Short communication

Dynamic TGA–FTIR studies on the thermal stability of lithium/graphite with electrolyte in lithium-ion cell

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Abstract

Graphite anode could initialize the thermal runaway of lithium-ion cells due to its spontaneous exothermic reactions above the critical temperature. In order to explore the mechanisms of these reactions, a series of experiments were carried out with on-line coupled thermogravimetric analyser–Fourier transform infrared spectrometer (TGA–FTIR). The reactions under study essentially involved metallic lithium reacting with electrolyte and the thermal decomposition of natural graphite GDR at various states of charge (SOC). It is found that metallic lithium reacts with ethylene carbonate (EC) violently at around 180 °C producing CO_2 and dilithio butylene dialkoxide which could further react with $LiPF_6$ and/or PF_5 to produce POF_3. At the relatively low temperature (about 60 °C), CO_2 produced from both 0% SOC and 100% SOC GDR samples is attributed to the decomposition of organic compounds in solid electrolyte interface (SEI) film. In addition, the amount of POF_3 produced from 0% SOC GDR sample is more than that from 100% SOC GDR sample. Further, fully intercalated GDR sample shows a structural collapse, a solid-state exothermic reaction at ∼260 °C. Based on the TGA–FTIR results obtained from these exothermic reactions, detailed thermal decomposition paths are proposed in this paper.

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Keywords: TGA–FTIR; Graphite anode; SEI film; Thermal runaway; Li-ion cell

1. Introduction

It is well known that the thermally unstable lithiated graphite can cause safety issues of Li-ion cells: primary SEI (P-SEI) film decomposition is an exothermic reaction which could initialize a series of exothermic reactions, such as the reaction between intercalated lithium and electrolyte to form a secondary SEI (S-SEI) film, and the structure collapse of lithiated graphite [1]. In this paper, the P-SEI film is the film electrochemically formed on the graphite surface during initial cycles, while the S-SEI film is the film chemically formed on the graphite surface during thermal runaway process [1,2]. Extensive studies have been carried out to investigate the thermal runaway mechanism, but most studies were only focused on the thermal behavior, e.g. onset temperature, peak temperature and enthalpy, via either DSC or ARC techniques [1–5]. Several possible reaction pathways [1,2] were proposed but without further verification. In addition, the

extremely complex compositions of the P-SEI film (such as lithium ethylene dicarbonate [6], lithium oxalate [7], lithium methoxide [7], and more), with electrolyte precipitates and inter-calated/trapped lithium, make the thermal runaway mechanism exploration more difficult. In order to clarify this mechanism, we performed the on-line coupled TGA–FTIR tests of various samples: metallic lithium with electrolyte and natural graphite GDR samples at various SOCs. TGA–FTIR makes it possible to study detailed thermal decomposition path by monitoring evolution of gas products as a function of temperature and weight change. Specifically, the reaction products and their relative abundance extracted from infrared spectra acquired during the TG analysis could be easily related to sample weight loss.

2. Experimental

The graphite anodes laminated on the 25 μm thick copper current collector were composed of 92% natural graphite GDR and 8 wt.% polyvinylidene fluoride (PVDF) binder with a loading of 4.37 mg cm^{-2} active material. Electrochemical cells were assembled in Argon filled glove box (water and oxygen contents

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<10 ppm). The electrochemical cells were made from Swagelok fittings with graphite anodes (1.6 cm^2 area), Li reference and counter electrodes, and a Celgard (3501) as the separator. The electrolyte used was 1.2 M LiPF$_6$/ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 wt.%) (Quallion). The graphite anodes were galvanostatically charged/discharged at a low rate of C/25 (60 μA cm^{-2}) using a battery cycler (BT-2043 Arbin cycler, College Station, TX) between 1 V versus Li/Li$^+$ and 10 mV versus Li/Li$^+$ for two formation cycles to build up the solid electrolyte interface. The cells were finally charged to different states of charge (0% SOC or 100% SOC), for TGA measurements. After opening the cell in the Ar-filled glove box carefully, the extra electrolyte was removed from the surface of the electrode and the electrode materials were recovered from the current collector and used as TGA samples. Metallic Li and 1 M LiPF$_6$/ethylene carbonate (EC) were used as received. The water content of the electrolyte is less than 10 ppm. All the sample handlings were performed in an inert atmosphere with no air exposure even momentarily.

The on-line TGA–FTIR is consisted of a thermogravimetric analyzer (TGA model 2960, TA Instruments) and a Fourier Transform Infrared Spectrometer (Nexus 470, Nicolet) equipped with a temperature controlled transmission gas cell. The coupling between TGA and FTIR is via quartz capillary array. Both FTIR gas cell and the capillary array were heated to 200 °C while running the experiments to prevent deposits on the gas cell and capillary walls. To ensure inert atmosphere environment, TGA and FTIR gas cell and the coupling line were all housed in Argon atmosphere (glovebag), while FTIR spectrometer was completely isolated from the gas cell, capillary array and TGA. Special care was taken to ensure that FTIR optical path was properly purged in such a way that background infrared signal from residual moisture and carbon dioxide (CO$_2$) is negligible during the experimental run. The inert working condition of on-line TGA–FTIR was checked with copper oxalate by following Mullen et al.'s [8] work.

The on-line TGA–FTIR measures the change in sample weight as a function of temperature under non-isothermal condition, 10 °C min^{-1}, while simultaneously monitoring the volatile components evolved from samples as a result of thermal decomposition. The gas phase products were continuously transferred to FTIR gas cell through capillary array by using Ar as carrier gas, containing less than 10 ppm of moisture, at a flow rate of 220 ml min^{-1}. The FTIR spectra were continuously acquired at a resolution of 4 cm^{-1} and summed over 32 scans during the thermogravimetric (TG) measurements. The mass loss reported in this work has 1% error. In all the experiments, the heat rate of TGA is 10 °C min^{-1} and the flow rate of Ar carrier gas containing less than 10 ppm moisture is 220 ml min^{-1}.

3. Results and discussions

Thermogravimetry (TG) and derivate thermal analysis (DTA) profiles of metallic Lithium with electrolyte (1 M LiPF$_6$ in EC) obtained, at a heating rate of 10 °C min^{-1}, is presented in Fig. 1A. The mass of the remaining solid residue is about 16 wt.% of its original mass when temperature reaches 300 °C.
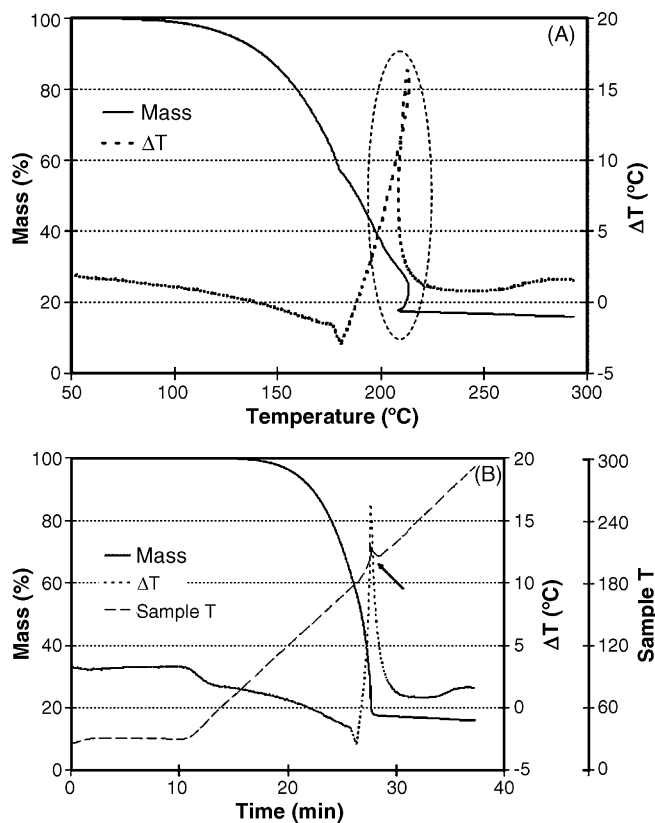

Fig. 1. (A) Mass loss (left) and derivative thermal analysis ΔT (right) vs. temperature during thermal decomposition of metallic with 1 M LiPF$_6$/EC electrolyte (1.452 mg Li + 19.834 mg electrolyte) at a heating rate of 10 °C min^{-1} in argon (flow rate: 220 ml min^{-1}) containing <10 ppm H$_2$O; (B) mass loss (left), ΔT (1st right) and sample temperature (2nd right) vs. experiment time in the same experiment.

The fluctuation observed between 200 °C and 220 °C in both TG and DTA curves (circled with the dashed line) can be attributed to a huge exothermic reaction happened at about 200 °C which causes a drastic increase in the sample temperature over the target temperature (over shoot). To clarify this, the TG, DTA and sample temperature are also plotted versus experiment time in Fig. 1B. The overshoot sample temperature is very clear in Fig. 1B as marked by the arrow. The overshoot sample temperature cools down to target temperature after the exothermic reaction which causes TG and DTA curves back and forth in Fig. 1A. The evolution of gas products as a result of sample thermal decomposition or volatilization was simultaneously monitored by FTIR during TGA experiment and is presented in Fig. 2A. The typical FTIR spectrum acquired at 208 °C, along with standard spectrum of gas-phase EC, PF$_5$, POF$_3$ and HF are shown in Fig. 2B. As seen clearly in Fig. 2B, only CO$_2$, POF$_3$ and EC are detected in the gas phase. No other species, such as PF$_5$ and HF are detected. The evolution of carbon dioxide starts from ∼60 °C, and constantly evolves at a rate of 0.00048 a.u. mg^{-1}, till ∼190 °C. Then the evolution rate of carbon dioxide dramatically increases and forms a sharp peak at 208 °C. There is a second small CO$_2$ evolution peak centered at 228 °C. The EC evaporation can be detected by FTIR in a broad temperature range, from 90 °C to 290 °C, with the peak temperature
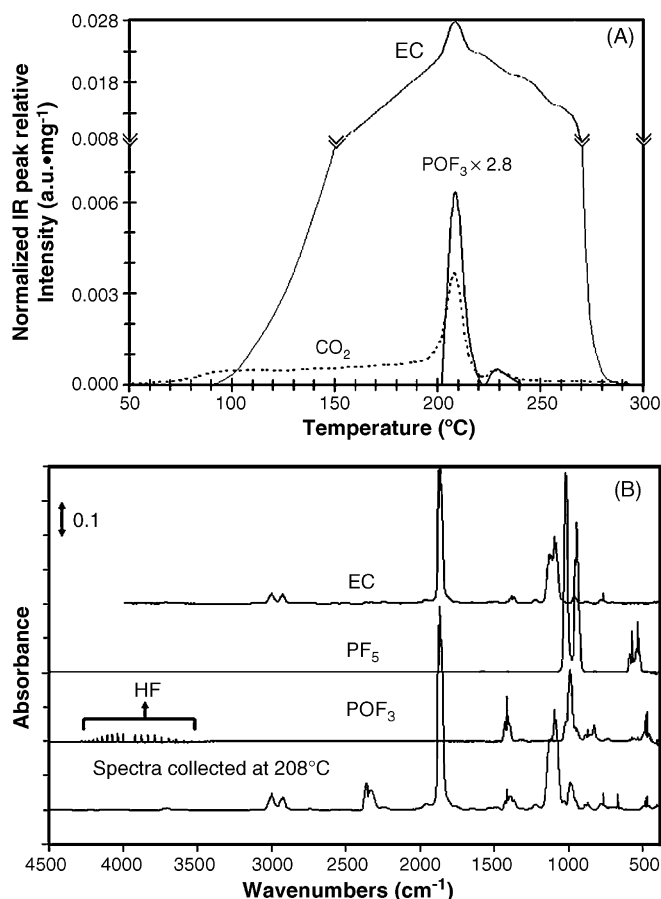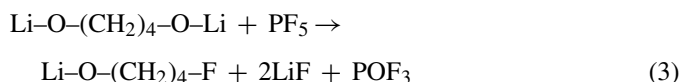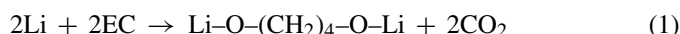
Fig. 2. (A) Evolution of gaseous products as a function of temperature during the same experiment as in Fig. 1. The following infrared peak intensities (EC 1876 cm^{-1}, POF$_3$ 1415 cm^{-1} and CO$_2$ 2362 cm^{-1}) were selected to represent each gas phase product (the same selected infrared peak intensities are applied in Figs. 3B and 4B); (B) the spectra collected at 208 °C during the experiment (bottom) and the standard FTIR spectra of the gas phase EC (top), PF$_5$ (second), POF$_3$ and HF (third).

at 208 °C. The evolution of POF$_3$ between 200 °C and 240 °C shows two maximums that correspond to two different reactions: the first sharp peak starting at 201 °C centers at 208 °C; the second small peak follows the first peak and centers at 228 °C. As observed from the results obtained, the exothermic peak in DTA curve (at about 200 °C) corresponds to the sharp peaks of CO$_2$ and POF$_3$ evolution in the FTIR curves which suggests that at least one of them, or both are produced by exothermic reactions. In our previous TGA–FTIR thermal studies of 1 M mLiPF$_6$ in EC [9], we clearly described that the salt decomposes to LiF and gas phase PF$_5$, while EC evaporates to gas phase without any decomposition or reaction. PF$_5$ further hydrolysis to POF$_3$ and HF when some moisture is present. However, in the presence of some metallic Li, small portion of EC decomposes to CO$_2$. Moreover, only POF$_3$, instead of PF$_5$, is detected as the gas phase product from the decomposition of salt. This POF$_3$ cannot be produced by involving moisture, since no HF is detected along with the POF$_3$. We propose the following reactions (1)–(3) for the above experiment data: metallic lithium reacts with EC to produce carbon dioxide and dilithio butylene dialkoxide; the PF$_5$ decomposed from salt reacts with dilithio butylene dialkoxide

to produce POF$_3$.

$$2Li + 2EC \rightarrow Li-O-(CH_2)_4-O-Li + 2CO_2 \quad (1)$$

$$LiPF_6 \rightarrow LiF + PF_5 \quad (2)$$

$$Li-O-(CH_2)_4-O-Li + PF_5 \rightarrow$$
$$Li-O-(CH_2)_4-F + 2LiF + POF_3 \quad (3)$$

Or salt reacts with dilithio butylene dialkoxide directly to produce POF$_3$,

$$Li-O-(CH_2)_4-O-Li + LiPF_6 \rightarrow$$
$$Li-O-(CH_2)_4-F + 2LiF + POF_3 \quad (4)$$
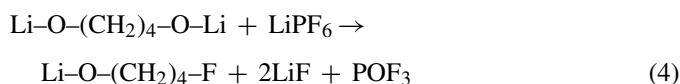
The mechanisms for the second CO$_2$ and POF$_3$ evolution peaks are not clear yet and need further exploration. The weight ratios of Li, LiPF$_6$ and EC in the initial sample are 6.8%, 12.3%, 80.9%, respectively. Their corresponding molar ratio is 0.2 mmol:0.017 mmol:0.2 mmol. Since no PF$_5$ or other fluoride compounds is detected in the gas phase, we can conclude that all salt decomposes to POF$_3$. In addition, the integrated areas of the evolution of CO$_2$ and POF$_3$ are 0.12 and 0.06, respectively, indicating that the amounts of reacted Li and EC in the current experiment, both are 0.034 mmol. Therefore the remaining mass is calculated as 17.8 wt.% of its original mass, which is very close to the experiment data of 16 wt.%.

Fig. 3A presents the TG, DTA and DTG profiles of 0% SOC GDR sample which contains fully delithiated graphite Li$_0$C$_6$, P-SEI film, and remaining electrolyte (mainly LiPF$_6$ and EC). The selected infrared peak intensity, representative of all the gas phase products from either evaporation of the electrolyte or thermal decomposition of the P-SEI film in moisture free environment are shown in Fig. 3B. In Fig. 3A, The TG curve shows that the mass loss of this sample has three clear stages. The first stage is the quick mass loss of 17 wt.% (i.e., 83 wt.% of its original mass in the temperature range from 50 °C to 156 °C). In addition, the DTA curve shows that the first stage is an exothermic reaction as *marked by the arrow*. In the DSC studies [1,3] of fully deintercalated graphite sample, an exothermic reaction was also detected in the similar temperature range. This exothermic peak has been attributed to the P-SEI film breakdown [1–3]. As shown in Fig. 3B, EC, CO$_2$ and POF$_3$ are the gaseous products detected by FTIR in this stage. The EC evaporates from 83 °C to 210 °C and centers at 164 °C. Most probably the EC remains intact without any decomposition since the graphite sample contains no lithium at fully discharge state. CO$_2$ evolution starts ~60 °C and reaches peak temperature of 115 °C. Another small CO$_2$ spike followed with the first sharp peak ends at 184 °C. We would like to attribute the CO$_2$ evolution peaks to the decomposition of metastable organic compounds in P-SEI film, such as lithium ethylene dicarbonate and/or lithium butylene dicarbonate, etc.

$$(R-OCOOLi)_2 \rightarrow (R-O-Li)_2 + 2CO_2 \quad (5)$$
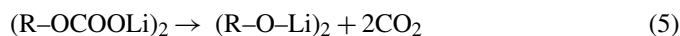
where R is either CH$_2$ or C$_2$H$_4$. The onset temperature of bulk lithium ethylene dicarbonate decomposition is 59 °C (unpublished data). The evolution of POF$_3$ starts from 150 °C and peaks
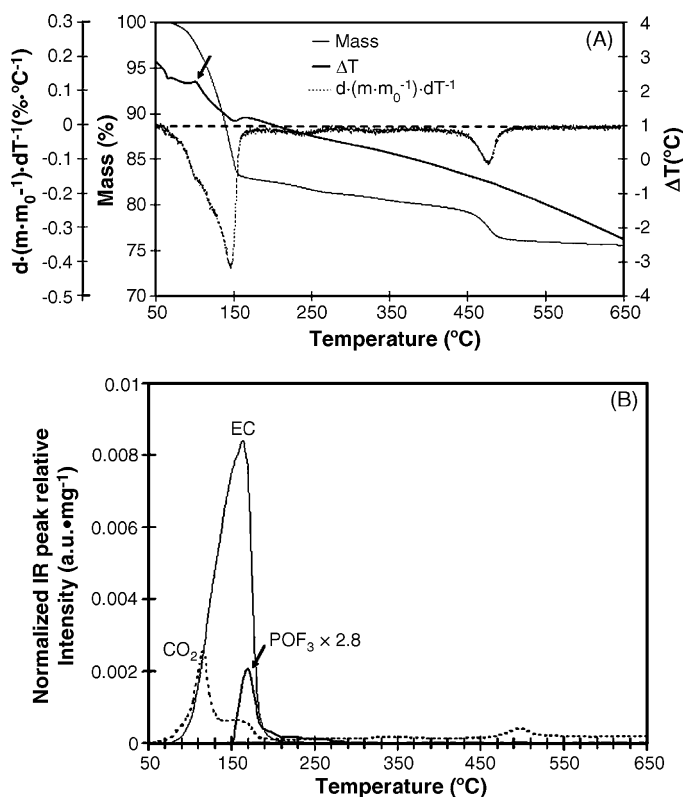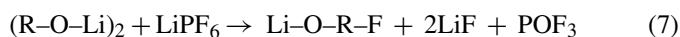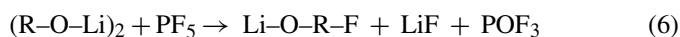
Fig. 3. (A) The rate of mass loss (1st left), mass loss (2nd left) and ΔT (right) profiles as a function of temperature during the thermal decomposition of 0% SOC GDR sample (Li_0C_6) at a heating rate of $10\,^\circ C\,min^{-1}$ in argon (flow rate: $220\,ml\,min^{-1}$) containing <10 ppm H_2O; (B) gaseous products distribution as a function of temperature obtained from the same experiment.
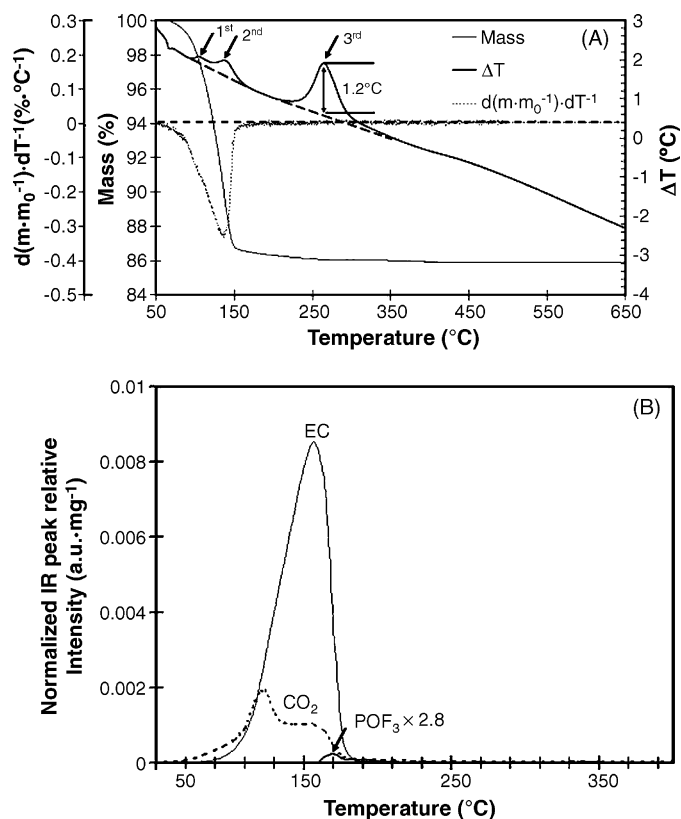

Fig. 4. (A) The rate of mass loss (1st left), mass loss (2nd left) and ΔT (right) profiles as a function of temperature during the thermal decomposition of 100% SOC GDR sample ($Li_{0.9}C_6$) at a heating rate of $10\,^\circ C\,min^{-1}$ in argon (flow rate: $220\,ml\,min^{-1}$) containing <10 ppm H_2O; (B) gaseous products distribution as a function of temperature obtained from the same experiment.

at $170\,^\circ C$. Our previous experiment clarified that POF_3 is produced by either PF_5 or $LiPF_6$ reacting with dilithio butylene dialkoxide. Therefore, in this case, we would like to attribute the evolution of POF_3 to that PF_5 and/or salt to react with the P-SEI compounds, such as lithium alkyl dioxide.

$$(R–O–Li)_2 + PF_5 \rightarrow Li–O–R–F + LiF + POF_3 \qquad (6)$$

$$(R–O–Li)_2 + LiPF_6 \rightarrow Li–O–R–F + 2LiF + POF_3 \qquad (7)$$

Since both EC evaporation and bulk lithium ethylene dicarbonate decomposition are endothermic, the exothermic heat detected in the first stage can only be associated with the reactions (6) and (7). Further mass loss of 4 wt.% (i.e., 83–79 wt.%) is observed in the second stage between $156\,^\circ C$ and $455\,^\circ C$ with traces of CO_2 evolution. This stage can be attributed to the continuous decomposition of many meta-stable SEI organic compounds. The last stage (79–76 wt.%) followed right after the second stage is also a quick mass drop in the temperature range of 455–$500\,^\circ C$. This stage is also accompanied with the evolution of CO_2 with the peak temperature at $500\,^\circ C$. The last CO_2 peak can be attributed to the decomposition of lithium alkyl oxide, such as lithium methyl oxide (onset T, $473\,^\circ C$, peak T, $513\,^\circ C$, unpublished data).

However, in the TGA test of 100% SOC GDR sample ($Li_{0.9}C_6$), there is only one mass loss stage starting from $71\,^\circ C$ and ending at $\sim190\,^\circ C$ as shown in Fig. 4A. The final remaining

mass of this sample, 86 wt.% of its original mass, is larger than that of 0% SOC sample (76 wt.%). This suggests that more compounds are trapped as solid residues when intercalated Lithium is present. As marked by the arrows, DTA curve shows two small exothermic peaks from $96\,^\circ C$ to $162\,^\circ C$. The first exothermic peak can be associated with the decomposition of the P-SEI film as we described in the previous part, while the second exothermic reaction can be attributed to the formation/decomposition of the S-SEI film [1,2]. Fig. 4B presents all the detected gas phase products. The EC evaporates from $83\,^\circ C$ to $190\,^\circ C$ and centers at $150\,^\circ C$. The integrated peak area of EC is 0.42 for 0% SOC sample (Fig. 3B), while it is only 0.23 for 100% SOC sample (Fig. 4B). The reason for less EC evaporated from the sample $Li_{0.9}C_6$ is that a part of the EC is consumed by the reaction between the intercalated Lithium to form the S-SEI film as indicated in reaction (1). To our surprise, except for the evaporation of EC, CO_2 is the main gas produced from the sample $Li_{0.9}C_6$. The evolution of CO_2 starts at $\sim60\,^\circ C$ and reaches peak temperature at $124\,^\circ C$, followed with a small *hump* which ends at $191\,^\circ C$. The CO_2 is produced by the decomposition of P-SEI film as reaction (5) and the reaction between intercalated lithium and EC as reaction (1). Only tiny amount of POF_3 is detected from $164\,^\circ C$ to $210\,^\circ C$. Since no other fluoride gaseous compounds are detected in the whole temperature range, it seems that most fluoride elements are trapped as the solid residues as

following:

$$POF_3 + 2x Li \rightarrow Li_x POF_{3-x} + x LiF \qquad (8)$$
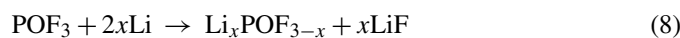
In the first experiment carried out with metallic lithium and EC, the above reaction is unlikely to occur. The reasons are listed as below: (i) the dilithio butylene dialkoxide formed by reaction (1) could cover the bulk lithium surface completely preventing the contact between POF_3 and lithium; (ii) the residual mass in this experiment is 16 wt.%, lower than 17.8% which is calculated without the reaction (8); the calculated residual mass would be even higher than 17.8% if reaction (8) occurred. Assuming reactions (1) and (8) are the main reactions to form the S-SEI film, the overall heat produced in the formation of this film should be proportional to the amount of consumed lithium. This is proved by Yang et al. [1] in their DSC studies of lithiated natural graphite Mag-10 samples by examining the overall enthalpy versus the amount of intercalated Lithium: when the P-SEI film decomposition and the S-SEI film formation are the only reactions occurring in the thermal runaway (this is valid when the intercalated lithium is less than 0.37 per C_6 for Mag-10), the overall enthalpy exhibits a good linear relationship with the amount of intercalated Lithium. In DTA curve (Fig. 4A), the third large exothermic peak detected from 225 °C to 310 °C and peaked at 269 °C can be claimed as the structure collapse of the lithiated graphite [1]. Obviously this is only a solid-state exothermic reaction since no mass loss or gas evolution has been detected. With the DSC and XRD techniques, it is proved that the lithiated graphite $Li_x C_6$ would lose its structure and release the intercalated Lithium at high temperature when x is more than 0.3.

$$Li_x C_6 \rightarrow x Li + 6C \qquad (9)$$

4. Conclusions

In the thermal studies of metallic lithium/electrolyte via on-line coupled TGA–FTIR technique, mild CO_2 evolution is detected from 60 °C which can be attributed to the lithium reacting with EC. This reaction becomes violent when temperature exceeds 190 °C. Moreover, the product from this reaction, dilithio butylene dialkoxide, reacts with $PF_5/LiPF_6$ very strongly at 200 °C to produce gaseous POF_3. Both reactions are exothermic and produce large amounts of heat. As for the fully delithiated GDR sample, the organic compounds in P-SEI film decompose and produce CO_2 from 60 °C to 650 °C. In addition, the organic compounds and/or their decomposition products react with $PF_5/LiPF_6$ producing POF_3 in the temperature range from 150 °C to 270 °C. However, for fully lithiated graphite sample, most POF_3 and partial EC are trapped as solid residues by exothermally reacting with intercalated Li to form the S-SEI film. Furthermore, the graphite structure collapse at 260 °C is proved to be a solid-state exothermic reaction. As a result, all these exothermic reactions, such as the decomposition of P-SEI film and the formation of S-SEI film, must be considered in order to improve the thermal stability and safety of lithium-ion cells.

Acknowledgements

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