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Thermal Studies of LiPF₆ and LiPF₆ Based Electrolytes by on-line TGA- FTIR

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Lithium hexafluorophosphate (LiPF₆) 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)^{1,2}, and computationally by Density Functional Theory (DFT) and Molecular Dynamics (MD) methods³.

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 LiPF₆, LiPF₆/EC and LiPF₆/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 LiPF₆ salt obtained, at a heating rate of 10 K·min⁻¹, in the carrier gas, containing < 10 ppm of H₂O (solid line) and 300 ppm of H₂O (dashed line) respectively, are shown in Fig.1. The influence of moisture level on thermal decomposition behavior of LiPF₆ 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 H₂O, is clearly illustrated.

To investigate the influence of high moisture level on the decomposition behavior of LiPF₆ 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 LiPF₆ in environment containing 300 ppm and less than 10 ppm of H₂O 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 LiPF₆ decomposition and decomposition products. Results of the TGA-FTIR studies of LiPF₆ 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 LiPF₆ in the presence of 300 ppm H₂O (dashed line) and less than 10 ppm H₂O (solid line).

Figure 2. FTIR spectra of initial decomposition products of LiPF₆ at 479 K in the presence of 300 ppm (A) and less than 10 ppm of H₂O.

Figure 3. Evolution of gaseous products as a function of temperature during thermal decomposition of LiPF₆ with a heating rate of 10 K·min⁻¹ in the presence of 300 ppm (dashed line) and less than 10 ppm H₂O (solid line).

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