Introduction

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.

Experimental Approaches

A series of combustion experiments on electrolytes were carried out by the means of the wick-LOC method which was modified from the LOI method. The limiting oxygen concentration (LOC) to sustain the flame can be determined by precise adjustment of oxygen. The schematic of the experimental setup used to determine the wick-LOC value is shown in Fig.1.

The wick combustion system comprises three main parts: the fuel supply system (left) to provide a continuous supply of electrolytes; the gas control system (right) to supply the well-mixed gas of N₂O₂; and the combustion chamber (middle) to generate a wick-stabilized flame under a constant external flow velocity. Along the centerline of the combustion chamber, the wick complying with the quality standards specified in ASTM D1322 [1] was supported by a stainless alloy tube (inner diameter: 6mm, outer diameter: 7mm) in the glass chamber. The wick height was set at 7 mm above the top end of the stainless tube. The capillarity effect helped to feed a liquid fuel (a mixed solvent) from the wick bottom to the wick tip.

The fuel supply system is shown on the right side of the schematic. It can keep a constant liquid level ensuring a stable and sufficient fuel supply rate during combustion. To avoid the wick self-trimming (baking wick fabric) due to the weak capillary effect, the liquid level of fuel was stabilized at 10 mm lower than the top end of the stainless tube in each test of this research. The gas supply system is illustrated on the left side of the schematic.

The supplied gas was comprised of nitrogen and oxygen. The nitrogen and oxygen were well mixed before feeding to the combustion chamber. The oxygen concentration of external gas was set in the range of 0 to 25 vol% with a small increment of 0.1 vol%. The mixed gas was uniformly supplied by a honeycomb flow straightener to the wick combustion region. The axial flow velocity, an average value of total flow flux divided by the cross-sectional area of the chamber, could be varied from 4 cm/s to 18 cm/s.

Under a specific experimental condition, the liquid fuel vapor burned at the tip of the wick and the diffusion flame was recorded by a digital video camera (Panasonic HDC-TM70). When a stable flame formed, an R-type thermocouple of 0.3 mm in diameter was placed on an X-Y motion stage to measure the flame temperature of each position. The fiber-optic spectrometer was utilized to measure the light emission intensities of the flames given by the electrolytes. The measurable wavelength range of the spectrometer is 200–800 nm. For each trial of flame spectrum measurement, the dark mode was recalibrated to avoid the effect from external light. The combustion residues from burned wick were characterized utilizing scanning electron microscopy (SEM) and X-ray diffraction (XRD) from Material Analysis and Structure Analysis Open Unit (MASAOU) in Hokkaido University.

Results and Discussion

In Chapter 3, validations and applications of the wick-LOC method were conducted [2]. 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. Then the 10cm/s axial flow and 7mm wick length were selected as the proper experimental conditions 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 results showed a broad correlation to the chemical-related properties and had a good consistency with other types of LOC values.

In Chapter 4, in-depth studies on the wick flame extinction affected by OPC additions were conducted [3]. 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, as shown in Fig. 4.

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, as shown in Fig. 2.

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, as shown in Fig. 3.

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”, as shown in Fig. 5.
In Chapter 5, the dimethyl carbonate (DMC)-based electrolytes with 1M addition of different lithium salts (LiPF₆, LiBF₄, 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 LiPF₆, 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 PF₆ anion played a similar role with the TMP additive in the gas phase flame inhibition. In the cases of LiPF₆ and LiBF₄, 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.

Conclusions

This thesis has validated the reproducibility and reliability of the wick-LOC method. The LOC of single solvents, binary solvents, and solvents with organophosphorus compound (OPC) additives have been 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 (LiPF₆, LiBF₄, and LiTFSI) on electrolyte combustion and wick flame extinction were investigated. The gas-phase flame inhibition of LiPF₆ 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.

References