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Study on thermal decomposition of lithium hexafluorophosphate by TG–FT-IR coupling method

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Abstract

Using TG–FT-IR coupling method, direct evidences of the decomposition process of lithium hexafluorophosphate had been obtained. Studies showed that $LiPF_6$ is stable under normal temperature when the content of water is very low. When heated, $LiPF_6$ would react with the trace water in the air. HF and OPF_3 would be released in the same time which could be detected from the FT-IR spectra collected in situ. The peak temperature of the decomposition of $LiPF_6$ varied from 192.93 °C (average heating rate 2.0 °C min^{-1}) to 223.83 °C (average heating rate 20.0 °C min^{-1}). Based on the on-line FT-IR spectra, the characteristic absorption bands of $PF_6{}^-$ in the decomposed substances were detected for the first time which might come from the reaction of trace HF with PF_5.
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1. Introduction

It is no doubt that the research of $LiPF_6$ is one of the hottest fields in Li-ion battery industry all over the world. Because of its high conductivity and good electrochemical stability, $LiPF_6$ is widely used in production of Li-ion batteries. But the thermal stability of $LiPF_6$ still confused most of researchers.

Ravdel et al. [1] had made a relatively thorough study on the thermal decomposition of $LiPF_6$ and its solutions in ethylene carbonate (EC), dimethyl-carbonate (DMC), diethylcarbonate (DEC) and ethylmethylcarbonate (EMC). Moshkovich et al. [2] had also mentioned the decomposition equilibrium of $LiPF_6$ in electrolytes. Other researchers, such as Oesten et al. [3] and Heider et al. [4] also had given similar conclusion of the decomposition mechanism of $LiPF_6$. Most of them have mentioned the reaction of $LiPF_6$ with water in the decomposition process, which can be shown as

$$LiPF_6 + H_2O \rightarrow LiF + OPF_3 + 2HF \qquad (1)$$

But there are lack of more direct and convictive evidences except Moshkovich et al. [2] proved that the peaks of $LiPF_6$, POF_3 and PF_5 were emerged using ^{31}P and ^{19}F NMR in oxidized $LiPF_6$ solutions after electrolysis at potentials around 5 V using ^{31}P and ^{19}F NMR. In their studies, most researchers had mentioned the heat flow changes in the thermal decomposition of $LiPF_6$, but none of them had presented more completed decomposition mechanism and reactions in the whole process.

In our work, FT-IR and TG coupling technique was used to obtain the on-line information during the thermal decomposition of $LiPF_6$.

2. Experimental

2.1. Materials

High purity $LiPF_6$ (99.99%) was obtained from Sigma-Aldrich, Inc. High purity (99.999%) argon was obtained from Qinghai Laoqian Gas Limited Corporation.

2.2. Processing conditions

All the samples were prepared in an argon atmosphere glove box (H_2O less than 10^{-6} mg L^{-1}, O_2 less than 10^{-6} mg L^{-1}) made by M. Braun Corporation. Two special 10 cm long stainless gas cells were designed to determine the FT-IR spectra of LiPF$_6$ outside the glove box. The KBr windows of the gas cells are the products of Thermo-Nicolet Corporation.

The in situ FT-IR measurements were performed on Thermo-Nicolet Model Nexus FT-IR spectrometer. Number of background and sample scans is 10 and 32 times, respectively. The resolution during the experiments is 4 cm^{-1}. Total number of scan points is 8480 and total time of collection is 60.28 min.

The in situ TG measurements were conducted using a TA Instruments SDT Q600. The LiPF$_6$ sample was measured in a 90 μL ceramic pan from 25 to 500 °C with the average heating rate of 2, 5, 10, 15 and 20 °C min^{-1}. All the pans were pretreated in a muffle furnace under 1000 °C.

The Nexus FT-IR spectrometer and SDT Q600 analyzer were coupled by a Thermo-Nicolet TGA Interface Model II, of which the stainless transfer line and quartz gas cell can be heated to as high as 300 °C and be kept at certain temperature separately.

The room temperature is 20 °C and the relative humidity is 45% during the experiments.

3. Results and discussion

In our former studies [5], the TG–DTG decomposition curves of LiPF$_6$ had three decomposition peaks which were in accordance with the studies of Ravdel [1]. But in this series of experiments, repeated experiments showed that there were only two decomposition peaks during the decomposition process of LiPF$_6$ shown as Fig. 1. The possible reason was that purity of argon in former studies was too low.
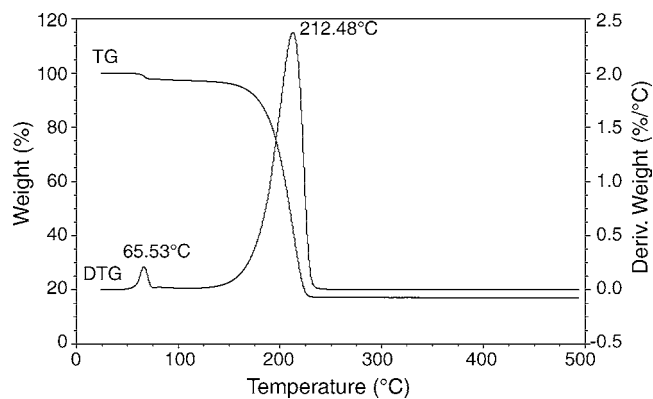

Fig. 1. TG–DTG curves of LiPF$_6$ heated from 25 to 500 °C (average heating rate: 10 °C min^{-1}).
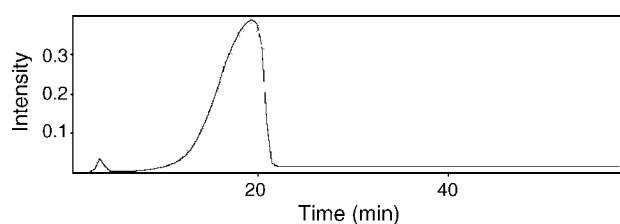

Fig. 2. Detected signals intensity of decomposed products during the decomposition process of LiPF$_6$.

What is more, the decomposition peak temperature of the LiPF$_6$ depended on the heating rate strongly. Table 1 showed the results of the relationship between the peak temperature and average heating rate.

Table 1 revealed that the decomposition peak temperature of LiPF$_6$ changed greatly when average heating rate changed. The gap of peak 1 is 21.64 °C and the gap of the peak 2 even goes to 30.9 °C at different heating rate.

As expected, the in situ FT-IR spectrometer had also shown two strong signals. Gram-Schmidt figure during the decomposition of LiPF$_6$ is shown as Fig. 2.
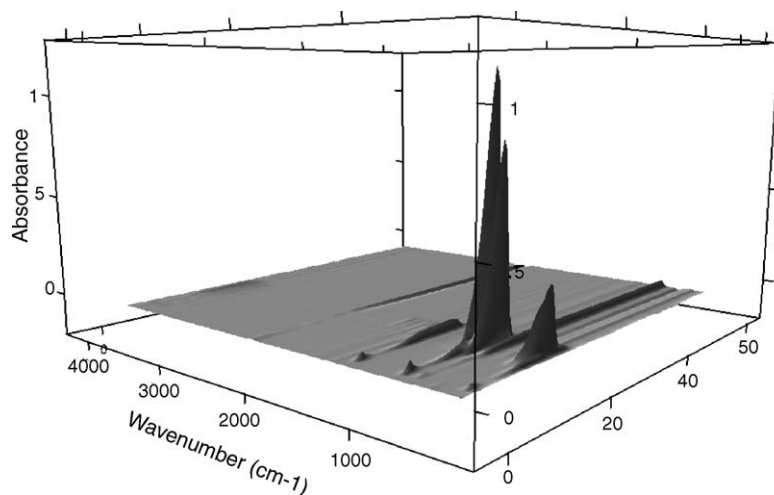

Fig. 3. The 3-dimension grams of LiPF$_6$ during the whole decomposition process.

Table 1
Relationship between average heating rate and decomposition peak temperature of LiPF$_6$

Average heating rate (°C min^{-1})	Temperature of peak 1 (°C)	Temperature of peak 2 (°C)
2.0	53.35	192.93
5.0	60.49	199.23
10.0	65.53	212.48
15.0	71.84	215.00
20.0	74.99	223.83

More directly, 3-dimension grams during the whole process were shown as Fig. 3.

According to Fig. 2, three typical FT-IR spectra were analyzed which were collected at the peak positions of 6.409, 21.374 min and one of the flat position (42.216 min). The three FT-IR spectra were shown as Fig. 4.

The spectrum at 6.409 min in Fig. 4 agreed well with that of OPF$_3$ except one peak in 345 cm^{-1}, which was shown in Table 2 [6].

Because the FT-IR spectrometer used in experiment can only determine the brand between 4000 and 400 cm^{-1}, the absorption peak of 345 cm^{-1} cannot be tested. But from the above spectrum, we still can conclude that there was OPF$_3$ in the first decomposition step of LiPF$_6$. The spectrum at 21.374 min in Fig. 4 was most probably caused by PF$_5$, the reported and theoretical absorption values of PF$_5$ and the values tested were shown in Table 3 [6,7].

Table 3 showed that the difference between the theoretical and the determined absorption values of PF$_5$ was great, but the reported values agreed better with the experimental values. Combined the characteristic absorptions with peak shape of PF$_5$ [7], spectrum at 21.374 min in Fig. 4 must be PF$_5$.
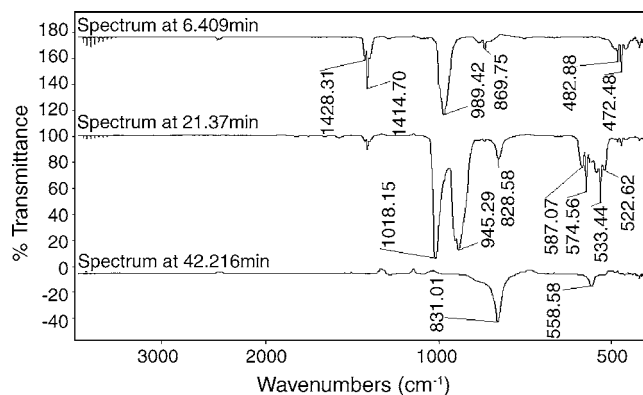

Fig. 4. FT-IR spectra of decomposed products of LiPF$_6$ at 6.409, 21.374 and 42.216 min.

During the end process (without mass loss) of the decomposition of LiPF$_6$, there should be no any other peaks i.e. no other new substance. But when the FT-IR spectra were collected and analyzed, the results showed that there was another new substance formed during the process which was shown as spectrum at 42.216 min in Fig. 4.

The two absorption bands at 831.01 and 558.58 cm^{-1} are in accordance with the absorption values of PF$_6^-$ which have two characteristic absorption bands at 820–860 and 550–565 cm^{-1} [8]. Theoretically, the substance detected could not be LiPF$_6$ in the end process. So the only possible substance should be HPF$_6$ which is caused by the reaction of PF$_5$ with trace HF decomposed via former step. The possible chemical reaction can be shown as Eq. (2). But why the HF was not totally blown off by argon needs further studies:

$$PF_5 + HF \rightarrow HPF_6 \qquad (2)$$

Table 2
Vibration modes and absorption values of OPF$_3$

Items	OPF$_3$					
Vibration modes	ν_1(A$_1$), ν(XY$_3$)	ν_2(A$_1$), ν(XZ)	ν_3(A$_1$), δ(XY$_3$)	ν_4(E), ν(XY$_3$)	ν_5(E), δ(XY$_3$)	ν_6(E), ρ_r(XY$_3$)
Reported value	873	1415	473	990	485	345
Tested value	869.75	1414.70	472.48	989.42	482.88	

Table 3
Relative FT-IR absorption values of PF$_5$

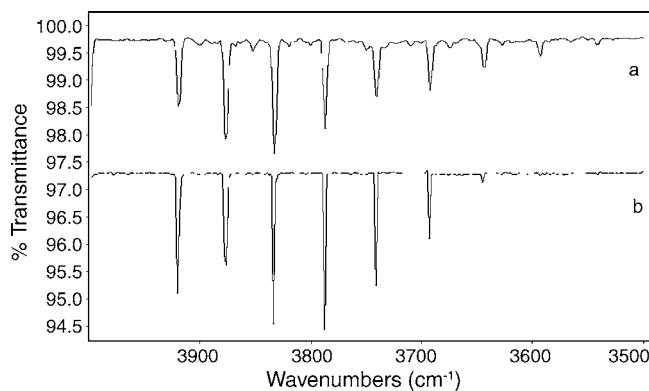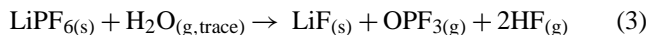| PF$_5$ vibration modes	Absorption values (cm^{-1})			
	Theoretical 1 (Hyper Chem)	Theoretical 2 (Spartan)	Reported	Determined
ν_1	185.61	145.86		
ν_2	185.80	375.46	300	
ν_3	472.07	375.46		
ν_4	472.64	534.78		
ν_5	505.24	593.45	575	574.56
ν_6	506.14	593.45	532	533.44
ν_7	545.13	599.26	640	587.07
ν_8	790.62	716.96	514	522.62
ν_9	867.08	867.38	817	828.58
ν_{10}	1163.85	1101.34	944	945.29
ν_{11}	1179.54	1103.97	1026	1018.15
ν_{12}	1180.10	1103.97		

Fig. 5. FT-IR spectra of enlarged former part of spectrum at 6.409 min (a) and HF in HR Nicolet TGA Vapor Phase libraries (b).

If we carefully observe all the three FT-IR spectra in Fig. 4, it seems to be another spectrum in all former part of three spectra. The search result showed that the detected FT-IR spectra are in accordance with the spectrum of standard HF. The FT-IR spectra of the enlarged former part of the spectrum at 6.409 min in Fig. 4 and the standard HF in the HR Nicolet TGA Vapor Phase libraries [9] were shown as spectrum a and b in Fig. 5.

It is obvious that the two spectra are exactly the same one, which proved that there was HF during the whole decomposition process of $LiPF_6$.

Up to now, we can safely conclude that the whole decomposition of $LiPF_6$ should be described as one hydrolysis step (Eq. (3)), one decomposition step (Eq. (4)) and the relative chemical reaction of PF_5 and HF (Eq. (5)):

$$LiPF_{6(s)} + H_2O_{(g,trace)} \rightarrow LiF_{(s)} + OPF_{3(g)} + 2HF_{(g)} \quad (3)$$

$$LiPF_{6(s)} \rightarrow LiF_{(s)} + PF_{5(g)} \quad (4)$$

$$PF_{5(g)} + HF_{(g)} \rightarrow HPF_{6(g)} \quad (5)$$

Because above experiments were conducted in TA Q600 analyzer which cannot isolate sample from air totally. And the above results revealed that the first decomposition peak in TG curves was caused by the reaction of $LiPF_6$ with trace water in air. So another series of experiments below were performed to further study the decomposition behaviors of $LiPF_6$.

Firstly, a special designed hermetic gas cell which can be put into the TGA interface was put into the glove box. Secondly, proper amount of $LiPF_6$ was loaded in the gas cell. Thirdly, the gas cell was carefully assembled and transferred into the TGA interface. At last, the FT-IR spectra of the sample were collected at certain desired temperatures.

Fig. 6 showed the several typical FT-IR spectra during the whole process. It is clear from Fig. 6 to see that $LiPF_6$ almost had no decomposition at 29 °C, but with the elevation of the temperature, the OPF_3 and PF_5 are forming gradually. When the temperature gets to 61 °C, the peaks of OPF_3 are already very sharp which agreed well with the TG curves. And when the temperature gets to 151 °C, the peaks of PF_5 are also very
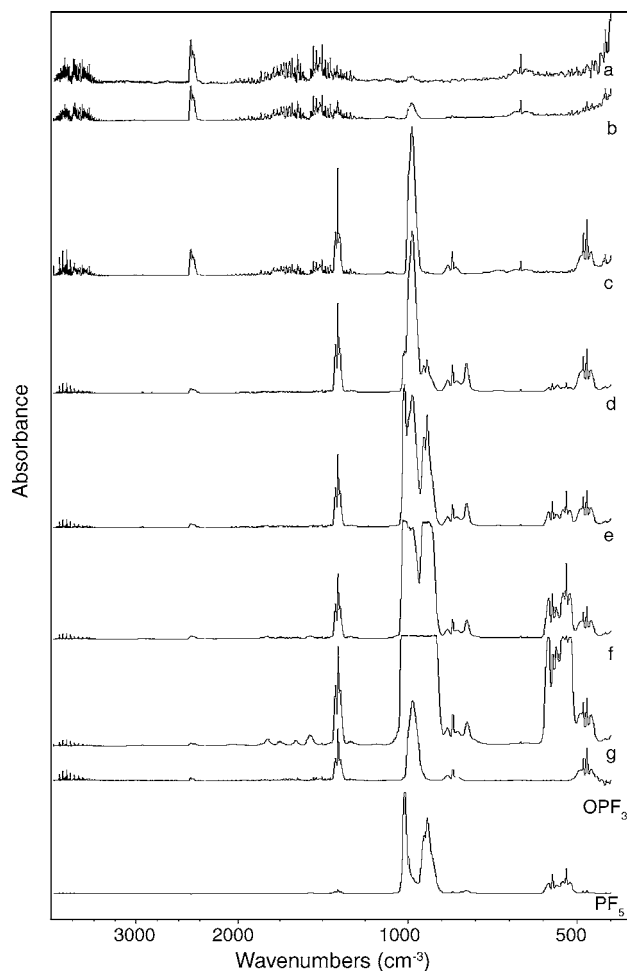

Fig. 6. Detected FT-IR spectra of decomposed products of $LiPF_6$ under different temperatures (gaseous phase part) and OPF_3, PF_5: (a) 29 °C, (b) 45 °C, (c) 61 °C, (d) 133 °C, (e) 151 °C, (f) 180 °C, (g) 200 °C.

clear. And when the temperature gets to 200 °C, the peaks of PF_5 are as strong as to appear as a flat one. What is more, from the very moment of the formation of PF_5, the characteristic peaks of PF_6^- are also formed at the same time which can be seen from Fig. 7.
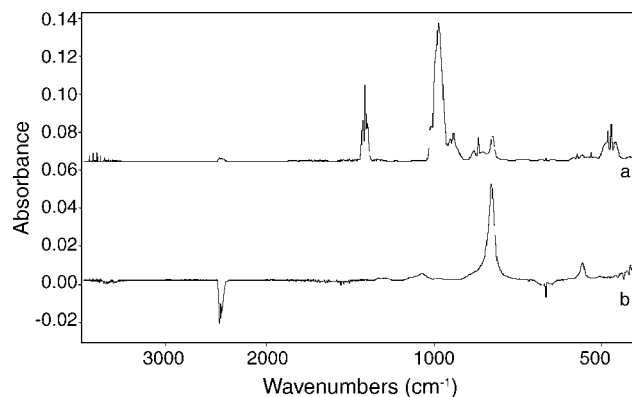

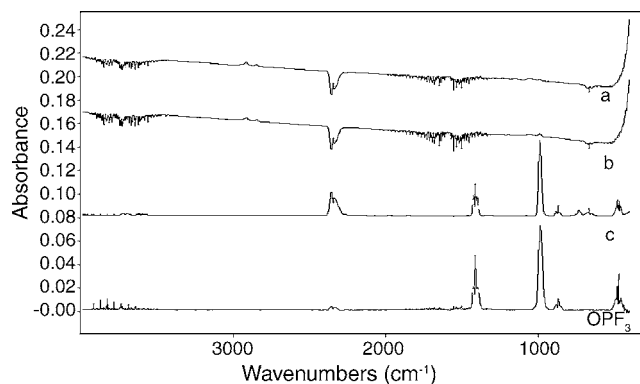Fig. 7. FT-IR spectra of $LiPF_6$ heated under 133 °C: (a) gaseous phase part and (b) HPF_6.

Fig. 8. FT-IR spectra of decomposed products of LiPF$_6$ heated under different temperature (kept for 1 h) and OPF$_3$: (a) 23 °C, (b) 30 °C and (c) 60 °C.

The reaction of LiPF$_6$ with trace water at elevated temperature would happen are further proved by another experiment.

In the experiment, LiPF$_6$ sample was loaded in another hermetic gas cell and kept under desired temperature for 1 h. The FT-IR spectra of 23, 30 and 60 °C were collected separately. The results were shown as Fig. 8.

Fig. 8 proved that LiPF$_6$ are very stable under room temperature if the amount of H$_2$O is very low (less than 1 mg L^{-1}). But when the temperature is elevated even as high as about 40 °C, although the amount of H$_2$O is very low (less than 1 mg L^{-1}), the hydrolysis of LiPF$_6$ would happen.

Acknowledgements

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