

## Preparation and characterization of lithium hexafluorophosphate for lithium-ion battery electrolyte

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**Abstract:** A promising preparation method for lithium hexafluorophosphate ( $\text{LiPF}_6$ ) was introduced. Phosphorus pentafluoride ( $\text{PF}_5$ ) was first prepared using  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  at  $280\text{ }^\circ\text{C}$  for 3 h.  $\text{LiPF}_6$  was synthesized in acetonitrile solvent by  $\text{LiF}$  and  $\text{PF}_5$  at room temperature ( $20\text{--}30\text{ }^\circ\text{C}$ ) for 4 h. The synthesized  $\text{LiPF}_6$  was characterized by infrared spectrometry and X-ray diffraction (XRD). Atomic absorption and ion chromatography results show that the purity of synthesized  $\text{LiPF}_6$  reaches 99.98%. Thermal stability of self-synthesized  $\text{LiPF}_6$  was analyzed by differential thermal analysis and thermogravimetry. The results indicate that the self-synthesized  $\text{LiPF}_6$  has higher purity, lower impurity contents and better thermal stability than the commercial  $\text{LiPF}_6$ .

**Key words:** lithium-ion batteries; lithium hexafluorophosphate; phosphorus pentafluoride; acetonitrile

### 1 Introduction

Lithium hexafluorophosphate ( $\text{LiPF}_6$ ) is a typical electrolyte salt for lithium-ion batteries. This salt has many advantages over conventional electrolyte salts such as  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$  and  $\text{LiClO}_4$ : 1) It can form suitable SEI membrane in electrodes, especially in cathode; 2) it can implement passivation for anode current collectors to prevent their dissolution; 3) it has wide windows of electrical stability; 4) it has excellent solubility and high conductivity in various solvents; and 5) it is environment-friendly [1–2].

Traditional preparation of  $\text{LiPF}_6$  continuously follows the HF solvent method. However, there are three major disadvantages for this method. First, high toxicity of HF brings great danger to preparation and rigorous demands for reaction devices; second, high energy consumption is essential because of deeply-cold reaction; third, large amount of impurity always remains in the product as a form of  $\text{LiPF}_6\cdot\text{HF}$ . In normal cases, it is very difficult to decrease the amount of HF to below  $10\text{ }\mu\text{g/mL}$ . The remaining HF causes erosion to electrodes, which directly affects the capacity of batteries. Therefore, the factors mentioned above all lead to the restriction of

HF method nowadays [1–4].

In this work, a promising preparation method of  $\text{LiPF}_6$  is introduced. In order to strictly control the influence of  $\text{H}_2\text{O}$ ,  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  are used to prepare  $\text{PF}_5$ , which is defined as a “thoroughly-dry method”. Acetonitrile with low toxicity is used instead of HF as a solvent, which has no pollution to environment and production. Acetonitrile is extremely beneficial to separation and purification of  $\text{LiPF}_6$ .

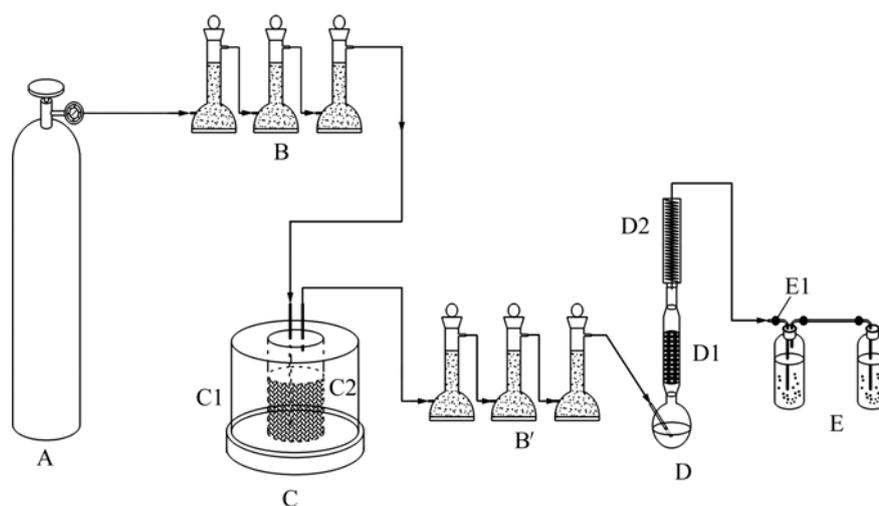
### 2 Experimental

#### 2.1 Reagents

$\text{LiF}$  (self-made [5]), anhydrous acetonitrile, anhydrous aether,  $\text{CaF}_2$ ,  $\text{P}_2\text{O}_5$  were all supplied by Tianjin Kemiou Chemical Reagent Co., China. Argon gas was supplied by Changsha Gaoke Gas Plant of China.

#### 2.2 Equipment

The equipment in the experiment was self-constructed. The whole equipment is schematically shown in Fig. 1. Reactor I (C) was mainly composed of a stainless steel cylinder vessel (C2) and crucible heater box (C1). Hermetical circles and liquid-sealing system were designed at the mouth of heater box to guarantee no



**Fig.1** Schematic diagram of equipment: A Carrier gas system; B, B' Drier towers; C Reactor I; C1 Crucible heater box; C2 Stainless steel cylinder; D Reactor II; D1 Circumfluence equipment; D2 Condenser; E Waste gas absorption equipment; E1 Desiccant

leak of gas in the experiment. Reactor II (D) comprised a two-neck round bottom flask equipped with a magnetic stirrer (D), circumfluence equipment (D1) and condenser (D2). Among them the circumfluence equipment was designed to increase the utility rate of materials, and the condenser was to prevent the volatilization of solvent in the flask. Argon gas of high purity in the carrier gas system (A) was used to build up protection environment for the whole experiment. Many drier towers (B, B') were set in various places in the experiment to satisfy rigorous demand for water. Waste gas multiple-absorption equipment (E) was adopted in the experiment.

### 2.3 Preparation of $\text{PF}_5$

The preparation process of  $\text{PF}_5$  in the experiment was monitored by Gas Chromatography-Mass Spectroscopy-Selected Ion Monitoring (GC-MS-SIM). Because only liquid sample can meet the request of determination in GC-MS-SIM,  $\text{PF}_5$  must be pretreated [6]. In the experiment,  $\text{PF}_5$  was dissolved in anhydrous aether. Firstly, anhydrous aether was enclosed in a two-neck round bottom flask equipped with a magnetic stirrer and a condenser. After the flask was placed in 0 °C-water-bath and the air in it was removed by dry argon gas,  $\text{PF}_5$  was dissolved into anhydrous aether for 0.5–1 h. Finally, the sample was fetched out from the flask for determination.

### 2.4 Preparation of $\text{LiPF}_6$

$\text{LiPF}_6$  was synthesized by  $\text{CaF}_2$ ,  $\text{P}_2\text{O}_5$  and  $\text{LiF}$  according to the following procedures. 1) 50.0 g  $\text{CaF}_2$  and 150.0 g  $\text{P}_2\text{O}_5$  were sealed in a pottery ball-grinding machine to be mixed for 2 h. The mixture was then quickly transferred to the stainless steel cylinder vessel

in crucible heater box. 2) 10.0 g  $\text{LiF}$  and 200 mL anhydrous acetonitrile were enclosed into the two-neck round bottom flask. They were stirred under magnetism to form suspending solution. 3) 8.0 g  $\text{LiF}$  was filled in the circumfluence tower by carrier of glass fibre. Two reactors were connected. 4) Air in whole system was removed by dry argon gas. 5) The temperature of reactor I was controlled between 280 °C and 300 °C. The temperature of reactor II was controlled between 20 °C and 30 °C. Reaction process was maintained for 3 h. 6) After the solution in the flask was heated at 50 °C for 4 h, it was filtrated quickly. 7) The received filtrate was cooled at -20 °C for crystallization. The product was dried in vacuum at 60 °C to obtain  $\text{LiPF}_6$ .

### 2.5 Characterization and determination

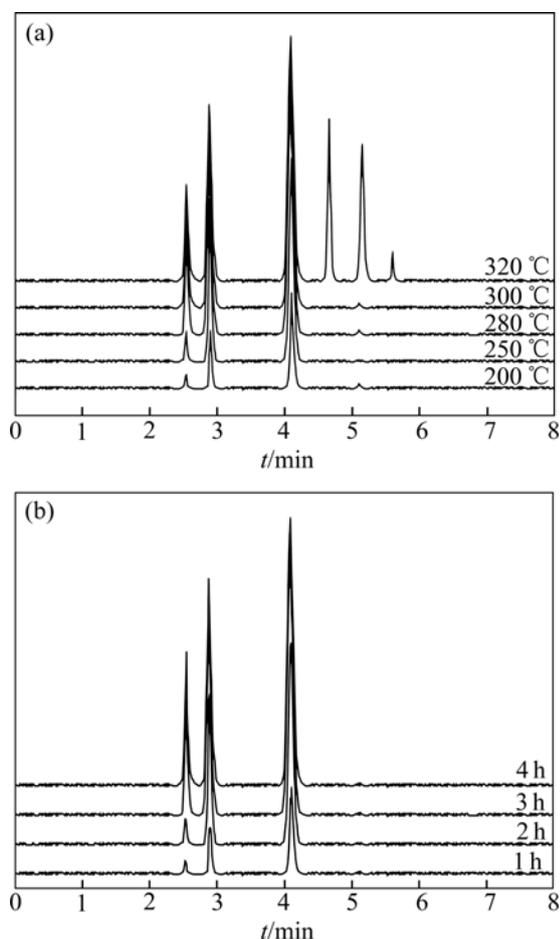
All the operation in the experiment was carried out in a glove box under  $\text{H}_2\text{O}$  and  $\text{CO}_2$  free atmosphere, which was provided by Scientific Instrument Plant of Nanjing University, China. Infrared spectrum was measured by AVATAR-360 FT-IR instrument provided by Nicolet Magna Co., USA. 1–2 mg  $\text{LiPF}_6$  was quickly transferred in agate mortar to be mixed with KBr for 5–6 min. It was then pressed into pieces for measurement. The structures of self-synthesized  $\text{LiPF}_6$  were characterized using  $\text{Cu K}\alpha$  radiation in the range of 10°–90° with a scanning rate of 2 (°)/min by D/max 2550 X-ray diffraction (XRD) instrument provided by Japan. Thermogravimetric (TG) analysis was done by SDT Q600 V8.0 instrument provided by USA. The quantity of  $\text{Li}^+$  was determined by atomic absorption spectrometry with the instrument provided by Beijing Rayleigh Analytical Instrument Co., China. The concentrations of  $\text{Li}^+$  standard solutions were 0.5, 1, 2, 4, 6, 8 mg/L,

respectively. 1 mL 2.0 g/L KCl solution was used as ionization buffering agent. The testing solution was self-made  $\text{LiPF}_6$ -aether after dilution. The quantity of  $\text{PF}_6^-$  was determined by Dionex 500 ion chromatography instrument from USA. The concentrations of standard solutions were 10.0  $\mu\text{g/mL}$   $\text{F}^-$ , 5.0  $\mu\text{g/mL}$   $\text{PO}_4^{3-}$  and 80  $\mu\text{g/mL}$   $\text{PF}_6^-$ , respectively. The preparation of  $\text{PF}_5$  was monitored by GC-MS Philigen series of Thermo Electron Corporation. The type of GC was Trace GC ultra. The GC column was db-5. The type of MS was Trace dsq. The adopted selected ions in the experiment were  $m/z=50, 69, 88, 104, 107$ .

### 3 Results and discussion

#### 3.1 Monitoring to preparation of $\text{PF}_5$

The monitoring figure of GC-MS-SIM to the preparation of  $\text{PF}_5$  at different temperatures is shown in Fig.2(a). It can be seen that the peak area at 200  $^\circ\text{C}$  is clearly small, which results from no reaction of materials at this temperature. The peak area reaches the maximum at temperatures between 280  $^\circ\text{C}$  and 300  $^\circ\text{C}$ . However, many impurity peaks appear when the temperature is



**Fig.2** GC-MS-SIM graphs of preparation of  $\text{PF}_5$ : (a) At different temperatures; (b) At 280  $^\circ\text{C}$  with different time

continuously increased over 300  $^\circ\text{C}$ . Therefore, the monitoring results reveal that continuously increasing temperature brings disadvantages to the preparation of  $\text{PF}_5$ . It is determined that the best heating temperature of  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  is between 280  $^\circ\text{C}$  and 300  $^\circ\text{C}$ . The monitoring figure of GC-MS-SIM with different time at 280  $^\circ\text{C}$  is shown in Fig.2(b). It can be obviously found that the best reaction time is 3 h. Therefore, the optimal preparation condition of  $\text{PF}_5$  is that  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  are heated between 280  $^\circ\text{C}$  and 300  $^\circ\text{C}$  for 3 h. Meanwhile, it can be concluded from MS information that  $\text{PF}_5$  prepared at optimal conditions is in high purity.

#### 3.2 Infrared spectrum characterization

$\text{PF}_6^-$  belongs to  $O_h$  point group. Six kinds of vibration modes are included in the molecule, whose basic frequency number is 15. The characteristic of  $O_h$  point group is listed in Table 1[7–8].

**Table 1** Characteristic of  $O_h$  point group

$O_h$	$I$	$8C_3$	$3C_2$	$6C_4$	$6C'_2$
$U_R$	7	3	3	3	1
$\zeta_{(R)}$	15	0	-1	1	1
$O_h$	$i$	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
$U_R$	1	1	5	1	3
$\zeta_{(R)}$	-3	0	5	-1	3

It can be calculated from Table 1 that:

$$\Gamma = A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$$

Then,

$$\Gamma^t = 2F_{1u}, \Gamma^v = A_{1g} + E_g + F_{2g} + F_{2u}$$

And,

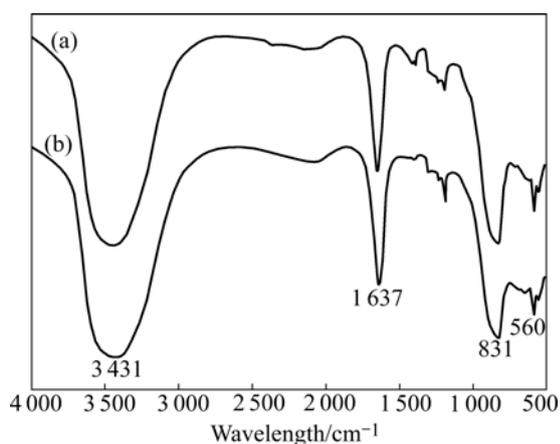
$$\Gamma\alpha = A_{1g} + E_g + F_{2g}$$

So, for  $\text{LiPF}_6$  molecule, two energy levels belonging to  $F_{1u}$  have infrared activity, which results from the flexing vibration and bending vibration of F—P bond, respectively[9–13]. Therefore, two strong absorption peaks of  $\text{LiPF}_6$  molecule should appear at 820–860  $\text{cm}^{-1}$  and 550–565  $\text{cm}^{-1}$ .

The infrared spectra of standard  $\text{LiPF}_6$  and self-synthesized  $\text{LiPF}_6$  are shown in Fig.3. It can be found that the position and intensity of peaks in the two spectra are the same. Strong absorption peaks appear at 560  $\text{cm}^{-1}$  and 831  $\text{cm}^{-1}$ , respectively. Therefore, it can be confirmed that the received production is  $\text{LiPF}_6$ .

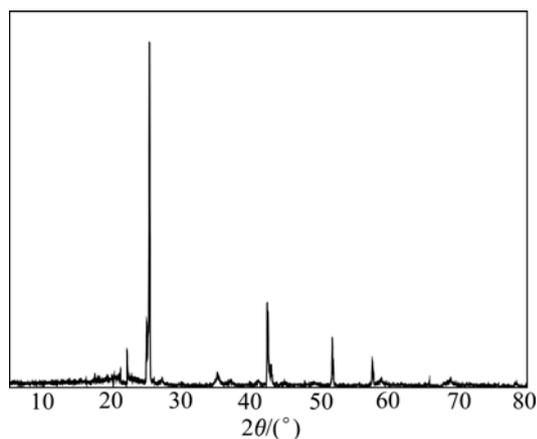
#### 3.3 XRD characterization

Strong lines of  $\text{LiPF}_6$  in standard PDF card appear at 21 $^\circ$ –26 $^\circ$ . Hypo-strong lines appear at 42 $^\circ$ , 51 $^\circ$ , 57 $^\circ$ , etc [14–15].



**Fig.3** Infrared spectra of  $\text{LiPF}_6$  tested at differentiate rate of  $4 \text{ cm}^{-1}$ , and scan degree of 32 times: (a) Standard  $\text{LiPF}_6$ ; (b) Self-synthesized  $\text{LiPF}_6$

The XRD pattern of self-synthesized  $\text{LiPF}_6$  is shown in Fig.4. It can be observed that the strong peaks of self-synthesized  $\text{LiPF}_6$  appear at  $22.00^\circ$  and  $25.24^\circ$ , and hypo-strong peaks appear at  $42.28^\circ$ ,  $52.72^\circ$  and  $57.72^\circ$ , which is the same as the standard PDF card. Meanwhile, it can be confirmed from the calculation results of diffraction peaks that the crystal structure of  $\text{LiPF}_6$  is hexagonal series and space group belongs to  $O_h$  point group. It can be also observed that the diffraction peaks are smooth and clear, and the diffraction peak of  $h/h_0=100$  appears at  $2\theta=26.83^\circ$ , which accounts for the integrated crystal structure of  $\text{LiPF}_6$ .



**Fig.4** XRD pattern of self-synthesized  $\text{LiPF}_6$  tested by  $\text{Cu K}\alpha$  radiation in range of  $10^\circ$ – $90^\circ$  with scanning rate of  $2^\circ/\text{min}$

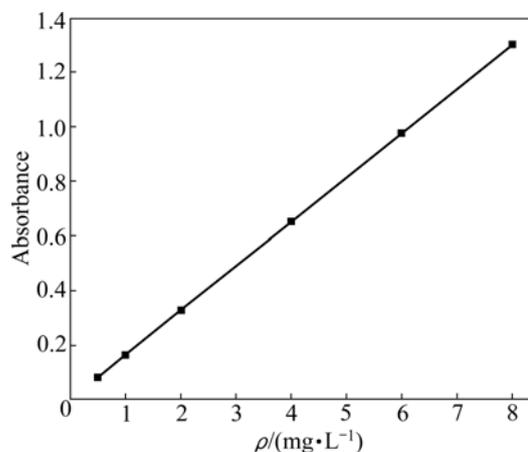
### 3.4 Atomic absorption analysis

Fig.5 shows the standard curve of  $\text{Li}^+$  solution, whose correlative coefficient is 0.999 92. 5.0 g self-synthesized  $\text{LiPF}_6$  was firstly dissolved in 1 000 mL anhydrous aether. It was then diluted for analysis at the same conditions as standard  $\text{Li}^+$  solution. The analysis result is  $\rho(\text{Li}^+)=0.291 \text{ mg/L}$ . The concentration of self-

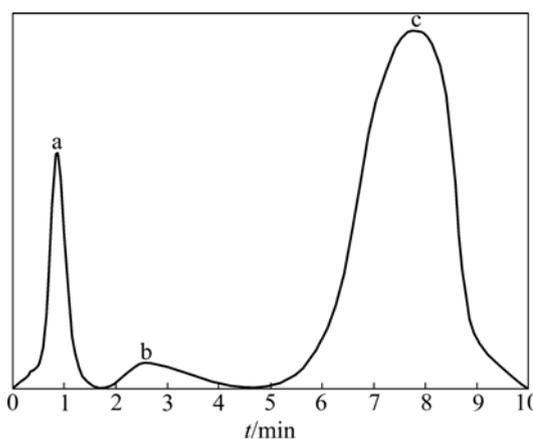
synthesized  $\text{LiPF}_6$  through conversion is  $\rho(\text{Li}^+)=0.291 \text{ g/L}$ . This final result indicates that self-synthesized  $\text{LiPF}_6$  has low amount of impurity metal ions.

### 3.5 Ion chromatography(IC) analysis

The standard IC graphs of  $10.0 \text{ }\mu\text{g/mL F}^-$ ,  $5.0 \text{ }\mu\text{g/mL PO}_4^{3-}$ ,  $80 \text{ }\mu\text{g/mL PF}_6^-$  are shown in Fig.6. 5.0 g self-made  $\text{LiPF}_6$  was firstly dissolved in 1 000 mL anhydrous aether. It was then diluted for analysis at the same conditions as standard solutions. The analysis result is  $\rho(\text{PF}_6^-)=47.07 \text{ }\mu\text{g/mL}$ . The concentration of self-synthesized  $\text{LiPF}_6$  through conversion is  $\rho(\text{PF}_6^-)=4.707 \text{ g/L}$ . The final result indicates that no other impurity ions (such as  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ) are testified, and the purity of self-synthesized  $\text{LiPF}_6$  reaches 99.98%.



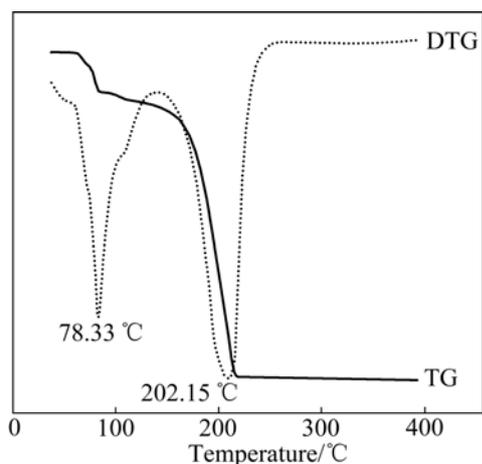
**Fig.5** Standard curve of lithium ion



**Fig.6** Standard IC graphs: (a)  $10.0 \text{ }\mu\text{g/mL F}^-$ ; (b)  $5.0 \text{ }\mu\text{g/mL PO}_4^{3-}$ ; (c)  $80 \text{ }\mu\text{g/mL PF}_6^-$

### 3.6 TG-DTG analysis

The thermal decomposition curve of self-synthesized  $\text{LiPF}_6$  is shown in Fig.7. It can be seen that strong decomposition peaks of  $\text{LiPF}_6$  appear at  $78.33^\circ\text{C}$  and  $202.15^\circ\text{C}$ , and the mass loss is 12.44% and 80.38%, respectively. However, it is reported in Refs.[1–2,16] that the initial decomposition temperature of  $\text{LiPF}_6$  is  $60^\circ\text{C}$



**Fig.7** Thermal decomposition curve of  $\text{LiPF}_6$  tested with heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under protection of  $\text{N}_2$  in corundum crucible

$^\circ\text{C}$ . Therefore, the thermal stability of self-synthesized  $\text{LiPF}_6$  is higher than the literature-reported  $\text{LiPF}_6$ .

## 4 Conclusions

1) A promising preparation method of  $\text{LiPF}_6$  was introduced. Phosphorus pentafluoride ( $\text{PF}_5$ ) was first prepared using  $\text{CaF}_2$  and  $\text{P}_2\text{O}_5$  at  $280\text{ }^\circ\text{C}$  for 3 h.  $\text{LiPF}_6$  was synthesized in acetonitrile solvent by  $\text{LiF}$  and  $\text{PF}_5$  at room temperature ( $20\text{--}30\text{ }^\circ\text{C}$ ) for 4 h.

2) The synthesized  $\text{LiPF}_6$  was characterized by infrared spectrometry and X-ray diffractometry (XRD). Atomic absorption and ion chromatography results show that the purity of synthesized  $\text{LiPF}_6$  reaches 99.98%. The thermal stability of self-synthesized  $\text{LiPF}_6$  was analyzed by differential thermal analysis and thermogravimetry. The initial decomposition temperature of self-synthesized  $\text{LiPF}_6$  is  $78.33\text{ }^\circ\text{C}$ , which is higher than the literature-reported decomposition temperature.

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