Gas evolution behaviors for several cathode materials in lithium-ion batteries

Weihe Kong, Hong Li, Xuejie Huang, Liquan Chen*

Laboratory for Solid State Ionics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China

Abstract

Several 18650 lithium-ion batteries using $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$ as cathode materials were assembled separately. Gas species of these batteries under normal cycling and overcharging to 4.5 and 5.0 V conditions were examined by means of GC–MS method. Under the normal charge and discharge voltage range, it is found that gas components are independent to the cathode materials. C_2H_5F gas was detected in all cases. A formation mechanism is proposed. Under overcharging condition, it is found that the gas components are different and there is a correlation between the C_2H_2 product and the oxidation ability of various delithiated cathode materials.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Gas evolution; Cathode; Lithium-ion batteries

1. Introduction

Lithium-ion batteries are widely used from portable electronic devices to electric vehicles. The safety of lithium-ion batteries, especially under abusive conditions, is a primary concern of battery manufacturers and their customers. In particular, the safety of overcharged batteries is an important aspect for the evaluation. In general, the safety state of lithium-ion batteries under overcharge condition is determined by the thermal behaviors and gas generation behaviors, including the quantity and the nature of generated gases, of the batteries [1,2]. The thermal behaviors and their infection to battery safety for various cathode materials have been studied by many researchers [1,3,4]. For the gas generation behaviors, many studies were focused on the reactions between carbonaceous anode and the electrolyte. It is known that the main origin of gas evolution is related to the reactions for forming the solid electrolyte interphase (SEI) films [5,6]. However, the gas generation behaviors in practical lithium-ion batteries, especially the influence from the different cathode materi-

als, are still not clear. There are a few experimental results on $LiCoO_2$ cathode materials. It is known that oxygen can be generated during overcharge and it can oxidize the electrolyte to form CO_2 [7]. Gas species, i.e. CH_4, CO, CO_2, O_2, C_2H_6, C_2H_4, C_3H_8, and C_3H_6 were detected out by GC–FID technique [5]. $LiMn_2O_4$ and $LiFePO_4$ are both promising cathode materials for lithium-ion batteries, because of their low cost, non-toxicity, and relative high safety in comparison with $LiCoO_2$. Therefore, it is interesting and important to understand the relationship between gas generation behaviors and these cathode materials in practical batteries.

In this paper, gas generation behaviors of various cathode materials in 18650 batteries under normal cycling and overcharge conditions have been investigated by using GC–MS technique.

2. Experimental

2.1. Electrode preparation

The cathode materials, i.e. $LiCoO_2$ (Nippon chemical), $LiMn_2O_4$ (Nippon chemical), and $LiFePO_4$ (Valance) were

* Corresponding author. Tel.: +86 10 8264 9046; fax: +86 10 8264 9050.
 E-mail address: lqchen@aphy.iphy.ac.cn (L. Chen).

Table 1
The basic design parameters of the batteries with different cathodes

Chemical system of battery	Weight ratio of active materials of anode and cathode	Designed capacity of battery (mAh)
CMS/LiCoO$_2$	1:2.1	1100
CMS/LiMn$_2$O$_4$	1:2.7	700
CMS/LiFePO$_4$	1:2.1	1000

commercial products. Cathodes were prepared by pasting the slurry composed of the active material powder with 5% polyvinylidene fluoride (PVDF), and 4% acetylene black and 2% graphite in a *N*-methyl pyrrolidone (NMP) solvent onto both sides of Al foil with 20 μm thickness. The total thickness of the cathode foil is 170 μm. In the case of LiFePO$_4$, the particles were coated with 6.5 wt.% carbon in advance. The anodes were prepared by pasting the slurry of carbon microspheres (CMS) (G15, Shanshan Keji) with 5% PVDF and 4% acetylene black onto both sides of Cu foil with thickness of 15 μm. The total thickness of the anode foil is 150 μm.

2.2. Battery preparation and measurements

The membrane electrode assembly (MEA) for 18650 batteries were wound semi-automatically by a winding machine and a 25 μm-thick porous polyethylene film (Celgard 2325) was used as separator. The MEA was put into the 18650 battery can. After drying under vacuum at 100 °C for 12 h, the electrolyte was injected and then the test battery was sealed. Battery assembly was conducted at 20 °C in a dry-room with relative humidity (RH) ⩽ 2%. The electrolyte is 1 M LiPF$_6$ dissolved in a ethylene carbonate (EC):dimethyl carbonate (DEC) solvent (1:1 in volume). In order to prevent the deposition of metal lithium on the surface of the anode during overcharging, the cathode was used as the capacity-limited electrode in the battery. The basic design parameters are listed in Table 1. It should be mentioned that for the convenience of

testing the gas species, the height of the electrodes inside the batteries and the capacity of batteries were reduced properly compared to standard 18650 batteries.

A small hole was drilled on the cap of the battery in advance for the GC–MS gas collection. The battery inside the can was sealed by an internal Al–plastic membrane.

After assembling, the batteries were cycled for one time with 0.1*C* rate in the voltage range of 2.7 V desired voltage (for LiFePO$_4$ it was 3.65 V, for LiMn$_2$O$_4$ it was 4.3 V, for LiCoO$_2$ it was 4.2 V) to form stable SEI layer on the surface of electrodes. Then the batteries were charged and discharged in the same voltage range for 100% DOD at 0.2*C* rate. After three cycles, the batteries were kept either at charged state, or overcharged to preset voltages using 0.2*C* constant current, and then charged under constant voltage until the current was decreased below 0.05*C*. All electrochemical experiments were carried out at room temperature and ambient conditions. After normal charging or overcharging, the batteries were used for GC–MS measurements.

2.3. GC–MS measurements

Gas chromatography was carried out on a Trance 2000 series GC instrument (Finnigan Inc.). The temperature of the GC oven was set at 50 °C and the inlet temperature was 50 °C for the gas samples. Helium (He) was used as carrier gas. The species from the column outlet were continuously ionized and analyzed with Trance MS mass spectrometer (Finnigan). The ionization voltage and emission current were set at 70 V and 350 μA, respectively. The range of mass collection was set to be 10–190 amu (atomic mass unit) for the gas samples. The range of retention time (RT) was 0–20 min for the gas. The setup of the retention time range was determined by extending the retention time to 30 min and making sure that no species could be detected out after 20 min for the gas samples.

After normal charging or overcharging, the gas generated in the battery was collected using a 100 μl syringe through
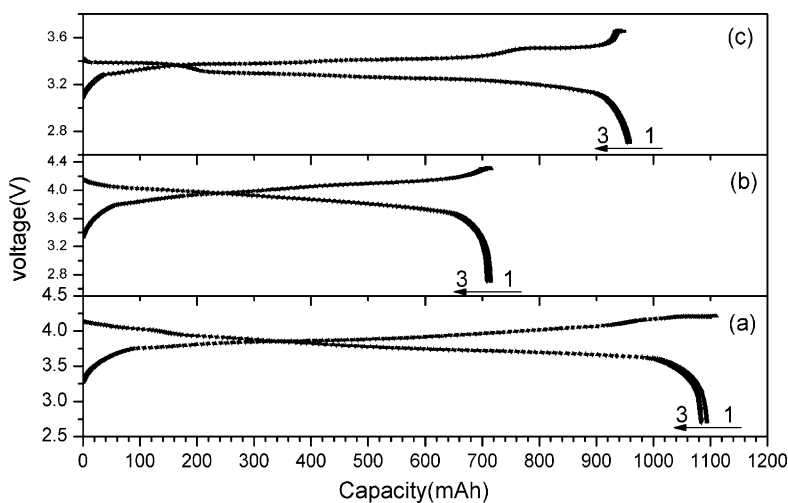

Fig. 1. The charge–discharge curves of three kinds batteries at the first three cycles. (a) CMS/LiCoO$_2$ battery; (b) CMS/LiMn$_2$O$_4$ battery; and (c) CMS/LiFePO$_4$ battery.
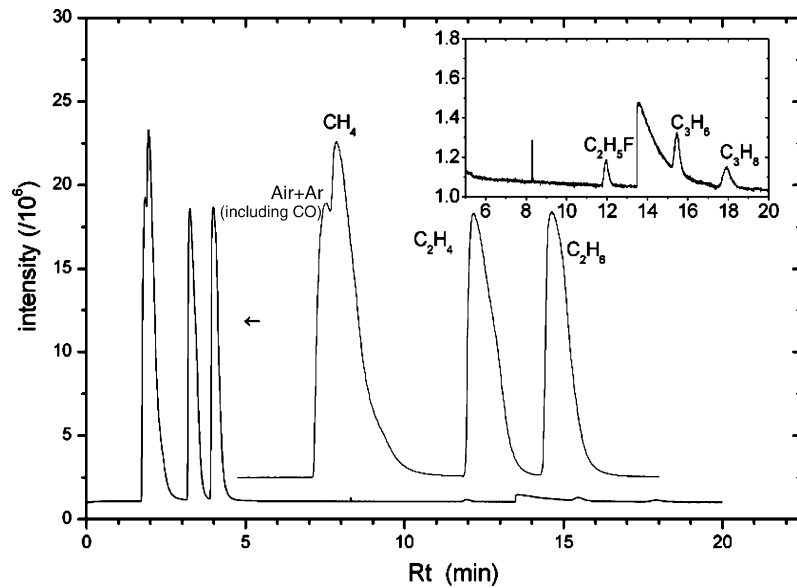
Fig. 2. The gas-chromatography of the CMS/LiCoO$_2$ battery under normal cycling condition (0.2C, 2.7–4.2 V). Species marked in the figures are determined by corresponding MS results.

the drilled hole and the Al–plastic sealing membrane, and then injected to the GC–MS equipment immediately.

3. Results and discussion

3.1. Battery performances

Fig. 1 shows charge and discharge curves of the battery with different cathode materials at 0.2C rate. It can be seen that the battery performances met the design requirements.

3.2. GC–MS result analysis

3.2.1. Gas generation behaviors inside the batteries under normal cycling conditions

GC–MS measurements were performed on three different batteries: CMS/LiCoO$_2$ (Fig. 2), CMS/LiMn$_2$O$_4$ (Fig. 3), and CMS/LiFePO$_4$ (Fig. 4). It can be seen that the gas species are same for all batteries under normal cycling conditions, including CO$_2$, CO, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$, and C$_2$H$_5$F, as identified by MS results. These components except the last species have been reported in the reference [5].
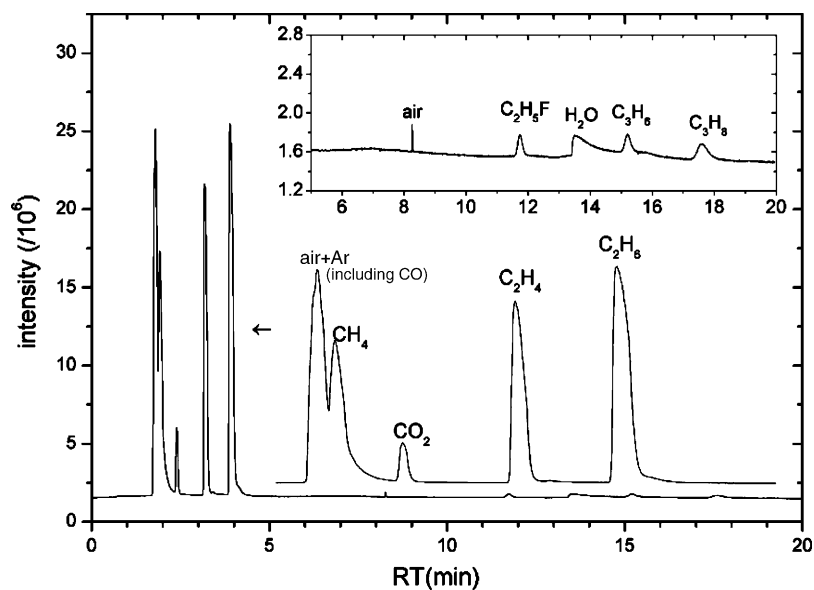

Fig. 3. The gas-chromatography of the CMS/LiMn$_2$O$_4$ battery under normal cycling condition (0.2C, 2.7–4.3 V). Species marked in the figures are determined by corresponding MS results.
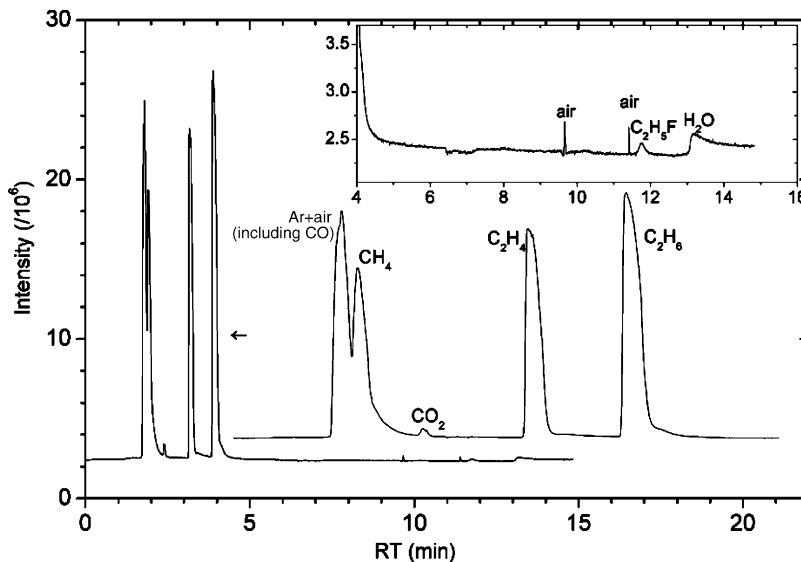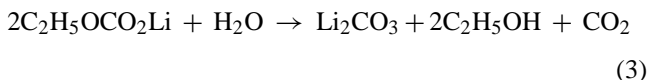
Fig. 4. The gas-chromatography of the CMS/LiFePO$_4$ battery under normal cycling condition (0.2C, 2.7–3.65 V). Species marked in the figures are determined by corresponding MS results.
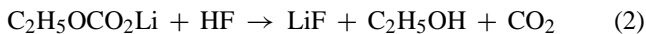
As discussed in the reference, CH$_4$, C$_2$H$_6$, C$_3$H$_6$, and C$_3$H$_8$ are produced from the reduction of DEC and radical on the surface of anode. CO and C$_2$H$_4$ are generated by the reduction reaction of EC. CO$_2$ gas could come from not only the air inside the batteries (dry room, containing CO$_2$ and O$_2$), but also can be generated in two different processes. One is the oxidation reaction of DEC with O$_2$ containing in the battery.

$$(C_2H_5O)_2CO + 6O_2 \rightarrow 5CO_2 + 5H_2O \tag{1}$$
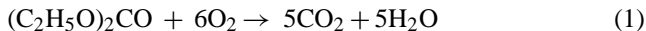
The other is the reaction of the ROCO$_2$Li with trace impurities (H$_2$O) and HF (decomposition product of LiPF$_6$) in the electrolyte (ROCO$_2$Li is produced by side reaction, which is a reaction of ROCO$_2$R with lithium ion [7]):

$$C_2H_5OCO_2Li + HF \rightarrow LiF + C_2H_5OH + CO_2 \tag{2}$$

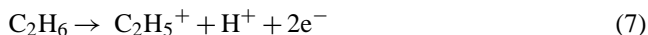$$2C_2H_5OCO_2Li + H_2O \rightarrow Li_2CO_3 + 2C_2H_5OH + CO_2 \tag{3}$$

Above results also show that the kind of gas product is not related to the type of the cathode materials.

The species of C$_2$H$_5$F is identified clearly by MS in Fig. 5. It is known that fluorinated alkylate (R–F) can be produced via the electrochemical oxidation of alkylate with HF. Actually, trace amount of HF is dissolved in the electrolyte due to the existence of trace H$_2$O inside the practical lithium-ion batteries. And C$_2$H$_5$$^\bullet$ radical and C$_2$H$_6$ are originated from the reactions of the anode with the electrolyte [5]. Therefore, there are two possible reactions to form C$_2$H$_5$F as listed below:

$$C_2H_6 \rightarrow C_2H_6^+ + e^- \tag{4}$$

$$C_2H_6^+ \rightarrow C_2H_5^\bullet + H^+ \tag{5}$$

$$C_2H_5^\bullet \rightarrow C_2H_5^+ + e^- \tag{6}$$

or

$$C_2H_6 \rightarrow C_2H_5^+ + H^+ + 2e^- \tag{7}$$

$$C_2H_5^+ + F^- \rightarrow C_2H_5F \tag{8}$$

These reactions should be occurred on the surface of cathodes, not related to the reactions between the anode and the electrolyte.

3.2.2. Gas generation behaviors inside the batteries under overcharge condition

Fig. 6 is the gas generation behavior under different charging voltages of the LiCoO$_2$/CMS battery. Under the low current density, for the overcharge condition, the species of generated gas for batteries with LiCoO$_2$ are not changed with different charging voltages ($\leq$5 V). But the amount
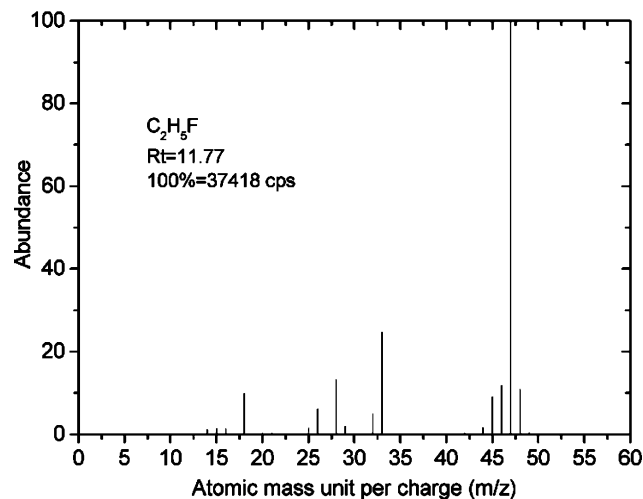

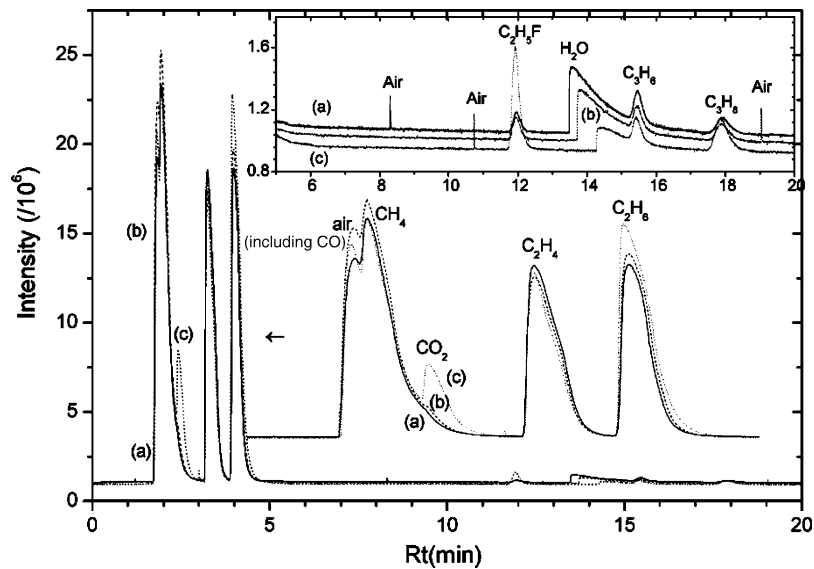Fig. 5. The MS of C$_2$H$_5$F detected out from the batteries.

Fig. 6. The gas-chromatography of the CMS/LiCoO$_2$ battery under different charging voltages (a) 4.2 V (solid), (b) 4.5 V (dash), and (c) 5.0 V (dot). Species marked in the figures are determined by corresponding MS results.

of gases increases with the rising of charging voltage, especially for CO$_2$ gas. It is known that O$_2$ is generated as a result of the decomposition of the overcharged delithiated LiCoO$_2$ [7] as in Eq. (9).

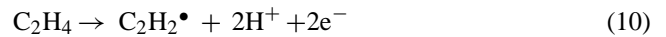$$3CoO_2 \rightarrow Co_3O_4 + O_2 \qquad (9)$$

It is obviously that higher charging voltage will lead to the production of larger amount of O$_2$ gas so that more CO$_2$ gas is produced from the reaction (1) consequently.

Fig. 7 shows the gas generation behaviors under different charge voltage of the LiMn$_2$O$_4$/CMS battery. When charged to 4.5 V, being different with the case of LiCoO$_2$ system, C$_2$H$_2$ is also detected out and its amount is increased with the

rising of charge voltage. As for LiFePO$_4$ cathode (see Fig. 8), when charged to 4.5 V, the relative intensity of C$_2$H$_2$ peak is higher. When charged to 5.0 V, more C$_2$H$_2$ gas product is produced. Based on above results, the production of C$_2$H$_2$ is related to the type of cathode materials and charging voltage.

We suggest that C$_2$H$_2$ is produced from the electrochemical oxidation reaction of C$_2$H$_4$ on the surface of cathode as Eq. (10).

$$C_2H_4 \rightarrow C_2H_2{}^{\bullet} + 2H^+ + 2e^- \qquad (10)$$

Under overcharging condition, comparing the oxidation ability of these cathode materials, delithiated LiCoO$_2$ generates more O$_2$ than others. The electrolyte and alkylates are
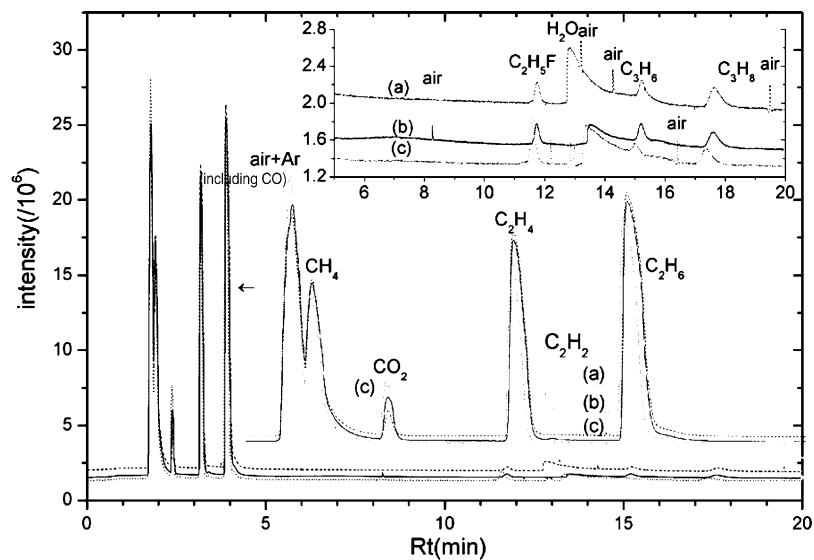

Fig. 7. The gas-chromatography of the CMS/LiMn$_2$O$_4$ battery under different charging voltages (a) 4.3 V (solid), (b) 4.5 V (dash), and (c) 5.0 V (dot). Species marked in the figures are determined by corresponding MS results.

Fig. 8. The gas-chromatography of the CMS/LiFePO$_4$ battery under different charging voltages (a) 3.65 V (solid), (b) 4.5 V (dash), and (c) 5.0 V (dot). Species marked in the figures are determined by corresponding MS results.
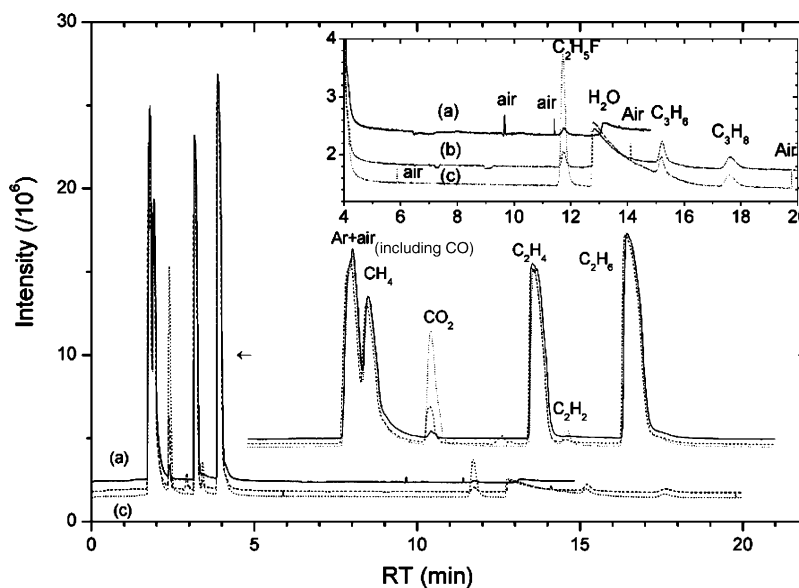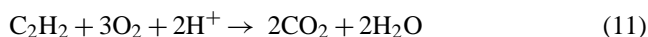
oxidized to form CO_2. Similarly to the reaction (1), C_2H_2 could be also oxidized further to transform into CO_2 as Eq. (11),

$$C_2H_2 + 3O_2 + 2H^+ \rightarrow 2CO_2 + 2H_2O \qquad (11)$$

Therefore, it is reasonable that C_2H_2 is not detected out and more CO_2 is found in the case of LiCoO$_2$ system. Obviously, reaction (11) is the third way to form CO_2 in the case of LiCoO$_2$-system.

While it is difficult for delithiated LiMn$_2$O$_4$ to give out O$_2$, the oxidation ability is not as strong as LiCoO$_2$. Therefore, it can oxidize alkylates partially to form CO_2 and C_2H_2 is still observed. As for LiFePO$_4$ cathode, the oxidation ability of this delithiated material is very poor even at overcharging state. Consequently, more C_2H_2 gas is detected in this case.

Based on above analysis, it is suggested that the amount of C_2H_2 inside the practical lithium-ion batteries under overcharging condition can be used to indicate the oxidation ability of delithiated cathode materials. Accordingly, oxidation ability of these three cathode materials is LiCoO$_2$ > LiMn$_2$O$_4$ > LiFePO$_4$.

It is well known that the safety order of the lithium-ion batteries for the same electrolyte and anode is LiFePO$_4$ > LiMn$_2$O$_4$ > LiCoO$_2$. According to above analysis and results, more fusible gas (C_2H_2) is produced in the case of LiFePO$_4$ battery. Therefore, the safety of a lithium-ion battery should be not related simply to the type of combustible gas species inside the battery, but probably the amount of the gas. The cathode materials with stronger oxidation ability may lead to the production of larger amount of gas, higher internal pressure of the battery, and large quantity of heat from the reaction, which decreases the battery safety.

4. Conclusions

It is found that gas generation behaviors under normal charging condition are not related to the type of cathode materials. While under overcharging condition, the amount and the type of gas species are influenced significantly by the oxidation ability of the cathode materials. More C_2H_2 is produced in LiFePO$_4$ battery due to its weak oxidation ability and more CO_2 is formed in LiCoO$_2$ battery because of its strong oxidation ability. The production of C_2H_2 can be used as a probe to compare the oxidation ability of the cathode material. It is found that the order of the oxidation ability for three cathode materials under overcharging state is LiCoO$_2$ > LiMn$_2$O$_4$ > LiFePO$_4$. In addition, C_2H_5F is also detected out as gas product in all batteries under normal or overcharging condition. It is produced from an electrochemical oxidation reaction from C_2H_6 with HF.

References

[1] D.D. MacNeil, Z. Lu, Z. Chen, J.R. Dahn, J. Power Sources 108 (2002) 8–14.
[2] A. Hammami, N. Raymond, M. Armand, Nature 424 (2003) 635.

[3] R.A. Leising, M.J. Palazzo, E.S. Takeuchi, K.J. Takeuchi, J. Power Sources 97–98 (2001) 681–683.

[4] Y. Saito, K. Takano, A. Negishi, J. Power Sources 97–98 (2001) 693–696.

[5] J.-S. Shin, C.-H. Han, U.-H. Jung, S.-I. Lee, H.-J. Kim, K. Kim, J. Power Sources 109 (2002) 47–52.

[6] G.A. Nazri, B. Yebka, in: C. Julien, Z. Stoynov (Eds.), Materials for Lithium-Ion Batteries, Kluwer Academic Publishers, 2000, pp. 161–178.

[7] K. Kumai, H. Miyashiro, Y. Kobayashi, K. Takei, R. Ishikawa, J. Power Sources 81–82 (1999) 715–719.