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学 位 論 文 題 名

Flammability study on electrolyte components in lithium-ion batteries using a wick combustion method

(灯芯燃焼法を用いたリチウムイオン電池用電解液成分の燃焼性に関する研究)

Fire safety becomes one of the most concern in the development of lithium-ion batteries (LIBs). The main contribution of the LIB fire can be traced back to the combustion of electrolytes. To mitigate the fire hazard of electrolytes, safer components (solvent, lithium salt, and additives) are expected. However, due to the conflict between flame retardancy and battery performance, it requires a quantitative flammability evaluation for a balanced electrolyte formula.

To quantify the flammability limits of organic electrolyte solvents used in lithium-ion batteries, a unique wick combustion system was developed in conjunction with limiting oxygen concentration (LOC) of candle-like flame, named wick-LOC method. By controlling the oxygen-nitrogen ratio of external flow of the wick diffusion flame, the flammability limits (LOC) of electrolyte solvents were determined experimentally.

This thesis first validated the reproducibility and reliability of the wick-LOC method. The LOC of single solvents, binary solvents, and solvents with organophosphorus compound (OPC) additives were quantified and discussed. To make an in-depth understanding of the effect of OPC additives in terms of flame extinction, flame stability limits were then studied. The blow-off regime and quenching regime were found in the flammability maps when OPC added. Finally, the influences of three typical lithium salts (LiPF_6 , LiBF_4 , and LiTFSI) on electrolyte combustion and wick flame extinction were investigated. The gas-phase flame inhibition of LiPF_6 addition was first found by the wick-LOC method. Furthermore, the solid-phase reactions due to the salt decomposition provided some inspirations in suppressing the electrolyte fire.

In Chapter 1, a brief overview of the LIB fire and the hazard of electrolyte components were introduced. Then, the methods of flammability evaluation for electrolytes were reviewed. Finally, the scope and structure of this thesis were presented.

In Chapter 2, the experimental setup of the wick-LOC method was presented. The experimental conditions and procedures to determine the LOC or flame stability limits were specified. The tested solvents, additives, salts and their combinations for each study were listed as well.

In Chapter 3, validations and applications of the wick-LOC method were conducted. To provide reproducible results under specified conditions, the effects of axial flow velocity, exposed wick length and elapsed time after ignition on the wick-LOC were studied, and the proper experimental conditions were selected for further applications. To validate the reliability of wick-LOC in flammability evaluation, correlation analyses to other flammability properties (flash point, auto-ignition temperature, the heat of combustion and other types of LOC) were conducted. The wick-LOC method was then applied

to quantify the flammability of mixed solvents. The linear changes of wick-LOC with mixing ratios were found in the mixture of linear and cyclic carbonates, while the non-linear trends were found in carbonate-ether mixed solvents. To evaluate the flame-retardant effectiveness of organophosphorus compounds (OPCs) as additives in electrolyte solvents, a series of tests were conducted. Results showed that small amounts of OPCs had significant flame-retardant effects, but the efficiency decreased with the higher OPC additions. The effectiveness of four OPCs was distinguished as well.

In Chapter 4, in-depth studies on the wick flame extinction affected by OPC additions were conducted. With the wick-LOC method, two modes of stabilized flame are found, namely, wake flame and full flame. In the case of higher OPC addition, two distinct branches of extinction processes occurred according to the different flame modes near extinction, and there was no transition from the full flame to wake flame. The flame stability limits are measured as a function of OPC addition for both flame modes. The wake flame is shown to be consistently more stable at low levels of OPC addition. However, once the OPC addition exceeds a critical amount, the full flame shows higher stability with a lower LOC than the wake flame. These phenomena in the two regimes are also found in other cases of high OPC addition (different type of OPC and electrolyte solvent). In terms of the most stable flame mode, the regime switches from the wake flame to the full flame with increasing OPC addition, and they are defined correspondingly as “blow-off regime” and “quenching regime”.

In Chapter 5, the dimethyl carbonate (DMC)-based electrolytes with 1M addition of different lithium salts (LiPF_6 , LiBF_4 , and LiTFSI) were studied comparing with pure DMC and trimethyl phosphate (TMP)-added solvents. The three lithium salts gave unique and distinct flame behaviors including flame shapes, colors and the changes of wick surface until self-extinguishing. The wick-LOC results indicated a considerable flame-retardant effect of LiPF_6 , while other salts have minor effects on the flame extinction. Utilizing the flame spectrum and combustion residue analyses, the roles of salts during combustion were characterized. The PF_6 anion played a similar role with the TMP additive in the gas phase flame inhibition. In the cases of LiPF_6 and LiBF_4 , the solid products (LiF) accumulation blocked the fuel supply from the wick to the flame region. The combustion complexity of LiTFSI on the cotton wick charring and heat release were considered as a potential hazard on solid combustible in the real fire cases.

In Chapter 6, conclusions of the present work and recommendations for the future work were summarized.