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Determination of flame stability limits of Li-ion battery electrolyte solvents with organophosphorus compounds addition by wick-LOC method

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Abstract

To evaluate the fire-retardant effectiveness of organophosphorus compounds (OPC) added to Li-ion battery electrolyte solvents, the limiting oxygen concentration (LOC) method is used in conjunction with a wick combustion system, called as wick-LOC method. With the wick-LOC method, two modes of stabilized flame are found, namely, wake flame and full flame. When OPC is added to the electrolyte, two distinct branches of extinction processes occur according to the different flame modes near extinction with no transition from full flame to wake flame in the case of higher OPC addition. 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 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". To explain the presence of these two regimes, the thermal balance effect is considered in the discussion of flame extinction mechanisms. The difference in flame volume near the extinction limit shows that the quenching mechanism dominates flame extinction under higher OPC addition. The thermal balance effect on flame stabilization or extinction can be the additional impact on the fire retardation abilities of OPC itself.

Keywords

Wick flame; Flame stability; Limiting oxygen concentration; Li-ion batteries; Organic liquid electrolyte; Organophosphorus compound

1. Introduction

Lithium-ion batteries (LIB) have been the dominant type of rechargeable batteries used in electronic devices owing to their high energy density and portability. However, some serious fire and explosion accidents associated with LIBs have been reported in recent years, and fire safety issue has been emphasized in the LIB industry.

The organic electrolyte solvents used in commercial LIBs are mostly linear and cyclic alkyl carbonates and their combinations, and their high volatility and flammability are the main causes of fire hazard [1]. According to LIB designers and producers, adding fire-retardant additives into electrolytes is an effective means of improving the fire safety of LIBs. Organophosphorus compounds (OPCs) are among the promising candidates with high fire -retardant effectiveness and low environmental impact compared to halogenated fire retardants [2–5]. While OPC addition has a negative impact on battery life and capacitance [6], it is expected that a balance between fire safety and battery performance will be achieved.

To meet the above expectations, in [7], a quantitative flammability evaluation method for LIB electrolyte solvents, called wick-LOC method, was proposed. The fire-retardant effect of OPC addition was indicated based on the limiting oxygen concentration (LOC) to sustain a flame in a wick combustion system. Different from the cup burner test for the gas-phase fire retardant effect [8,9] or limiting oxygen index (LOI) test for polymers [10,11], the wick-LOC method was designed for mixed liquid fuels. A wick impregnated with the electrolyte solvent generates a typical diffusion flame. The extinction limits (indicated by LOC) were obtained by decreasing the oxygen concentration under constant external flow velocity of N_2/O_2 atmosphere. The LOC results showed a significant fire-retardant effect with the addition of a small amount of OPC, while higher OPC addition (5–10wt%) led to a marginal effect. This implies that a balance point can be found from the quantitative LOC results considering the positive (fire suppression) and negative (decreased battery performance) effects of OPC addition.

In a previous study [7], the LOC results were determined standardly under the same mode of stabilized flame before extinction, that is, the flame was stabilized in the wake region of the wick (wake flame). However, in addition to the wake flame, another mode in which a side-stabilized flame enveloped the entire wick (full flame) was observed during experiments. With increasing OPC addition (up to 10 wt.%) into the electrolyte solvents, the flame could be extinguished directly from the full flame, and the corresponding LOC was lower than the LOC for extinction from the wake flame, which showed that full flame is more stable in the high OPC addition case.

The wake flame and the full flame modes were already discovered in the flame downward spread and extinction of solid material based on the LOI test method [12–14], and they have always been called wake-stabilized flame and side-stabilized flame for a candle-like solid slab/rod sample, respectively. By reducing the oxygen concentration of the external flow in the traditional LOI test, the flame extinction process has always been reported as follows. The base of the side-stabilized flame is pushed by external flow toward the downstream until the wake region with a shortening flame height; then, the flame proceeds to extinction. Extensive researches focusing on the change in extinction limits at different flow velocities, sample widths/thicknesses, and gravity [14–17] conditions have been conducted, and in these researches, the wake flame was always more stable as a consequence of the side-stabilized flame (or full flame). This phenomenon is commonly ascribed to the higher residence time of the wake flame compared to the side-stabilized flame according to the Damköhler number, which is widely used to explain the blow-off mechanism of the side-stabilized flame [18–21].

The flame in the wick-LOC method shows a configuration similar to that of downward flame propagation on a candle-like solid material during extinction. However, with increasing OPC addition, the flames are separated into two extinction processes given by the full and the wake flames near extinction. Moreover, the different extinction processes behave in a manner opposite to the common understanding mentioned in previous paragraph, according to which the full flame becomes more stable with increasing OPC addition, and its LOC decreases to be lower than that of the wake flame (refer to Supplementary materials). To clarify the influence of OPC addition to electrolyte solvent on the wick flame extinction in the wick-LOC method, the flame stability limits of two modes of stabilized flame (full flame and wake flame) were determined depending on OPC addition in the present work. Then, the extinction mechanism of each flame mode considering electrolyte solvent added OPC was discussed.

2. Experimental approach

2.1. Experimental setup and operation conditions

A schematic diagram of the experimental system used for flame stability limit measurement by the wick-LOC method is shown in Fig. 1, which is the identical to that in the previous work [7]. The experimental setup comprises three main parts, fuel supply system, gas control system, and combustion duct. The glass combustion duct is 220 mm in height above the honeycomb with a diameter of 80 mm to protect the flame. Along the central axis of the combustion duct, a cotton wick (5 mm diameter, following ASTM specification [22]) is inserted in the stainless support tube (8 mm outer diameter) at 7 mm above the top end of the tube. The wick is saturated with the electrolyte solvents, which can be supplied continuously at a constant level (10 mm lower than the top end of the tube) during the experiment. The nitrogen and oxygen flows can be adjusted to set the oxygen concentration and total flow rate manually, and well-mixed gas is supplied to the combustion duct through the mixing vessel and the honeycomb.

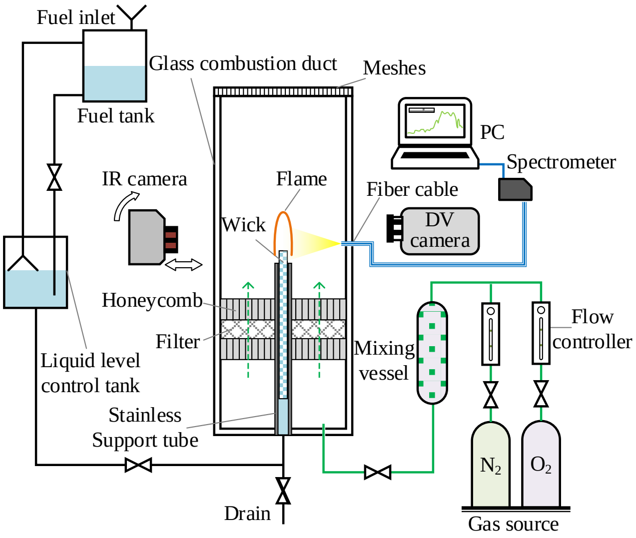


Fig. 1. Schematic of experimental system for flame stability measurement in wick-LOC method

In the experiments conducted herein, the oxygen concentration was adjusted under a constant axial flow velocity (10 cm/s). Complete flame extinction processes were directly recorded using DV camera. The flame stability limits given by the full and the wake flames were obtained by decreasing the oxygen concentration in steps of 0.1% until flame extinction. An infrared (IR) camera (spectral range of 8–13 μm) was used to capture the IR emission of the stabilized flames near limit condition. In this work, three linear alkyl carbonates, namely, DMC (dimethyl carbonate, $H_3COCOOCH_3$), EMC (ethyl methyl carbonate, $C_2H_5OCOOCH_3$) and DEC (diethyl carbonate, $(C_2H_5O)_2CO$), were tested as the typical electrolyte solvents used in LIBs, and three types of typical OPC addition, namely, TMP (trimethyl phosphate, $(CH_3O)_3PO$), TEP (triethyl phosphate, $(C_2H_5)_3PO_4$) and DMMP (dimethyl methylphosphonate, $CH_3PO(OCH_3)_2$), were examined. The results of DMC with TMP addition were analyzed as representative examples.

2.2. Approach to determining flame stability limits

Both the full and the wake flame stability limits were obtained during oxygen decrease in steps of 0.2% when approaching the limits. The waiting time after each step change of oxygen was set to more than 1 min to confirm the stable state of flame, which is longer than the time for new gas flow to replace the entire flow path (<10 sec). Each flame stability limit was determined as the average value of at least four repeated tests under an external flow of 10 cm/s, and deviations from the average value were recorded in the form of error bars, which are presented in this paper.

After several preliminary tests, the flame stability limits could be estimated approximately. The wick was ignited at a higher O_2 concentration to generate a full flame; then, O_2 was reduced in steps until an unstable flame base led to direct extinction or transition to wake flame; finally, the minimum O_2 concentration to sustain a stable full flame was considered the full flame stability limit. The approach to determining the wake flame stability limit depends on whether the full flame can transition to wake flame under decreasing O_2. With successful transition, the wake flame limit can be obtained by further decreasing O_2 until flame extinction. Otherwise, the full flame is extinguished directly. In this case, a stable wake flame should be re-established through ignition above the tip of the wick with a proper oxygen fraction. By reducing the oxygen carefully, the wake flame stability limit can be found at the minimum O_2 concentration at which the wake flame oscillates and shrinks to extinction.

3. Experimental Results

3.1. Observation of extinction processes

During the flame stability limits measurement of each pure electrolyte solvent and its mixtures with different proportions of OPCs, the extinction processes of each stabilized flame were observed by reducing oxygen in the external flow. Typical examples of pure DMC and DMC with TMP addition are shown in Fig. 2. During the extinction process of pure DMC flame in Fig. 2(a), the full flame is stable at a higher oxygen concentration; then, with decreasing oxygen concentration, the full flame becomes unstable and it turns into the wake flame, followed by extinction with further decrease in oxygen concentration. During the transition from full to wake flame, flame oscillation can be observed, which is a common behavior in candle flames [23,24]. The flames of the other pure electrolyte solvents (EMC and DEC) showed similar behaviors as that of the pure DMC flame in the extinction test.

However, when more OPC was added to the electrolyte, two distinct branches of the extinction process were observed. In the case of DMC with 10%TMP addition, once the stabilized full flame was obtained, it extinguished directly (blow-off) without transition to the wake flame, as shown in Fig. 2(b). When a stable wake flame was obtained by ignition at the tip face of the wick, the flame proceeds to extinction through oscillating motion, without transitioning to the full flame when the oxygen decreased, as shown in Fig. 2(c). These two branches of the extinction process can be found in the other high-OPC-addition cases as well.

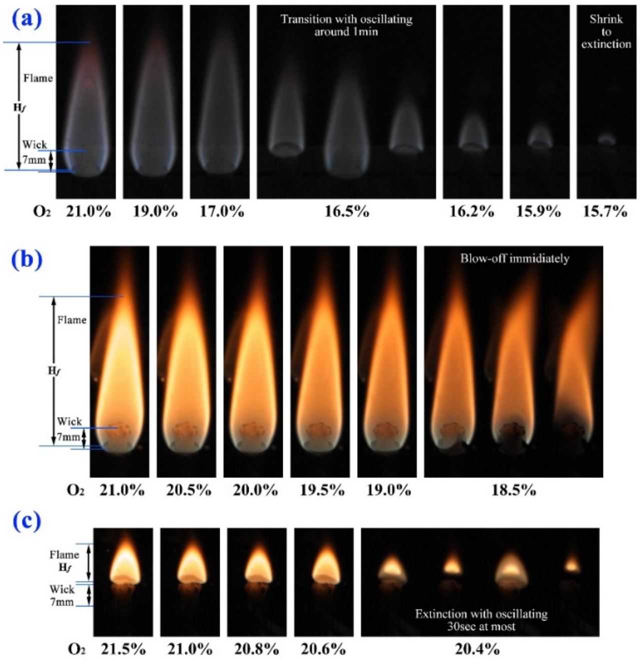


Fig. 2. Photographs of flame extinction process under continuous decrease of O_2 concentration. (a) pure DMC, extinction with transition from full to wake flame; (b) DMC+10%TMP, full flame direct extinction (blow-off); (c) DMC+10%TMP, wake flame extinction

The flame height was measured as the length from the visible flame base to the flame tip, as marked in Fig. 2. To clearly illustrate the different extinction phenomena of the wick flame in the case of pure DMC and DMC+10%TMP mixture, the changes in averaged luminous flame height during O_2 concentration decrease were recorded and plotted, as in Fig. 3. The solid lines with left-pointing arrows represent the change in flame height under decreasing oxygen concentration; the dashed lines with right-pointing arrows reflect flame growth from wake to full flame under increasing oxygen concentration. The barriers show the range of existence of each flame mode. The changes in the pure DMC wick flame indicate a common mutual transformation between the full and the wake flames. These findings are consistent with the numerical results obtained for a thick solid slab by using LOI method [14], where the hysteresis phenomenon was observed in the transition region. By contrast, the flame of DMC+10%TMP showed only unidirectional change from wake flame to full flame with increasing oxygen concentration; the stability limit of the full flame was lower than that of the wake flame.

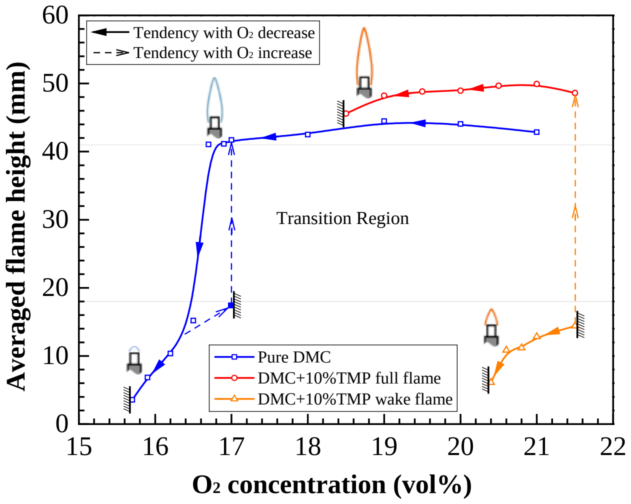


Fig. 3. Averaged flame height changes for full flame and wake flame in the cases of pure DMC and DMC+10wt.% TMP with oxygen change rate of 10cm/s in external flow

3.2. Flame stability limits of electrolytes with OPC addition

The definition of flame stability limit in this paper is the lowest oxygen concentration required to stabilize each flame mode (wake or full flame). This means there are two stability limits for a specific fuel corresponding to the two flame modes.

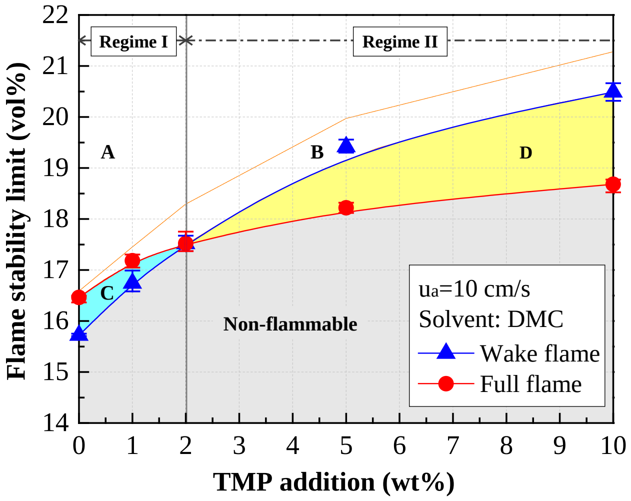
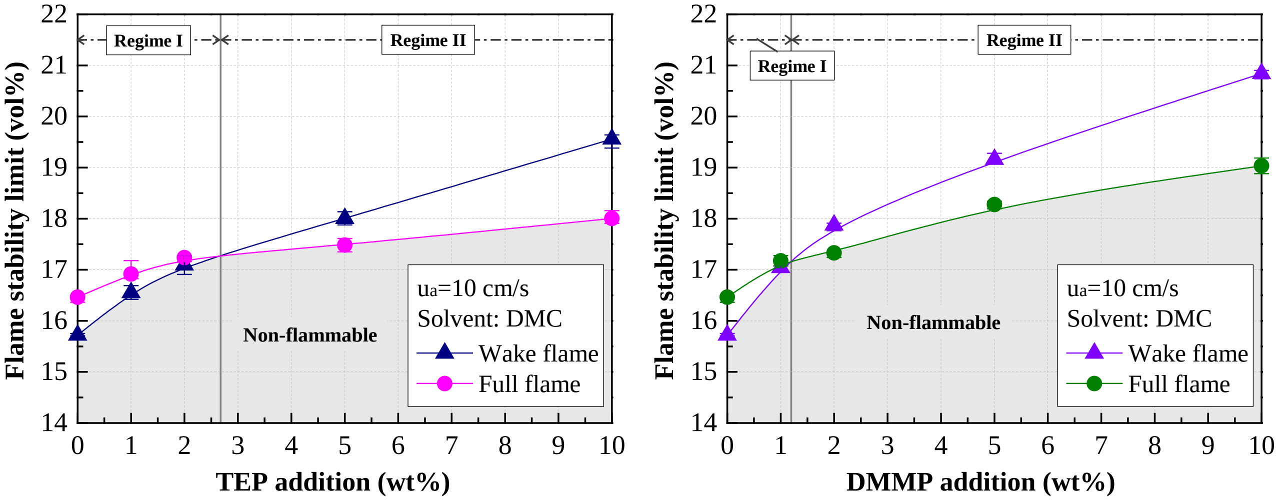


Fig. 4. Flammability map given by flame stability limits of DMC-based electrolyte as a function of TMP addition

The flame stability limits of DMC with added TMP (as a typical case) were first plotted, and a flammability map with five parts, as in Fig. 4, was obtained. Both flame limits increased with TMP addition, but the growth rate of flame limits declined, reflecting the marginal effectiveness of fire-retardation ability. The rise in wake flame limits of DMC with TMP addition showed strong sensitivity to TMP addition, which is consistent with the LOC results reported in [7]. However, the ascent of the full flame limits with the addition of TMP was less sensitive to the amount of TMP added. This comparison between the wake flame and the full flame showed that the wake flame was always more stable with no or low TMP addition, until the amount of added TMP exceeded the critical amount of around 2wt.%. After the addition of this critical amount of TMP, the full flame becomes more stable, as evidenced by the lower limiting oxygen concentration than that of wake flame, and with the increased TMP addition, the discrepancy between the limits of the full and the wake flames increases. As a result, the point of intersection of the full and the wake flame limit curves divides the figure into two regimes, Regimes I and II.

Combined with the stabilized flame modes at various oxygen levels, a flammability map with TMP addition can be formed in five parts, as in Fig. 4. The flammable zone is composed of parts A–D, while the bottom part is the non-flammable zone. The full flame exists solely in a higher oxygen levels in part A; and the zone of coexistence of the full and the wake flame is marked as B; only wake flames at lower oxygen levels occupy part C; part D indicates that only full flame can exist in this lower-oxygen region. The wake flame has a very limited range of existence according to areas of parts B and C. The fact that there is only one zone each in which the wake and the full flames exist under the lower oxygen condition is attributed to the dominant mechanisms in Regimes I and II, respectively.

To compare the influence of the type of added OPCs on the flame stability limits, TEP and DMMP were added separately to DMC for additional investigation. The flame stability limits of the DMC-based electrolyte with TEP and DMMP are plotted as a function of OPC addition in Fig. 5 (a) and (b), respectively. The increase in flame stability limits due to the addition of TEP and DMMP in DMC show trends similar to those in the case of TMP addition, albeit their respective effectiveness levels differ. Compared with the effect of TMP addition on the flammability of DMC, TEP not only shows a weaker fire-retardant effect on DMC but also has a later switch point between the two regimes (around 2.6% TEP addition compared to 2% TMP addition), and the discrepancy between the full and the wake flame limits under the addition of large amounts of TEP is smaller than that in the case of TMP addition. By contrast, DMMP is more effective than TMP in terms of flame retardation, and the switch to the second regime occurs with a lower amount added DMMP addition (1.2wt.%) than that in the case of TMP addition.

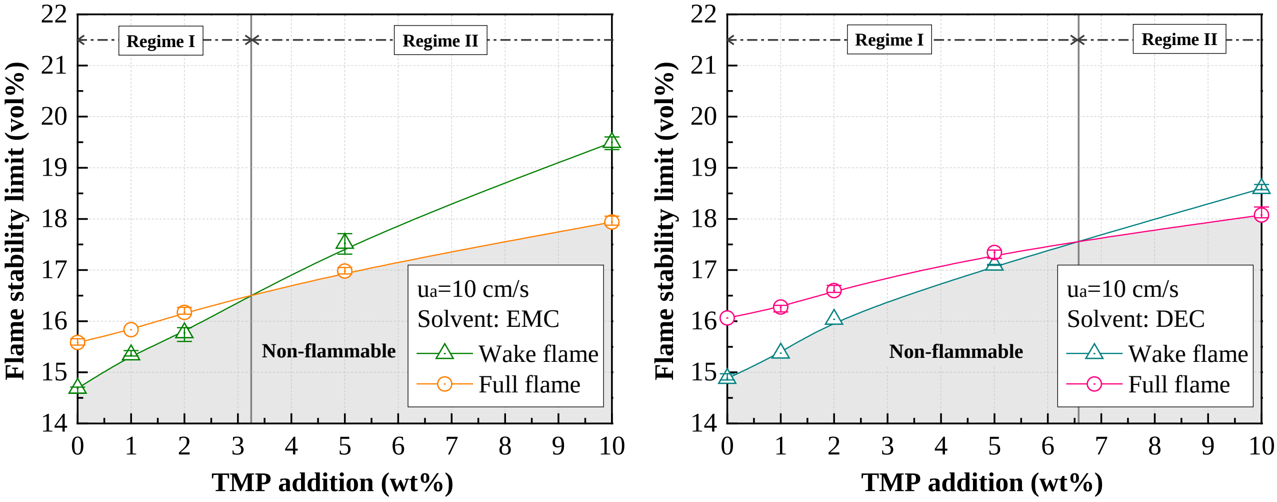


(a) (b)

Fig. 5. Flame stability limits of DMC-based electrolyte as a function of OPC addition. (a) DMC+TEP; (b) DMC+DMMP.

A comparison of flammability among the different electrolytes under the same level of OPC addition was made as well. EMC and DEC were selected as the same series of linear alkyl carbonates for comparison with DMC, and these three compounds have two, one, and zero ethyl groups, respectively. The flame stability limits of EMC and DEC with TMP are shown in Fig. 6 (a) and (b) for comparison with the DMC-based electrolyte solution. Although similar trends of the full and the wake flame limit curves is obtained, the absolute values of flame stability limits and the switch points of the two regimes are different. From these three tested electrolytes, the full flame limit shows sensitivity similar to that achieved with the TMP addition (around 2vol.% increase by adding 10wt.% TMP), whereas the wake flame becomes less sensitive than that in the DMC case, especially with the addition of DEC. Even though pure DEC has a slightly higher LOC than EMC, the fire-retardation effect of high TMP addition on DEC is weaker than that on the other electrolytes owing to the insensitivity of

DEC to the TMP addition.



(a)

(b)

Fig. 6. Flame stability limits with the addition of TMP to other linear alkyl carbonates: (a) EMC and (b) DEC.

4. Discussion

In the previous section, two extinction limit branches corresponding to different flame modes (full flame and wake flame) were presented as a function of OPC addition. With addition of OPC, not only does the fire-retardant effect decrease, but also the most stable flame switches from the wake flame to the full flame. This is contrary to the case (and ordinary experience) without any retardant in a candle-like flame configuration. High OPC addition was found to be marginally effective in terms of the retardation of gas-phase flames based on the condensation of phosphorus-containing intermediates and the fuel effect of OPC, which was found in extinguishment tests on a cup burner flame by using OPC-containing extinguish agents [8,9,25]. However, the aforementioned works did not consider reversal of the flame stability limits of the full and the wake flames. In the following section, the mechanisms of the reversal of the order of extinction limits in the two different regimes is discussed.

It is known that there exist two branches of the extinction limit for a candle-like flame (under LOI method configuration) [21,26]. The first branch is blow-off and the second branch is quenching extinction.

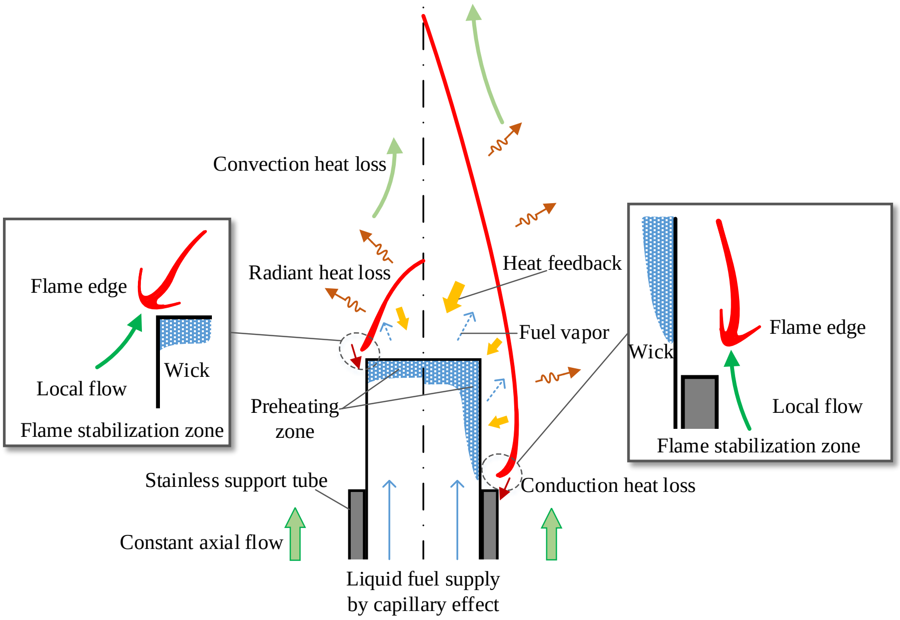


Fig. 7. Schematic description of stabilization of wake (left) and full flame (right) over wick configuration

From the viewpoint of fluid dynamics, flame propagation speed at the flame base (flame leading edge) is comparable to the local flow velocity required to maintain the flame position [27,28]; otherwise, blow-off extinction occurs (see Fig. 7). Generally, the local flow velocity of the wake flame at the flame base is less than that for the full flame because of small flame size and the resulting weak buoyancy-induced flow. Furthermore, if the flame is stabilized behind the top end of the wick, local flow velocity should be much less in the wake of the wick. Therefore, if we explain the extinction limit based solely on this blow-off mechanism, the extinction limit with the wake flame should be always lower (in other words, more stable) than that of the full flame because the local flow velocity near the flame base is lower with the wake flame, as explained above. The order of the stability limits in the low-OPC-addition range is consistent with this understanding (in Regime I), and this is also true in the case of the solid material flammability limit obtained using the LOI method based on ISO4589-2 [11–14,17]. By contrast, it cannot be explained by the order of flame stability is switched in the high-OPC-addition case, also called Regime II, according to the above understanding. In this case, the quenching mechanism could potentially be the key to understanding the switching mechanism.

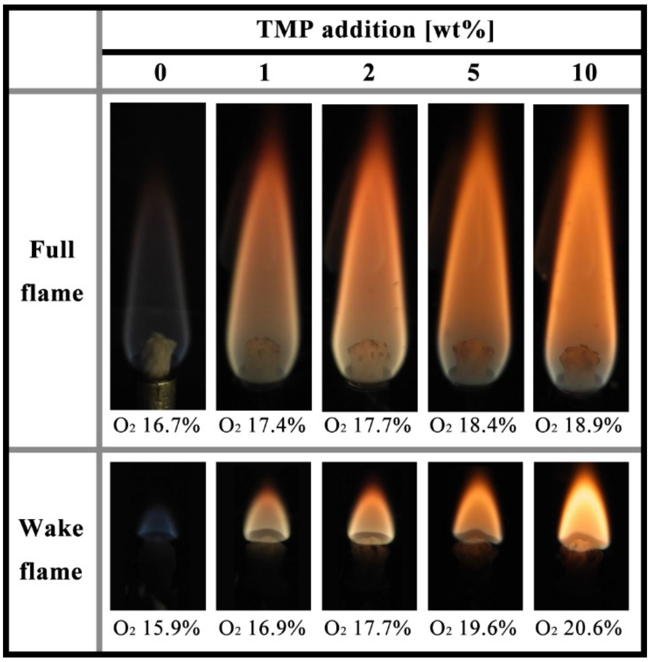


Fig. 8. Images of stabilized flames of DMC/TMP mixture near stability limits (LOC + 0.2%)

An example of the stabilized flames of DMC with various amounts of TMP addition near the extinction limits (LOC + 0.2%) is shown in Fig. 8. A blue translucent flame is generated from pure DMC, whereas a more luminous and yellow flame is generated with increasing TMP addition in the case of the full flame and the wake flame. The presence of the luminous flame is mainly attributed to the increased formation of phosphorus-containing particles from the added OPC [8,9]. In addition, we previously reported that the flame temperature increases with OPC addition at the same O_2 concentration [7], which could be explained by enhanced transitions from radical species (such as OH and H radicals) to stable species (typically H_2O) with aid of phosphorus compounds in gas-phase combustion. Similar facts have been reported by Korobeinichev as the promotion effect on flame temperature of OPC, in addition to its chemical inhibition effect [29,30]. Owing to such increases in temperature, OPC addition should lead to an increase in total heat loss from the flame to the surroundings, with an increased temperature gradient. Generally, it is understood that in combustion phenomena, the heat generated by a flame is a function of the flame volume, whereas the conductive heat loss to the environment is proportional to the flame surface area. Because conductive heat loss accounts for the major part of the total heat loss from a small-scale flame under normal gravity conditions [14,15], the ratio of heat loss to heat generation is dominated by the surface volume ratio (S/V) of the flame. The unique feature of the wake flame can be ascribed to its smaller size than that of the full flame, which results in a large S/V ratio. Therefore, the impact of OPC addition on the wake flame in terms of the temperature drop from the adiabatic flame temperature is quite significant in comparison to that in the full flame case. As a result, OPC addition degrades the stability of the wake flame to a greater extent than that of the full flame owing to the larger temperature drop in the former case. In this scenario, the flame extinction limit in the case of the wake flame should be higher (more unstable) than that in the case of the full flame.

As discussed above, flames are divided into two regimes based on the critical amount of OPC addition, as follows: Regime I represents the scenario in which the local flow velocity dominates the extinction limit of the two types of stabilized flame, and it is called the "blow-off regime." By contrast, regime II represents the scenario in which the smaller flame is at a disadvantage owing to excessive heat loss, and it is called the "quenching regime."

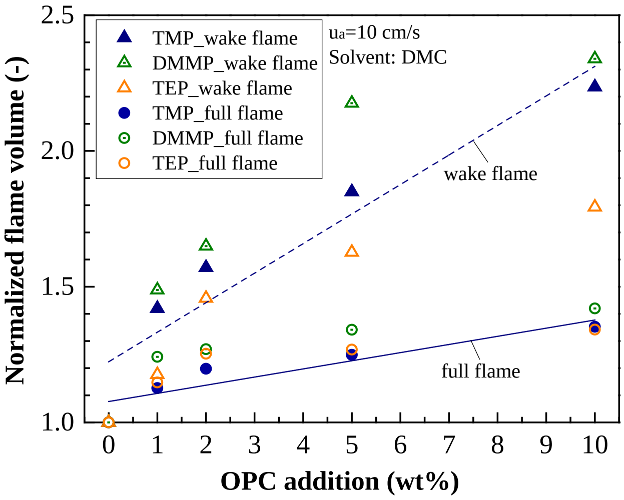


Fig. 9. Normalized flame volume of near-limit stabilized flames as a function of OPC addition in DMC

As already discussed, the wake flame has a higher ratio of heat loss to heat generation than that of the full flame owing to its smaller size. Assuming there exists a critical heat loss ratio at which the flame is maintained, flame volume should increase with increasing flame temperature. As the flame temperature increases with increasing OPC addition [7,29,30], we can expect the flame volume to increase with increasing OPC addition to sustain combustion, even near the extinction limit. Fig. **9** shows the change in normalized flame volume near the extinction limit as a function of OPC addition for the wake flame and the full flame. As can be seen in the figure (straight-line-fitting of TMP case), the rate of increase in flame volume is considerably larger in the case of wake flame, implying that quenching is the dominant mechanism governing extinction of the wake flame.

Because quenching dominates extinction of the wake flame in regime II, the extinction limit in terms of oxygen concentration is higher than that of the full flame because with increasing flame temperature, the smaller flame size is not favorable from the viewpoint of the flame stability.

5. Conclusions and future works

In this study, the low oxygen limits of typical electrolytes mixed with different types and amounts of OPC retardants were investigated using the wick-LOC method. Two modes of the wick-stabilized flame were found near extinction, namely, wake flame and full flame (side-stabilized enveloping flame). It was discovered that the wake flame can be less flammable than the full flame when the OPC addition exceeds a critical value, which is contrary to the case without OPC. The major findings are as follows:

(1) Flame extinction processes were observed under decreasing oxygen concentration. In case of the blue flame of pure DMC, the full flame successfully transitioned to the wake flame and, finally, extinguished with decreasing oxygen concentration. By contrast, in the 10% TMP addition case, no transition was found; instead, the extinction limit of the full flame was lower than that of the wake flame.

(2) Flame stability limits were determined to compare the two stabilized flames with OPC addition. The reversal points of the two flame stability limits were found at 2wt.% TMP addition in DMC solvent, which divided the flammability map into two regimes with different regions of existence of the two stabilized flames near extinction.

(3) Comparison experiments were conducted to show the effects of the type of OPCs and electrolyte solvents on flame stability limits. TEP showed weaker fire retardation and a higher regime switching point (2.6wt.%)

than TMP, while the effect of DMMP addition in DMC was the strongest, with the regime switching point occurring at 1.2wt.%. Lower sensitivities of the wake flame to TMP addition to EMC and DEC were found, as manifested in the higher regime switching points (3.2wt.% to EMC and 6.6wt.% in DEC).

(4) The flame extinction mechanisms were discussed to clarify the reversal of the flame stability limits of the full and the wake flames. In addition to blow-off mechanism, heat loss in the flame was emphasized based on the flame volume near the extinction limit. The flammability map is divided by the critical amount of OPC addition into two regimes: “blow-off regime” and “quenching regime,” which can explain the influence of OPC addition on the flame stability in each flame modes.

For the flammability test in the wick-LOC method, the addition of OPC flame retardant can change the contribution ratio of chemical reaction, kinetics, and thermal balance in terms of the flame extinction mechanism. For further use of the wick-LOC method for evaluation of LIB electrolyte flammability, additional discussion on which flame stability limit is more suitable for practical application is required, along with numerical works, in the future.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version.

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