperature shifts to lower values: the thermal runaway reaction occurs at 210°C for $LiNiO_2$, three exothermic peaks are observed at 240, 280, and 350°C; the decomposition temperature of $LiCoO_2$ shifts from 340 to 240°C; $LiMn_2O_4$ decomposes at 230°C and shows exothermic peak at 260°C. Fig. 5 gives the DSC traces for Li_xMnO_2, V_2O_5, and V_6O_{13} composite electrode after discharging to a capacity of 115 mA h/g, corresponding to $Li_{0.7}MnO_2$, $Li_{0.8}V_2O_5$, and $Li_{2.2}V_6O_{13}$. The results indicate that the intercalated 3 V cathodes are much more stable than the pristine materials: both vanadium oxide composite electrode are stable up to 300°C; Li_xMnO_2 shows greatly decrease in the exothermic peaks at 250°C, the decomposition mostly occurs at 350°C. Summarily, it is certain that the 4 V cathode materials are less stable in contact with PEO-based polymer electrolyte, particularly in their charge states, whereas the 3 V cathode materials show high thermal stability in contact with the polymer electrolyte.

It is worthy to be noted that there is no significant difference in the decomposition temperature of delithiated 4 V composite electrodes in contact with a liquid and a polymer electrolytes. The decomposition temperature of delithiated electrodes in presence of liquild electrolyte
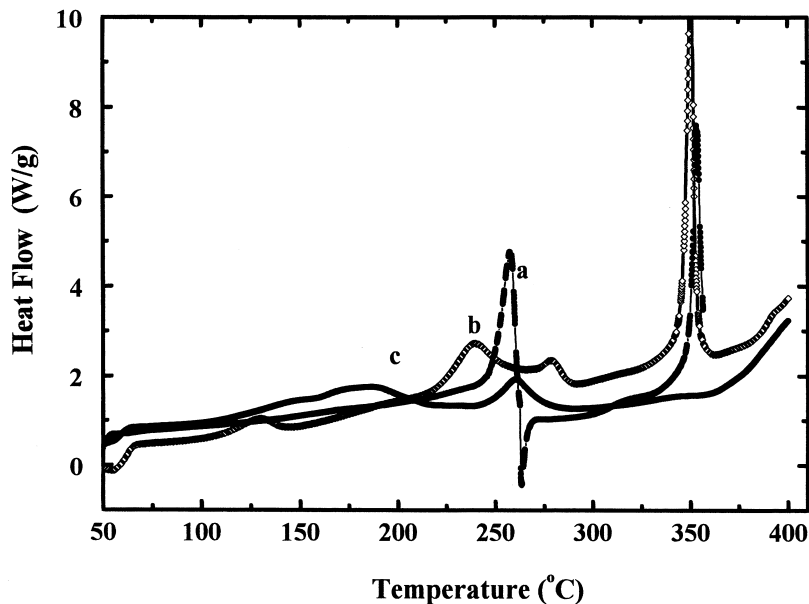
Fig. 4. DSC traces for 4 V composite electrodes after partial charge: (a) $Li_{0.6}CoO_2$; (b) $Li_{0.6}NiO_2$; and (c) $Li_{0.23}Mn_2O_4$. Ramp rate $10°C/min$.

was also reported at ca. 200°C (200°C of $Li_{0.25}NiO_2$, 225°C of $Li_{0.25}Mn_2O_4$, and 230°C of $Li_{0.25}CoO_2$) [11]. However, the composite electrodes show multiple exothermic peaks in contact with the polymer electrolyte instead of one large exothermic peak in presence of liquid electrolyte, suggesting a slow decomposition rate to thermal runaway. More recently, we found that the multiple exothermic peaks of the partly charged or discharged electrode (Li_xMO_2) are linked to the different oxidation state metal ion coexisting. The higher or lower oxidation state metal ion is reduced separately by the polymer electrolyte [12]. For example, $Li_{0.6}CoO_2$, the exothermic peak at 360°C may result from

the reaction of Co^{3+} and polymer electrolyte, and the peak at 260°C from Co^{4+}; the peak at 240°C for $Li_{0.7}MnO_2$ from Mn^{4+}, and 370°C from Mn^{3+}. We have confirmed that fully discharged lithiated MnO_2 ($LiMnO_2$) showed only one exothermic peak at 360°C [13]. Further work to determine whether or not the 4 V cathodes have a less tendency for thermal runaway reaction in polymer electrolyte than that in liquid electrolyte are being carried out by accelerating rate calorimetry (ARC).

The decomposition temperature each composite electrode before and after charge or discharge were summarized in Table 2 together with the average valance of metal ion M^{x+}
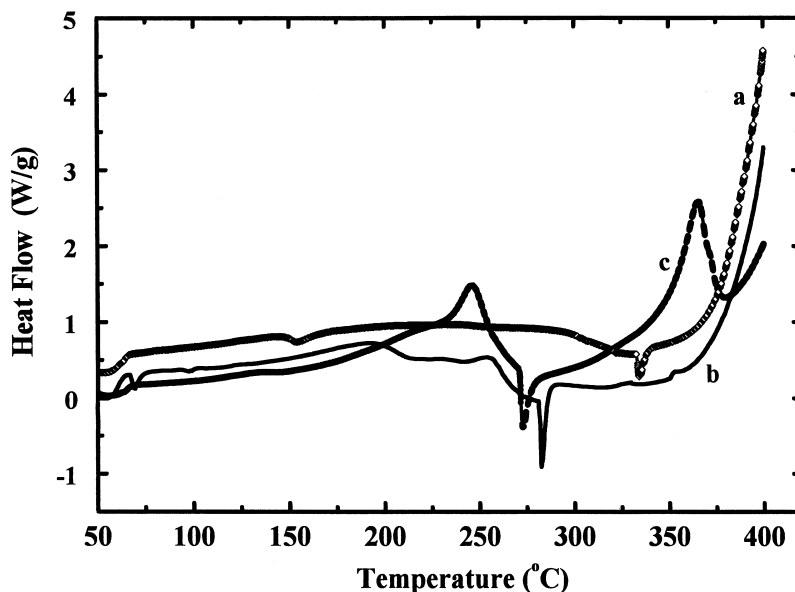

Fig. 5. DSC traces for 3 V composite electrodes after partial discharge: (a) $Li_{2.2}V_6O_{13}$; (b) $Li_{0.8}V_2O_5$, and (c) $Li_{0.7}MnO_2$. Ramp rate $10°C/min$.

Table 2
Thermal decomposition temperature and exothermic heat of cathode materials in $PEO_{20}LiN(CF_3SO_2)_2$ electrolyte

Cathode material	Open-circuit voltage (V vs. Li^+/Li)	Average valance of M	Decomposition temperature (°C)	Exothermic peak temperature (°C)	Exothermic heat (J/g)
$LiCoO_2$	3.18	3+	340	367	660
$Li_{0.6}CoO_2$	3.94	3.4+	240	257, 353	600
$LiNiO_2$	3.30	3+	250	348	926
$Li_{0.6}NiO_2$	3.72	3.4+	210	240, 280, 350	640
$LiMn_2O_4$	3.45	3.5+	275	302	312
$Li_{0.23}Mn_2O_4$	4.07	3.89+	230	260	420
$Li_{0.33}MnO_2$	3.43	3.67+	200	240	554
$Li_{0.7}MnO_2$	2.87	3.3	275	246, 370	200
V_2O_5	3.50	5+	210	247, 300	277
$Li_{0.8}V_2O_5$	2.64	4.6+	280	–	–
V_6O_{13}	3.58	4.3+	280	325	84
$Li_{2.2}V_6O_{13}$	2.48	4+	325	–	–

and the open-circuit-voltage (OCV) versus Li/Li^+. The results in Table 2 show that each cathode material at oxidation state which shows a higher OCV gives lower decomposition temperatures than that at reduced state. Fig. 6 gives a plot of the decomposition temperature against the OCV. Hardly it is to fit a line or curve describing accurately the correlation between the decomposition temperature and OCV, but it clearly shows that cathode active materials with higher potential have a tendency for more readily oxidizing the polymer electrolyte.

To further confirm whether or not the decomposition mechanism is related to an oxidation reaction of the polymer electrolyte with the active material, X-ray diffraction technique was applied to determine the phase composition of the thermal decomposition products. XRD patterns of each composite electrode after thermal analysis are given in

Figs. 7 and 8. The thermal decomposition product of $LiCoO_2$ composite electrode is characteristic of CoO phase as evidenced by the peaks of $2\theta=36.42, 42.32, 61.52$, and $73.76°$ (curve d in Fig. 7); $LiNiO_2$ composite electrode is reduced to NiO phase as evident from the peaks at $2\theta=37.14, 43.24$, and $63°$ (curve e in Fig. 7); $LiMn_2O_4$ is reduced into Mn_3O_4, a lower Mn valance oxide but Mn_2O_3, as the peaks at 2θ of 18.18, 28.74, 32.22, 35.96, and $59.76°$ are ascribed to the signature of Mn_3O_4 phase. XRD patterns of thermal decomposition of Li_xMnO_2 composite electrode in Fig. 8(d) show a quite different patterns of $LiMn_2O_4$, suggesting the reduction compound is not indexed to Mn_3O_4 rather than MnO phase with major diffraction peaks at $2\theta=34.94, 40.58$, and $58.70°$. The thermal decomposition product of both V_2O_5 and V_6O_{13} exhibit the very similar XRD patterns: both compounds are most likely reduced into VO_2 as evidenced
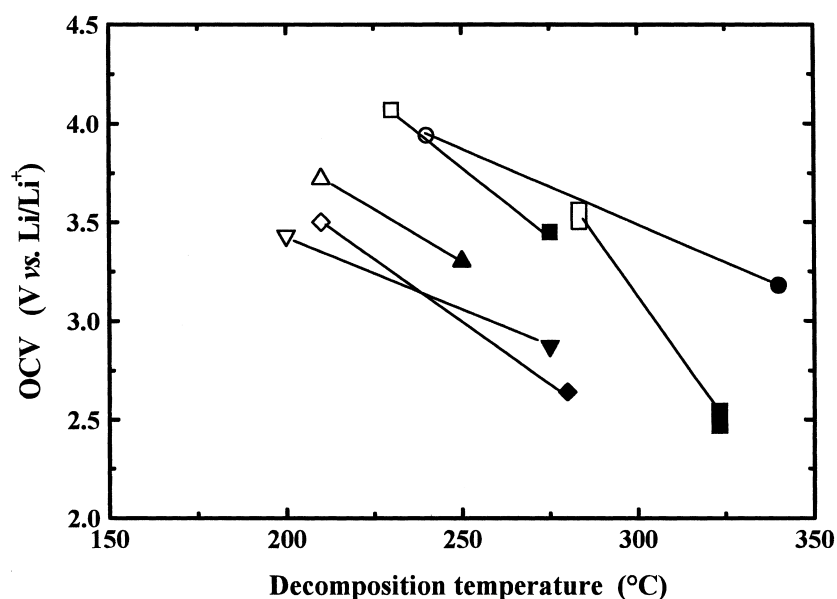

Fig. 6. Plots of decomposition temperature of composite electrode vs. open-circuit-voltage. Discharged state in the solid symbol, and charged state in the open symbol. (●) $LiCoO_2$, (■) $LiMn_2O_4$, (▲) $LiNiO_2$, (▼) Li_xMnO_2, (◆) V_2O_5, and (◨) V_6O_{13}.
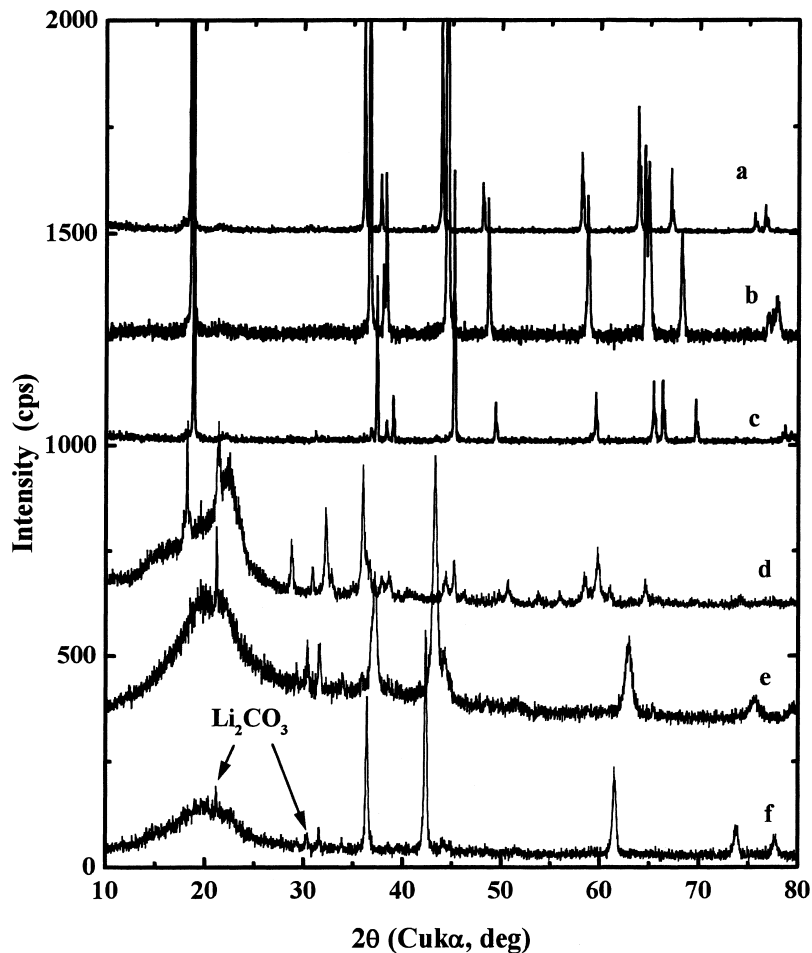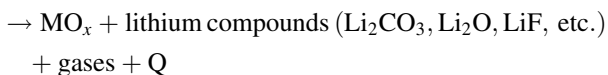
Fig. 7. X-ray diffraction patterns of the 4 V composite electrodes before and after thermal decomposition: (a,d) $LiMn_2O_4$; (b,e) $LiNiO_2$, and (c,f) $LiCoO_2$.

by the peaks of $2\theta=14.22$, 25.06, 28.96, 33.58, and 44.20°. From all the above results, the possible decomposition mechanism is proposed as follows:

$$LiMO_2 + polymer\,electrolyte$$
$$\rightarrow MO_x + lithium\,compounds\,(Li_2CO_3, Li_2O, LiF, etc.)$$
$$+ gases + Q$$

The exothermic heat of each pristine cathode material in comparison with that after their charge/discharge was summarized in Table 2. Hardly it is to find any relationship between the exothermic heat and the OCV or average M valance. The results indicated that 3 V cathodic materials show smaller exothermic heat after discharge than pristine electrode. However, 4 V cathodic materials did not show any definite tendency. Normally, it is easy to envisage that the exothermic heat is link to the changes in oxidation power of metal ion: 4 V cathode materials after charging should undergo a greater thermal runaway because of having a much stronger oxidation ability than that of pristine material. By contrast, 3 V cathode material shows lower exothermic heat after discharge as they are reduced into a lower M valance. Unfortunately, at this state, we do not have enough

evidence to further address this issue, because it is quite difficult to separate the composite electrode from with polymer electrolyte film (serve as a separator). Composite electrodes was incorporated into the electrolyte film during charge/discharge at 80°C. Moreover, the exothermic reaction between cathode material and polymer electrolyte is much complex. The exothermic heat most likely depends on several factors, such as the heating rate, the surface area of cathode material, and the catalytic properties of metal ion besides of the oxidation ability of metal ion. Regardless of these, we can still conclude that the 4 V cathode materials are less stable in contacted with PEO-based polymer electrolyte, whereas the 3 V cathode materials show enhanced stability.

3.3. Thermal stability of Li_xMnO_2 with various polymer electrolyte

As described above, it is obvious that the decomposition temperature and the exothermic heat are critically depends on the kind of cathode active material employed and on its charge/discharge state. Another question remains whether or not the thermal runaway is associated with the polymer
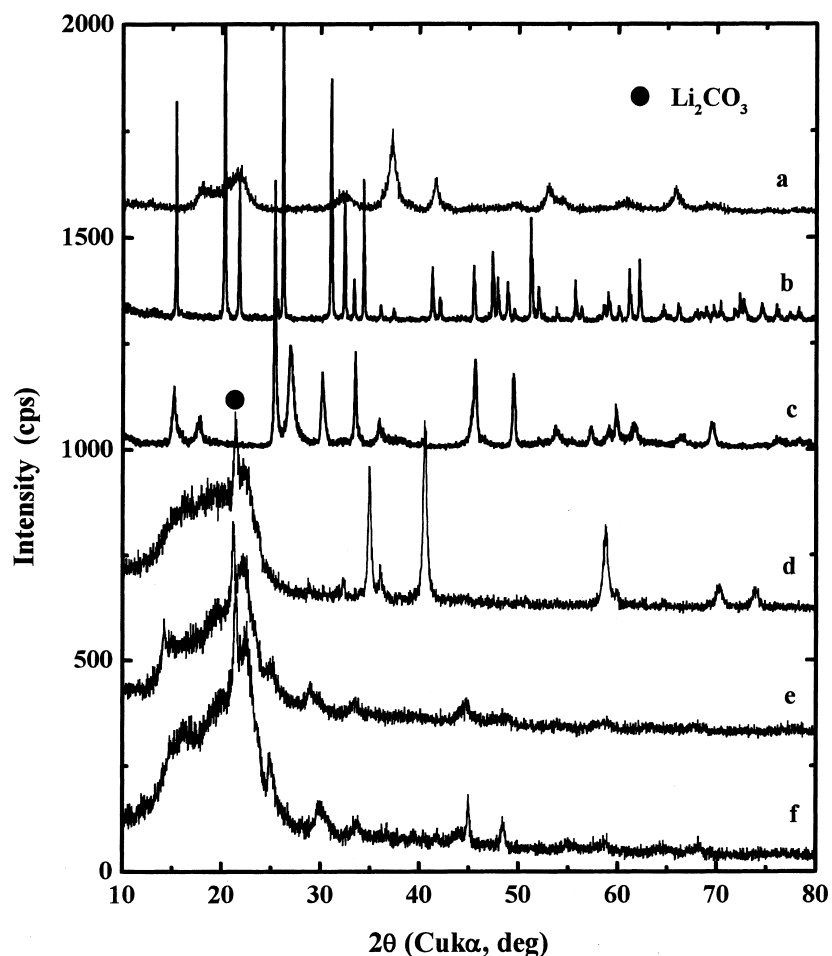
Fig. 8. X-ray diffraction patterns of the 3 V composite electrodes before and after thermal decomposition: (a,d) Li_xMnO_2; (b,e) V_2O_5, and (c,f) V_6O_{13}.

employed. Three kinds of polymer were selected to compare their thermal behavior when combined with Li_xMnO_2 cathode: polyethylene oxide with a molecular weight of 4×10^6 (PEO), poly(ethylene glycol) with a molecular weight of 2000 (PEG), and hyper-branched poly[ethylene oxide-co-2-propyl glycidyl ether] (P(EO/EM-2=95/5)). DSC curves of composite electrodes containing Li_xMnO_2, $LiN(CF_3SO_2)_2$, and carbon with the above three polymers are given in Fig. 9. There is no pronounced difference either in the exothermic heat or in the decomposition temperature. This strongly supported the fact that the exothermic reaction between cathode material and polymer electrolyte is critically dependent on the cathode active materials, rather than polymer electrolyte.

3.4. Electrochemical stability of PEO-based polymer electrolyte

The electrochemical stability of the electrolyte for oxidation process is relevant for the interface with the cathode and, is another important issue for the selection of a polymer electrolyte for battery application. Oxidation of polymer will increase cell resistance, as well as give rise to gas, thus

affect the battery profile or result in safety problems. Sylla et al. have reported that PEO/$LiN(CF_3SO_2)_2$ system are stable up to 4.5 V versus Li/Li^+ on a smooth blocking electrode (stainless steel working electrode) [14]. However, in a real battery system, polymer electrolyte works with a composite electrode rather than a smooth inert electrode. In the cathode the polymer electrolyte is in contact with the active material and conductive material, e.g. carbon black, acetylene black, graphite, etc. Fig. 10 show the linear sweep voltammogram of Li/SPE/stainless and Li/SPE/carbon composite at a scan rate of 50 μV/s. PEO$_{20}$LiN(CF$_3$SO$_2$)$_2$ electrolyte is at least stable up to 4.5 V versus Li/Li^+ on the stainless electrode, which is in good agreement with that reported previously [14]. However, its decomposition starts at 3.8 V versus Li/Li^+ on a carbon composite electrode, which is about 1 V below the value obtained with a smooth inert electrode. The interpretation of the difference is high possible that the catalysis of carbon with a large surface facilities the polymer decomposition. This is also a fundamental problem preventing the so-called 4 V cathode materials use as cathode materials for lithium battery batteries under the current condition, whereas the 3 V cathode materials show much higher potential for such batteries.
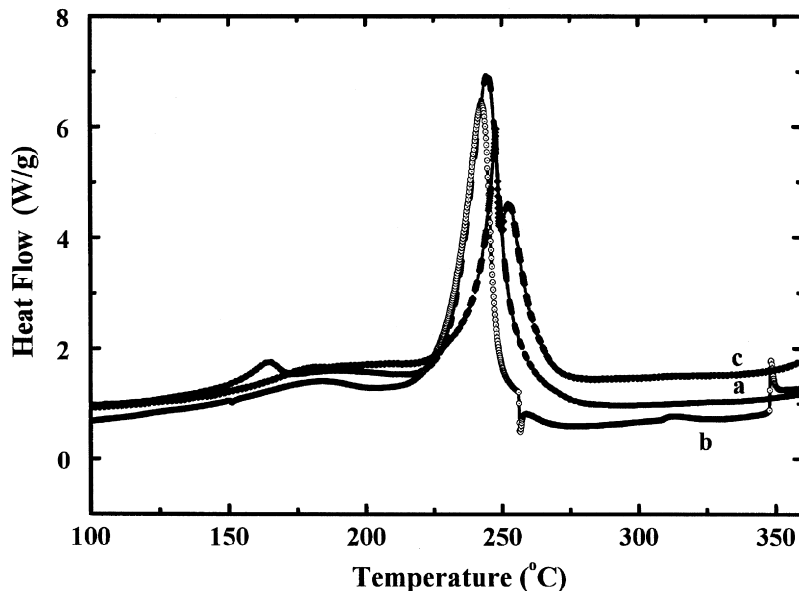
Fig. 9. DSC curves of Li_xMnO_2 based composite cathode with various polymer electrolytes: (a) PEO-LiN(CF$_3$SO$_2$)$_2$; (b) PEG-LiN(CF$_3$SO$_2$)$_2$, and P(EO/EM-2=95/5)-LiN(CF$_3$SO$_2$)$_2$.

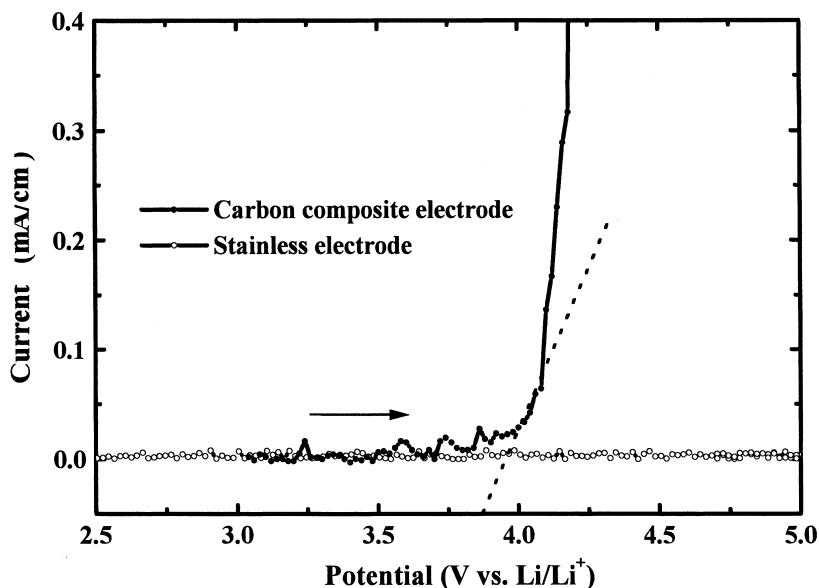Fig. 10. Linear sweep voltammogram of a PEO$_{20}$LiN(CF$_3$SO$_2$)$_2$ electrolyte sandwiched between a lithium disc and (a) a stainless disc or (b) a carbon composite electrode. The scan rate was 0.05 mV/s, and T=80°C.

4. Conclusion

PEO-LiCF$_3$SO$_3$ and PEO-LiN(CF$_3$SO$_2$)$_2$ polymer electrolytes are thermal stable up to 300°C, which are more safe as compared to liquid electrolyte. However, they become unstable and undergo thermal runaway reaction when in contact with cathode materials: Both LiNiO$_2$ and LiCO$_2$ exhibited significant exothermic reaction. LiMn$_2$O$_4$ was less reactive. 3 V cathodes, Li$_x$MnO$_2$, V$_2$O$_5$, and V$_6$O$_{13}$ also showed to be reactive with electrolyte, but the overall heat values were lower than that of the nickel and cobalt oxides.

The XRD results indicated that the thermal decomposition products of the cathode materials were metal oxides at the low valance, suggesting the exothermic reaction occurs via an oxidation reaction of the polymer electrolyte by the active material. The decomposition temperature depends on the potential of the cathode active materials. A cathode active material with higher potential more readily oxidizes the polymer electrolyte. These 4 V cathode materials become much unstable in their charge state, and the decomposition temperature shifts to low values. By contrast, these 3 V cathode materials become more stable in their discharge states.

Linear sweep voltammetry reveals that PEO based solid polymer electrolyte is stable up to 5.0 V versus Li/Li$^+$ at a blocking electrode, while it decomposes at ca 3.8 V at a carbon composite electrode. This is also a fundamental problem preventing the so-called 4 V cathode materials use as cathode materials for lithium battery batteries under the current condition, whereas the 3 V cathode materials show much higher potential for such batteries.

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