

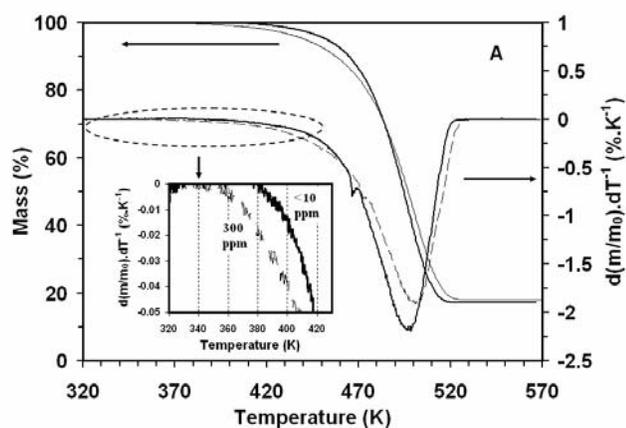
## Thermal Studies of LiPF<sub>6</sub> and LiPF<sub>6</sub> Based Electrolytes by on-line TGA- FTIR

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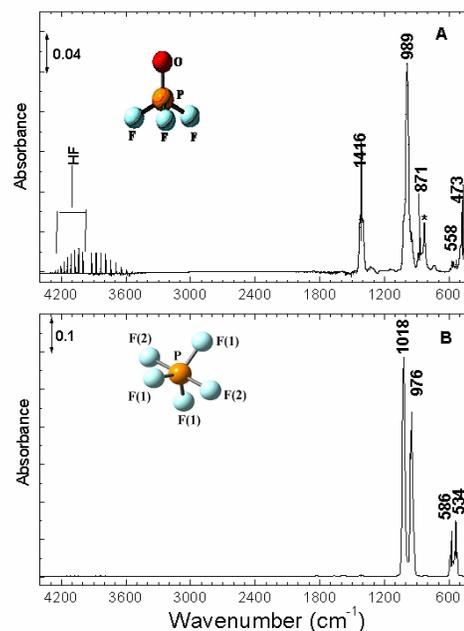
Lithium hexafluorophosphate (LiPF<sub>6</sub>) is the most widely used salt in the electrolytes for commercial Li-ion cells, due to many advantages such as its high ionic conductivity and electrochemical stability. Its thermal stability and its interaction with electrolyte organic components, such as ethylene carbonate (EC) and propylene carbonate (PC), at elevated temperature, have been studied experimentally by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)<sup>1,2</sup>, and computationally by Density Functional Theory (DFT) and Molecular Dynamics (MD) methods<sup>3</sup>.

In the present work, we report our thermal study by using on-line TGA-Fourier Transform Infrared (FTIR) to characterize the thermal behaviors and gases evolution of neat LiPF<sub>6</sub>, LiPF<sub>6</sub>/EC and LiPF<sub>6</sub>/PC mixtures. This technique makes it possible to follow the thermal decomposition path by monitoring evolution of volatile products as a function of temperature and weight change. Thermogravimetric (TG) profiles of pure LiPF<sub>6</sub> salt obtained, at a heating rate of 10 K•min<sup>-1</sup>, in the carrier gas, containing < 10 ppm of H<sub>2</sub>O (solid line) and 300 ppm of H<sub>2</sub>O (dashed line) respectively, are shown in Fig.1. The influence of moisture level on thermal decomposition behavior of LiPF<sub>6</sub> is apparent in the derivative thermogravimetry (DTG). From which decreasing of mass loss onset temperature (inset of Fig.1) by ca. 27 K in the presence of 300 ppm H<sub>2</sub>O, is clearly illustrated.

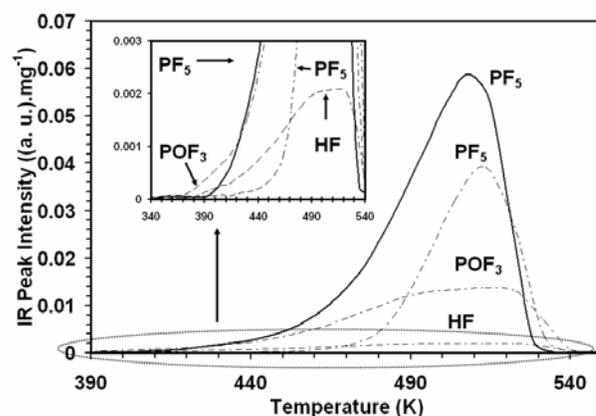
To investigate the influence of high moisture level on the decomposition behavior of LiPF<sub>6</sub> at molecular level, the evolution of gas products as a result of sample thermal decomposition or volatilization was simultaneously monitored by FTIR during TGA experiment. The typical FTIR spectra (at T = 479 K) of initial decomposition products of LiPF<sub>6</sub> in environment containing 300 ppm and less than 10 ppm of H<sub>2</sub>O are presented in Fig. 2A and 2B, respectively. The relative abundance of thermal decomposition products, in the presence of low (solid line) and high (dashed line) moisture level, extracted from infrared spectra acquired during the TG analysis is illustrated in Fig. 3. These results clearly demonstrated that moisture is the key factor to the onset temperature of LiPF<sub>6</sub> decomposition and decomposition products. Results of the TGA-FTIR studies of LiPF<sub>6</sub> and cyclic carbonates (EC, PC) in the presence of moisture will also be presented and discussed in detail.



**Figure1.** Thermogravimetric (TG) and thermogravimetry (DTG) profiles of thermal decomposition of LiPF<sub>6</sub> in the presence of 300 ppm H<sub>2</sub>O (dashed line) and less than 10 ppm H<sub>2</sub>O (solid line).



**Figure 2.** FTIR spectra of initial decomposition products of LiPF<sub>6</sub> at 479 K in the presence of 300 ppm (A) and less than 10 ppm of H<sub>2</sub>O.



**Figure 3.** Evolution of gaseous products as a function of temperature during thermal decomposition of LiPF<sub>6</sub> with a heating rate of 10 K•min<sup>-1</sup> in the presence of 300 ppm (dashed line) and less than 10 ppm H<sub>2</sub>O (solid line).

## References

1. S. E. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, and K. Kinoshita, *Electrochem. Solid-State Lett.*, **4**, A42 (2001).
2. K. S. Gavritchev, G. A. Sharpataya, A. A. Smagin, E. N. Malyi and V. A. Matyukha, *J. Thermal Analysis and Calorimetry*, **73**, 71 (2003).
3. K. Tasaki, K. Kanda, S. Nakamura and M. Ue, *J. Electrochem. Soc.*, **150**, A1628 (2003).

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