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Journal of Power Sources 68 (1997) 326–327

JOURNAL OF POWER SOURCES

Application of thermogravimetric studies for optimization of lithium hexafluorophosphate production

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Accepted 3 March 1997

Abstract

Lithium hexafluorophosphate, isolated from hydrogen fluoride solution (anhydrous) by decanting and filtering, is an adduct of composition $LiPF_6^* HF$. By thermogravimetric investigations the dynamics of HF removal from $LiPF_6$ by $LiPF_6^* HF$ thermal decomposition was studied. Based on the experimental data the constants entering into the equations as $C = C_0^* \exp(t^* K_0^* \exp(-E/RT))$ were calculated, explaining the thermal decomposition processes of $LiPF_6^* HF$ and $LiPF_6$. © 1997 Elsevier Science S.A.

Keywords: Lithium hexafluorophosphate; Thermal decomposition; Thermogravimetric investigations; Reaction rate constant

1. Introduction

Lithium hexafluorophosphate ($LiPF_6$) is the most promising complex lithium fluoride used essentially as the ionic component of electrolytes for rechargeable chemical cells. The most important figures of merit for this salt, except for the base material content, are the low content of moisture and free acid (in terms of HF). Given increasing demand for $LiPF_6$ in the world market the design of a high-efficient practice for production of this salt is of prime importance.

In our view, the synthesis method in the following system is of the greatest interest for large-scale production of the salt:

$$LiF + PF_5 \xrightarrow{HF} LiPF_6 \quad (1)$$

The selection of this reaction system depends on the scope for using exclusively pure starting components for attainment of the high-quality end product. The Siberian Group of Chemical Enterprises (SGCE) has exclusively developed production practices of pure lithium fluoride with impurity content of less than 0.1 wt.% and spectroscopically pure phosphorus pentafluoride, produced by the efficient process of direct fluorination of elemental phosphorus by gaseous fluorine. Also, the SGCE uses anhydrous hydrogen fluoride (less than 0.03 wt.% of moisture).

The most important steps in the production of high-quality $LiPF_6$ salt in system (1) are pure salt isolation and the removal of residual hydrogen fluoride.

There are two methods for these operations:

- evaporation of HF solution and vacuum drying of the solid residue;
- decanting of HF through a filter, using vacuum or pressure, with subsequent drying of the precipitate.

2. Results

The evaporating of excess hydrogen fluoride was found to cause partial decomposition of the desired product. It appears that the hexafluorophosphoric acid (anhydrous) formed in system (1) on $LiPF_6$ solvation is subject to decomposition.

$$HPF_6 \xrightarrow[T]{HF} HF + PF_5 \quad (2)$$

As a result, the PF_6^- ion content in the desired product decreases, and the lithium fluoride content increases appreciably.

The removal of hydrogen fluoride by decantation at temperatures of −80 to +20°C resulted in the production of the solid residue constituting free-flowing bulk material including an HF content of 8–11 wt.%.

To study the dynamics of HF removal from the material produced on HF decantation and the optimization of the $LiPF_6$ production process conditions, thermogravimetric studies were carried out.

Thermogravimetric characteristics were determined for 100–300 mg $LiPF_6$ samples, produced after HF decantation.

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PII S0378-7753(97)02652-9

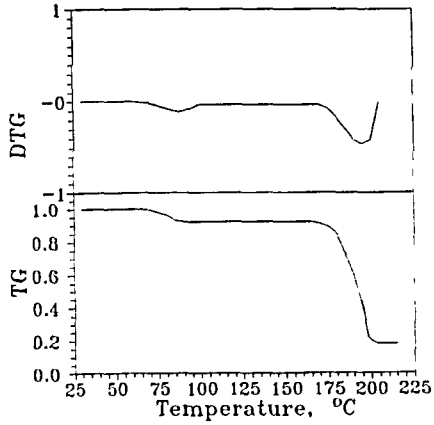

Fig. 1. The characteristic form of the thermogravimetric curves.

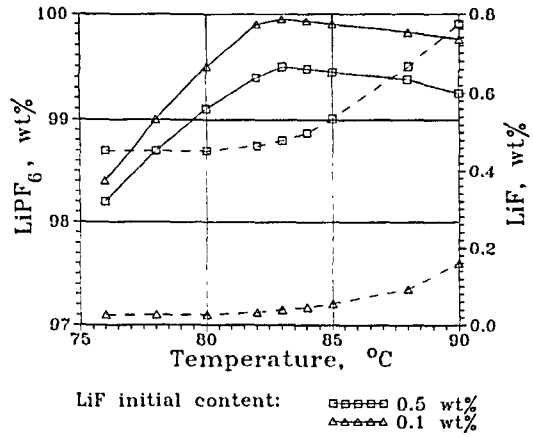

Fig. 2. Base material (———) and LiF (- - -) impurity content in $LiPF_6$ against drying temperature of samples with varying LiF initial content.

The measurements were made in dried nitrogen medium (dew point, −60°C).

The heating rate of the samples was 1–10°C/min.

The characteristic form of the thermogravimetric curves is shown in Fig. 1. The first peak in the DTG curve, observed over the temperature range from 85 to 95°C, defines hydrogen fluoride removal and is due to the thermal decomposition reaction:

$$LiPF_6^*HF \xrightarrow{T} LiPF_6 + HF \quad (3)$$

The second peak in the DTG curve, corresponding to the temperatures 185–195°C, is due to the thermal decomposition of the base material $LiPF_6$:

$$LiPF_6 \xrightarrow{T} LiF + PF_5 \quad (4)$$

If processes (3) and (4) are assumed to be first-order reactions, then the TG and DTG curves (per unit) may be explained in terms of the concentration of the removed components (HF and PF_5):

$$TG = C_{HF}(T,t) + C_{PF_5}(T,t) \quad (5)$$

$$DTG = d(C_{HF})/dt + d(C_{PF_5})/dt \quad (6)$$

such that:

$$C_{HF}(T,t) = C_1^* \exp(t^* K_1^* \exp(-E_1/RT)) \quad (7)$$

$$C_{PF_5}(T,t) = C_2^* \exp(t^* K_2^* \exp(-E_2/RT)) \quad (8)$$

where

- $C_{HF}(T,t)$ (C_1) = HF variable (initial) concentrations;
- $C_{PF_5}(T,t)$ (C_2) = PF_5 variable (initial) concentrations;
- K_1, K_2 = preexponential in the expression for the rate constant of process (3) and (4), respectively;
- E_1, E_2 = apparent activation energy of HF and PF_5 removal processes, respectively;
- T = temperature, K;
- t = time, min;
- R = 1.987 cal/mol K, gas constant.

The coefficients K_1, K_2 and E_1, E_2 of functions (7), (8) were calculated by the numerical approximation method for the experimental samples and the following results were derived:

$LiPF_6^*HF$ decomposition, process (3), is described by the expression:

$$K(T) = K_1^* \exp(-E_1/RT) \quad (9)$$

where

- $K_1 = (4–5) \times 10^{26}$, min^{-1};
- E_1 = 46700–46800, cal/mol.

$LiPF_6$ decomposition, process (4), is described by the expression:

$$K(T) = K_2^* \exp(-E_2/RT) \quad (10)$$

where

- $K_2 = (1–2) \times 10^7$, min^{-1};
- E_2 = 18700–19400, cal/mol.

The calculated curves of the content in $LiPF_6$ of the base material and the LiF impurity against the drying temperature at the LiF initial content in the product amounting to 0.1 and 0.5 wt.% are shown in Fig. 2.

The above evaluated constants K_1, E_1, K_2, E_2 of the $LiPF_6^*HF$ and $LiPF_6$ decomposition processes in the starting material were used for the curve calculations.

3. Conclusions

Optimization of the $LiPF_6$ drying process produces a high-quality product with the following characteristics:

- Base material content, wt.% $LiPF_6$, more than 99.9
- HF, ppm, not more than 100
- LiF, wt.%, not more than 0.08