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Influence of lithium salts on the combustion characteristics of dimethyl carbonate-based electrolytes using a wick combustion method

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Highlights

- The influence of three lithium salts on DMC-based electrolyte combustion was studied.
- Self-extinguishing of the wick flames always occurred in salt containing electrolytes.
- LiPF_6 had a remarkable flame-retardant effect to increase the flame extinction limits (wick-LOC).
- The radicals from salts have different effects on the flame behaviors in gas phase.
- Solid-phased reaction like surface accumulation of LiF caused wick flame extinguishing.

Abstract

Flammability studies of electrolytes are required for screening safer materials used in lithium-ion batteries. To clarify the influence of lithium salts on the electrolyte flammability, experimental analyses were conducted using a unique wick combustion system in conjunction with the limiting oxygen concentration (LOC) test, called wick-LOC method. 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. In the case of LiTFSI , the serious charring of the cotton wick was considered as a potential hazard on solid combustibles in the real fire scenarios.

Keywords

Flammability; Lithium-ion battery; Electrolyte; Lithium salt; Wick combustion

1. Introduction

Lithium ion batteries (LIBs) have been widely used in portable electronic devices, electric vehicles, large energy storage systems and other fields due to their high energy density and portability [1]. However, the fire and explosion accidents associated with LIBs have been reported frequently in recent years, and the fire safety issue has been emphasized in the LIB industry [2]. The main contribution of the LIB fire can be traced back to the combustion of electrolytes [3]. As the organic solvents (carbonates or ethers) are used in commercial battery electrolytes, their flammability can bring a larger combustion energy than the electro-chemical energy of the battery cell [4]. To mitigate the fire hazard of electrolytes, the flammability and thermal instability evaluations are always required including different organic solvents and multi-component electrolytes with lithium salts or some functional additives.

Researchers in LIB community have conducted numerous flammability tests and thermal instability analysis on electrolytes and their components. With the typical flammability tests of solvents or mixed solutions, a higher flash point (FP) and auto ignition temperature (AIT) or a shorter self-extinguishing time (SET) are expected for screening safer materials and formulations [5,6]. While such properties are always dominated by the evaporation process of liquid solvents, the effect of lithium salts addition cannot be clearly identified in the experimental results [7,8]. On the other hand, thermal stabilities of lithium salts and their based electrolytes have been widely investigated at elevated temperature (usually up to 350°C) [9–13]. The onset of thermal decomposition and endo-/exothermic processes of salts are always of interest to these studies. Lithium hexafluorophosphate (LiPF_6), even as the most popular salt in the commercial LIBs, has an unsatisfying thermal stability and easily hydrolyzes [14–16]. While, lithium tetrafluoroborate (LiBF_4) and lithium bis(trifluoromethanesulfonyl)imide [LiTFSI ,

LiN(CF₃SO₂)₂] showed better thermal stabilities attempting to replace the LiPF₆ in the battery cell [17–19]. The thermal stability and traditional flammability tests above focus more on the prevention of electrolytes ignition and thermal runaway; however, it might be inadequate to reflect the role of lithium salts on burning cases of electrolytes.

Besides the ignition-related properties, the flame propagation-/extinction-related properties are equally important to the material flammability, especially for fire suppression and damage control; however sometimes they are not consistent to each other [20]. The ideal thermal stability of lithium salts is required to be comparable to that of other electrolyte components without exceeding the operative temperature of LIBs [21]; while in a fire case of much higher temperature, the salts can play a distinct role which may affect the fire suppression and toxicity [22,23]. To understand how the addition of salts affecting the fire growth and extinction fundamentally, the combustion analyses are expected. The pool fire of electrolytes with LiPF₆ addition have been investigated using a cone calorimeter by Fu and co-workers [24], while heat release rate and flame geometry results can hardly reflect the effect of salts explicitly. Eshetu and co-workers have used Tewarson calorimeter to study the lithium salts effect on fire behaviors under an oxygen-rich environment. Their results showed that the heat release rate profiles and toxic gas products differed in electrolytes of LiPF₆ and Lithium bis(fluorosulfonyl)imide (LiFSI) [25]. Variations of limiting oxygen index (LOI) tests were also applied in screening safer electrolyte formulations [26–30], however the insights into salts effect on electrolytes combustion are still in development.

In this paper, a wick combustion apparatus in conjunction with limiting oxygen concentration (LOC) method was utilized to investigate the combustion characteristics and flammability of electrolytes, called wick-LOC

method [31,32]. Three typical lithium salts, LiPF₆, LiBF₄ and LiTFSI, were dissolved in dimethyl carbonate (DMC) solvent as 1 mole per liter (1M) addition to compare the influence of salts on combustion characteristics of DMC based electrolytes. The flame behaviors, extinction limits and combustion residues were compared. The potential hazards were discussed referring to the pure DMC combustion and flame-retardant-added cases as well.

2. Experimental approaches

2.1 Preparation of electrolytes

Dimethyl carbonate [DMC, OC(OCH₃)₂], the simplest linear carbonate commonly used in LIB electrolytes, was selected as the solvent in this comparative study to unify the solvent effect. Three kinds of typical lithium salts, (LiPF₆, LiBF₄ and LiTFSI) were selected as 1M addition in DMC. As the control groups, pure DMC, DMC with 1 and 10 wt% trimethyl phosphate [TMP, PO(OCH₃)₃] additions were tested as well, in order to show closer flame extinction limits (LOC) to the salt-added cases. The DMC solvent (purity > 99.5%) and salts (purity > 99.5%) were obtained from Kanto Chemical Co., Inc.; the TMP (purity > 98%) was obtained from TCI Co., Ltd. Six DMC-based solutions/solvent were prepared as shown in Table 1.

Table 1 DMC-based solutions with/without salts for experiments.

Designation	Solvent	Flame retardant addition	Lithium salts addition
A	DMC	--	--
B	DMC	1 wt% TMP	--
C	DMC	10 wt% TMP	--
D	DMC	--	1M LiPF ₆
E	DMC	--	1M LiBF ₄
F	DMC	--	1M LiTFSI

2.2 Experimental setup

The combustion experiments on electrolytes were carried out by the means of the wick-LOC method which was modified from LOI method in our previous work [31,32]. The limiting oxygen concentration (LOC) to sustain the flame can be determined by precise adjustment of oxygen. As shown in Fig. 1, the experimental setup of wick-LOC method comprises three main parts: the fuel supply system (left) to provide a constant altitude of liquid fuel; the gas control system (right) to supply the well-mixed gas of N_2/O_2 ; and the combustion chamber (middle) to generate a wick-stabilized flame under a constant external flow velocity (10 cm/s).

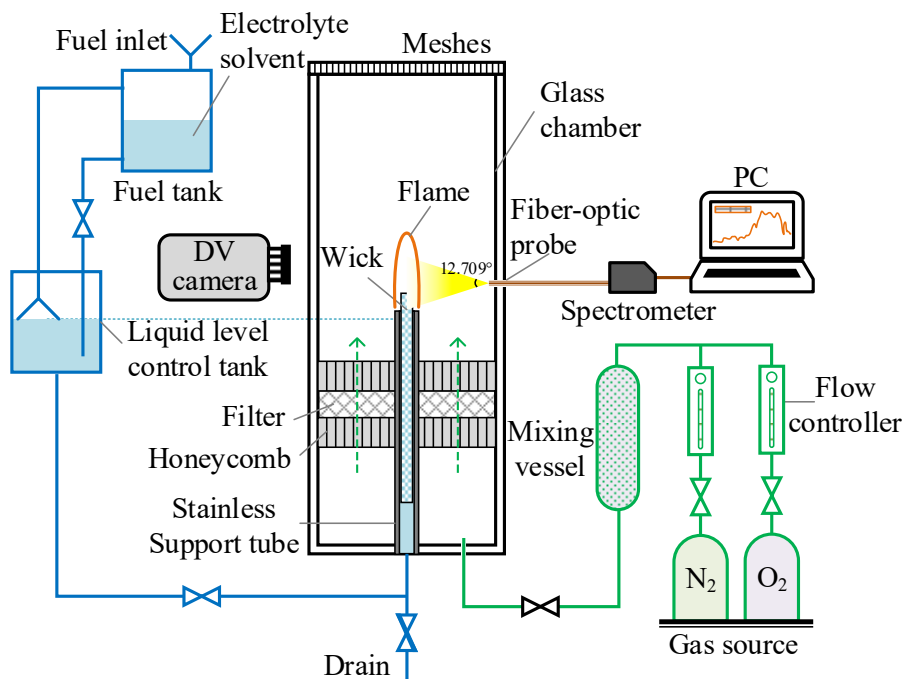


Fig. 1. Schematic of experimental setup (wick-LOC method).

Considering the layered nature inside the battery cell (liquid jelly roll or prismatic-cell configuration) [1,23,33], we chose to burn the electrolytes through a porous media (a cotton wick) for investigating the interaction of the

flame and combustible solid media. The cotton wick (7mm in height, 5mm in diameter) impregnated with the electrolytes can generate a candle-like diffusion flame. To avoid the aging and combustion deposition on the wick surface, the wick was refreshed for each trial by trimming the burned part.

For the flame suppression experiments, the DV camera was used for observing the evolution of the flame. 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, which has been commonly applied in combustion research [34,35]. The combustion residues from burned wick were characterized utilizing scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2.3 Experimental procedure

The flame extinction limits of DMC-based solvents/electrolytes were given as the limiting oxygen concentration of the wick-stabilized flame (wick-LOC). The wick-LOC is defined as the lowest oxygen concentration to sustain the candle-liked diffusion flame with the wick configuration, and it was obtained under a constant axial flow velocity (10 cm/s) in this paper. The experimental procedure of wick-LOC method followed the LOI method (ISO4589-2) in principle. Due to the unique fueling system and wick flame configuration, following detailed procedures were specified as developed in the previous work [31,32].

After fueling, the air tightness of the fueling system (blue part in Fig. 1) and the stable liquid level should be ensured. Then the tip of the wick was touched by a filter paper to check the saturation of the wick surface. After a steady supply of the external air flow (10 cm/s) at a higher oxygen level (more than 20 vol%), the lighter was placed on the tip of the wick to ignite it. For the electrolyte solvents without salt addition, the steady state of flames can be sustained at a constant oxygen level. With a gradual reduction of oxygen concentration in the

constant external flow rate, the flame would shrink to extinction. However, for the salt-added cases, preliminary experiments under 21 vol% oxygen were conducted to find the unique flame behaviors. The procedure to determine the wick-LOC of salt-added cases was improved in next section.

3. Results and discussion

3.1. Flame observation

To compare the flame behaviors, the preliminary experiments for different DMC-based mixtures were conducted at 21 vol% oxygen concentration with the external flow velocity of 10 cm/s. The flame behaviors of different solvents or electrolytes were shown in Fig. 2 (corresponding to the Supplementary materials). The stable flames of pure DMC, DMC with 1 wt% and 10 wt% addition of TMP were shown in Fig. (a), (b) and (c), respectively. In contrast, the flames of electrolytes with lithium salts addition (LiPF_6 , LiBF_4 and LiTFSI) can hardly sustain the steady state and finally went to self-extinguishing, as indicated in Fig 2 (d), (e) and (f) correspondingly. The solid residue of each salt-added case was recorded as the last image of each row.

Comparing with the blue flame of pure DMC, luminous yellow/orange flames of DMC with 1 wt% and 10 wt% TMP addition can be found. The luminous flame reflected the formation of phosphorus-containing particles in the flame due to the addition of organophosphorus compound as a flame retardant [36]. With more addition of TMP, the luminosity and height of the flame slightly increased. The cotton wicks in all salt-free solvents flames showed no trimming or charring during the combustion.

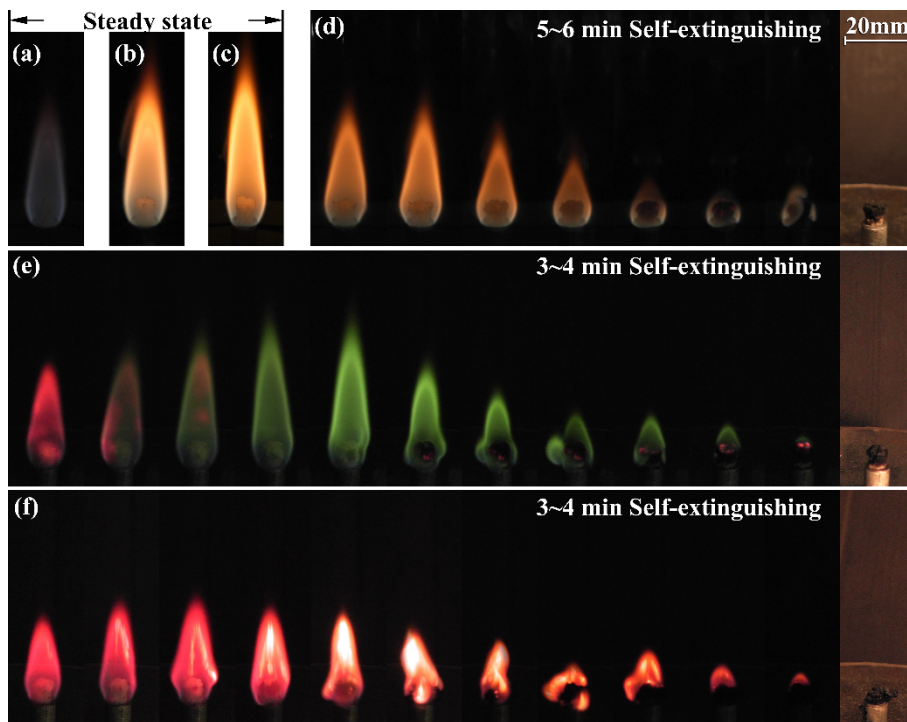


Fig. 2. Flame colors and burning behaviors of different DMC-based mixtures: (a) pure DMC, (b) DMC+1wt% TMP, (c) DMC+10wt% TMP, (d) DMC+1M LiPF₆, (e) DMC+1M LiBF₄, (f) DMC+1M LiTFSI.

Similarly, the electrolyte of DMC+1M LiPF₆ initially gave a yellow/orange flame, but the flame height and luminosity are lower than that of TMP-added cases. As some white solid products were formed and accumulated on the surface of the wick, the flame shrunk gradually due to insufficient fuel vapor release. Finally, the wick was charred, and the flame went to extinction. The main solid product was inferred to be lithium fluoride (LiF) as a thermal decomposition product from LiPF₆ [19]. Further residue analyses were conducted to confirm it in the later section.

The flame of DMC+1M LiBF₄ showed a unique color change during combustion. A red flame was obtained right after igniting, then it gradually changed to a green flame within 1 min, the flame height slightly increased as well. After the transition of flame color, a similar flame self-extinguishing process was observed due to the

accumulation of solid products.

For the flame behavior of DMC+1M LiTFSI, the red flame can be seen throughout the burning process. Then, some bright yellow parts of the flame were generated and expanded, accompanied by the erosion and charring of the wick. Different from LiPF₆ and LiBF₄, no accumulation of white solid products can be observed with the presence of LiTFSI, while the black viscous (char- and tar-like) residue took place because of cotton wick pyrolysis. Finally, the flame went to self-extinguishing by serious charring and insufficient fuel vapor release.

3.2. Comparison of flame extinction limits

According to the preliminary experiments above, the solid products from lithium salts decomposition would damage the surface of the wick in a continuous burning. As the fuel vapor release can be blocked by the surface accumulation of the solid products, the wick-LOC values would be overestimated when the burning time was long.

Therefore, a specific procedure to determine the extinction limit (wick-LOC) with shorter burning time was required until the surface effect can be neglected. First-step was finding the approximate range of LOC by adjusting the O₂% for ignition to check whether the flame can be ignited. In the second-step, the wick soaked with electrolytes was ignited from the near-LOC conditions to generate a small flame stabilized on the top of the wick; then quickly decreasing the oxygen with small decrement until flame extinction. Before each new ignition, the exposed wick should be cut and refreshed. The wick-LOC results were determined as the average value of at least four repeated tests. As a result, the wick-LOC of DMC-based solvents or electrolytes were summarized in Fig. 3, and the images of stabilized flame near extinction limit (at LOC+0.2 vol%) were recorded

correspondingly.

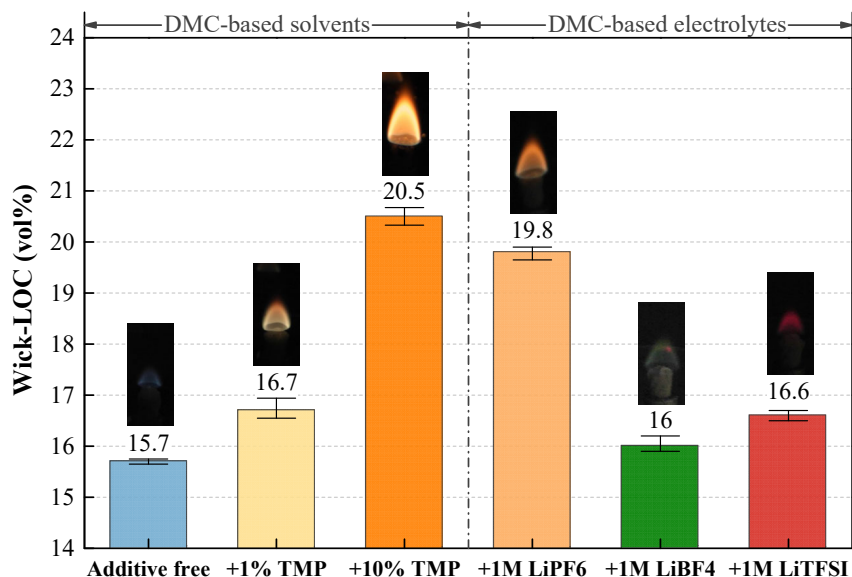


Fig. 3. Wick-LOC of DMC-based solvents and electrolytes.

With the addition of TMP as a flame-retardant additive, the wick-LOC of DMC-based solvents increased obviously. In comparison, a higher extinction limit of DMC+1M LiPF₆ showed a similar flame-retardant effect as the case of +10% TMP possibly due to the presence of phosphorus-containing compound in the flame. However, the wick-LOC results of DMC+1M LiBF₄ indicated the negligible effect of LiBF₄ on electrolyte flammability, even fluorine existed in the salt. The addition of 1M LiTFSI to DMC also gave a limited effect on the flame extinction, with about 1 % LOC increase.

3.3. Flame spectrum analysis

According to the different burning behaviors and flame extinction limits of electrolytes with three lithium salts additions, the flame spectrum analysis was conducted to clarify the salts effects on combustion, especially in

flame. The light emission intensities of flames given by DMC-based solvents and different salt-added electrolytes were indicated in the following figures. Some radicals can be identified depending on the spectral bands at some specific wavelengths. The light emission intensity of each radical is not only related to its concentration but also to the flame temperature.

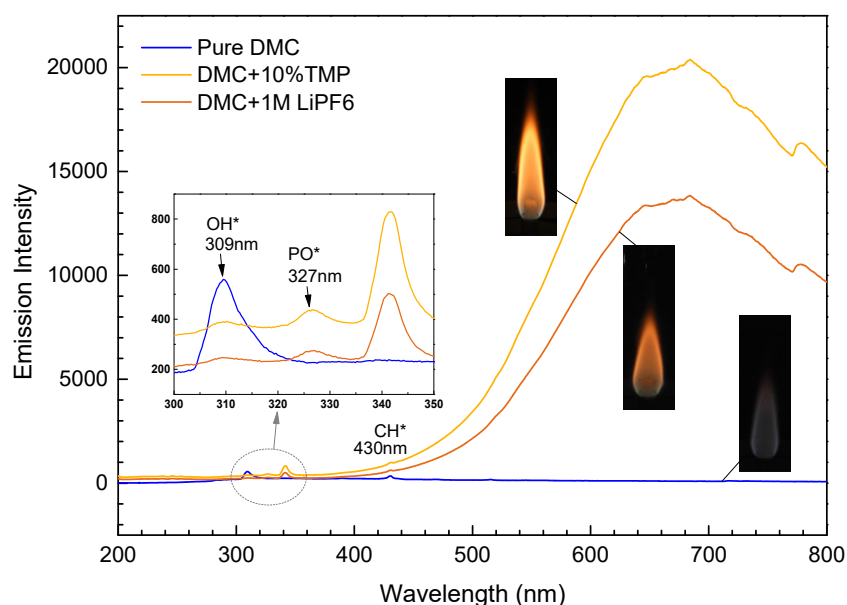


Fig. 4. Measured flame spectrum from different fuels: pure DMC, DMC+10 wt% TMP and DMC+1M LiPF₆.

In Fig. 4, the flame spectrum of pure DMC as a baseline only had two small peaks at 309nm and 430nm corresponding to the OH and CH radicals, respectively [37–39]. The flame spectrum profiles of DMC+10 wt% TMP and DMC+1M LiPF₆ were quite similar, both showed weakened emission intensities of OH and strong continuous emission of visible light. With the presence of phosphorus compounds like HPO₂, PO, PO₂ and HPO in the flame, the radicals OH and H can be captured to suppress the gas-phase combustion [40–42]. The small PO emission around 327 nm [43,44] and PO₂ involved in visible continua [45] suggested a similar role of LiPF₆

and TMP in gas-phase combustion. Such behaviors were also consistent to the flame inhibition and particle formation in cup burner flame when the phosphorus containing compounds added into the oxidizers [36].

As the radical recombination were catalyzed by phosphorus oxides and acids in the flame, the effective amount of phosphorus atoms from the phosphorus element sources (LiPF_6 and TMP) dominate the effectiveness of flame inhibition. Generally, the molar fraction of phosphorus atoms is higher in DMC+1M LiPF_6 than that in DMC+10 wt% TMP, which is 1 mol/L and 0.846 mol/L, respectively. However, the flame spectrum intensities and extinction limits gave reversed results. The potential reason is that the major part of the P atoms was lost as a noneffective compound (gaseous PF_5) during the thermal decomposition of LiPF_6 . Although LiPF_6 contains lithium, there was no light emission from Li radicals in the flame at 670.4 nm [35]. Most of the lithium was considered to form the most stable solid product, lithium fluoride (LiF), on the wick surface with no transport into the flame region. Therefore, the LiPF_6 addition gave two effects on the electrolyte combustion: one is the extinction limit of DMC flame due to the phosphorus from the anion; the other is the solid products formation from the lithium. The solid residues will be clarified in the later section.

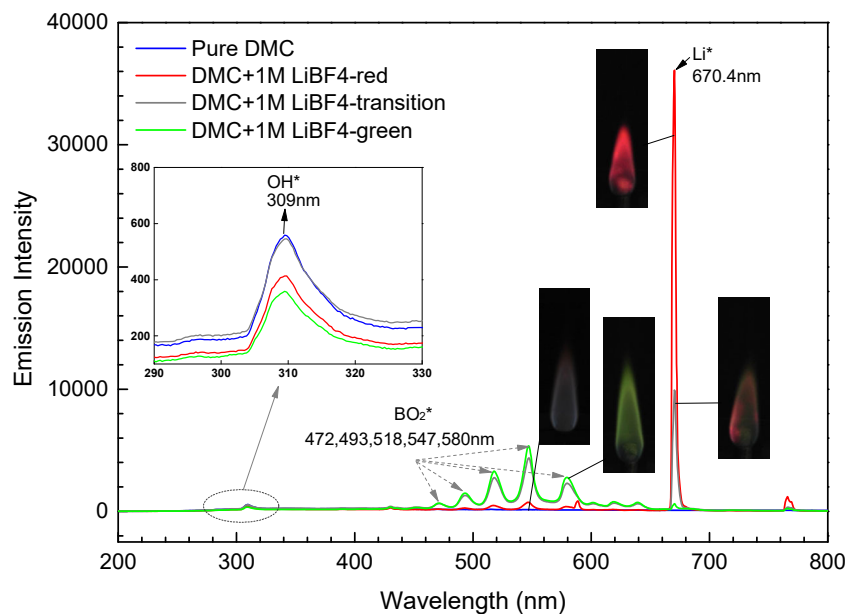


Fig. 5. Measured flame spectrum of DMC+1M LiBF₄ in different stages of combustion: red flame, transition and green flame.

Comparing with pure DMC, the flame spectrum of DMC+1M LiBF₄ in three different states (red flame at initiation, transition state from red to green flame, and green flame after transition) were presented in Fig. 5. Initially, the red flame had a strong emission intensity at 670.4 nm corresponding to Li radicals but very small intensities on the other wavelengths. During the transition of flame color, the emission intensity at 670.4 nm dropped dramatically, and some peaks from 472~580 nm becomes stronger reflecting the boron component (BO₂) release [46]. While after the transition, the clear green flame occurred because of BO₂ release. Most of the lithium were captured on the surface of the wick to form solid products (LiF), and it finally affected the self-extinguishing of the wick flame. As shown in enlarged spectrum of OH embedded in Fig. 5, small difference of OH intensity can be found for pure DMC and LiBF₄ added electrolyte. Therefore, the LiBF₄ addition, especially boron atoms, had a negligible effect on the flammability of electrolyte in the gas-phase combustion.

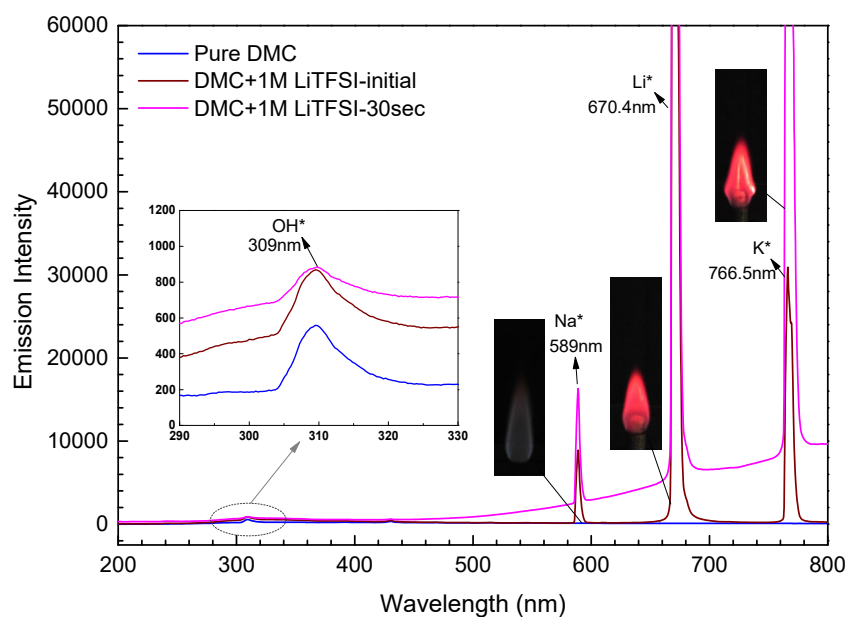


Fig. 6. Measured flame spectrum of DMC+1M LiTFSI in different stages of combustion: initial state and 30s after ignition.

In Fig. 6, as the red color existed throughout the burning of DMC+1M LiTFSI, strong intensities (exceed the boundary) at 670.4 nm showed a band emission of Li radicals found continuously during the experiment. After 30sec combustion, the emission intensity peaks at 589 nm and 766.5 nm wavelength increased significantly, along with the occurrences of bright yellow part in the flame and charring of the wick. These two peaks were related to the light emissions of Sodium (Na) and Potassium (K) radicals, respectively [35], which were attributed to the pyrolysis (charring) of cotton wick [47]. The intensities of OH radical implied that the local flame temperature increases with LiTFSI addition, but the reaction rate decreased slightly when wick charring. As it has been reported that the decomposition of LiTFSI was exothermic [17,19], such heat release could support charring of the wick. Concerning the layered structure of a LIB cell, the separator made by nonwoven fibers or polymer films could be affected by such exothermic reaction in combustion. A potential hazard is that the other solid combustibles in cell could be involved into the overall combustion and make larger damage. On

the other hand, the charring could be regarded as a flame-retardant effect in solid phase to prevent the heat and oxidizers. Yet the mechanism has not been fully understood, further investigations are expected.

3.4. Combustion residues

The self-extinguishing of the wick flame has been found in the three salt-added cases at 21 % oxygen. Due to the solid phase behaviors on the wick surface: solid products accumulation in LiPF_6 and LiBF_4 cases, and charring in LiTFSI case, the flammable vapor was blocked from the wick to prevent its reaction with the oxidizer. To characterize the combustion residues, the SEM images were taken in comparison with the original cotton wick, as shown in Fig. 7.

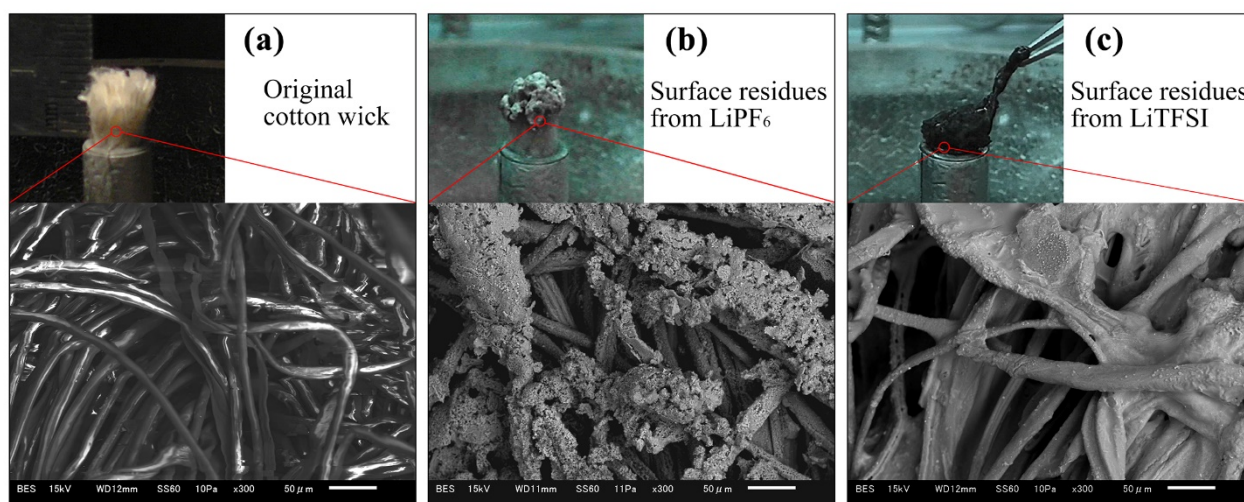


Fig. 7. Direct and SEM images of combustion residues on the cotton wick (a) original cotton wick, (b) LiPF_6 , (c) LiTFSI .

The SEM image of the original cotton wick [Fig. 7(a)] showed a clear fibrous structure, the pores can provide the outlets to supply the fuel and vapor. During the combustion of LiPF_6 - and LiBF_4 -added electrolytes, the grayish-white solid products were formed on the surface of the wick. The SEM image (b) showed the solid

product accumulated on the wick fibers and gradually covering the pores on the surface. In the cases of LiPF_6 and LiBF_4 addition, the wick as a porous media seemed not to react with the solid products, but it was just baked before flame self-extinguishing. The wick for LiTFSI-added electrolyte combustion, by contrast, was charred seriously with some tar-like products formed, as can be seen in Fig. 7(c). In the SEM image, the tar-like residues melt and finally covered the pores on the wick surface as well. Combining with the existed results, LiTFSI gave more complicated behaviors during the electrolyte combustion: reactive with solid combustible (cotton wick) leading to a larger damage; charring effect to suppress the flame in the later period. Due to the complexity of the combustion residues of LiTFSI-added electrolyte, more investigation on the intermediate products from LiTFSI in flame are expected in the future.

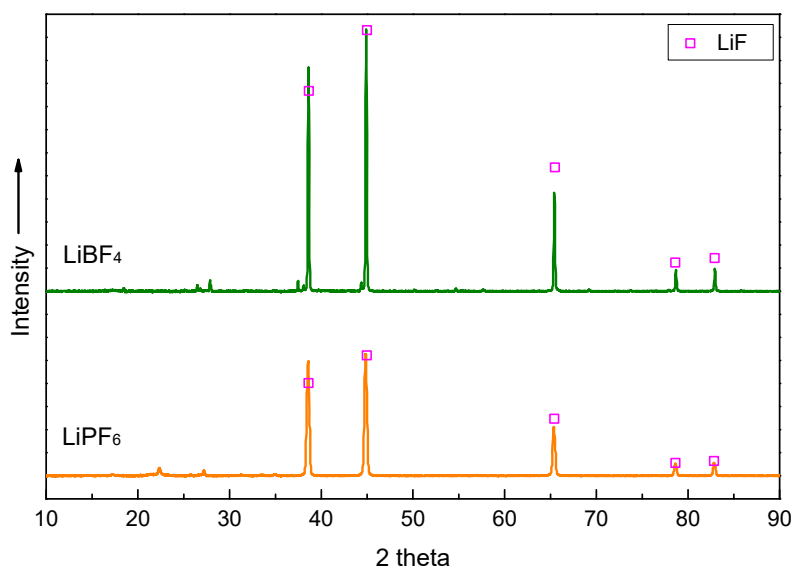
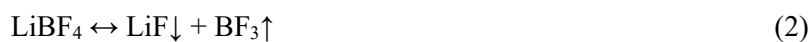


Fig. 8. XRD patterns of combustion residues of electrolytes adding LiBF_4 (green line) and LiPF_6 (orange line).

To identify the combustion residues of LiPF₆- and LiBF₄-added electrolytes, the accumulated solid residues were collected for the further XRD analysis, as shown in Fig. 8. Referring to the XRD pattern of lithium fluoride (LiF) [48], the crystalline material of combustion residues in both cases are mainly composed of LiF. The XRD results confirmed the decomposition products of LiPF₆- and LiBF₄-added electrolytes even in combustion scenarios. According to the overall thermal decomposition reactions reported by Kawamura [49] and Hong [19] below, the forward reactions are promoted during combustion.



Along with the crystalline LiF accumulated on the surface, the gas products PF₅ or BF₃ released to the flame region, and some complex intermediate reactions with O₂, H₂O and DMC followed. Inferring from the flame spectrum results, the intermediate compounds like phosphorus oxides and acids can further affect the combustion chain reactions of DMC. Therefore, the possible path of LiPF₆ involved in the DMC combustion on a porous wick configuration can be suggested in Fig. 9. Part of the released PF₅ contributed to the chemical flame inhibition in the gas phase, and the LiF solid covered the porous media to suppress the flame physically. Utilizing such behaviors, we can make a bolder concept to apply a porous media for the LIB fire protection, especially in electrolyte leaking cases of large scaled LIB pack. During a fire scenario, if the leaked liquid electrolyte can be absorbed by the incombustible porous media and burned, the fire can be controlled and finally self-suppressed by the LiF accumulation on the surface of porous media. Besides, porous protection can provide a better pressure release than sealed shell protection during thermal runaway. However, this concept should

consider how fast of the LiF salt can be produced on a porous media and which kind of porous material can fulfill the requirements of LIB protection. More discussions are expected in the future.

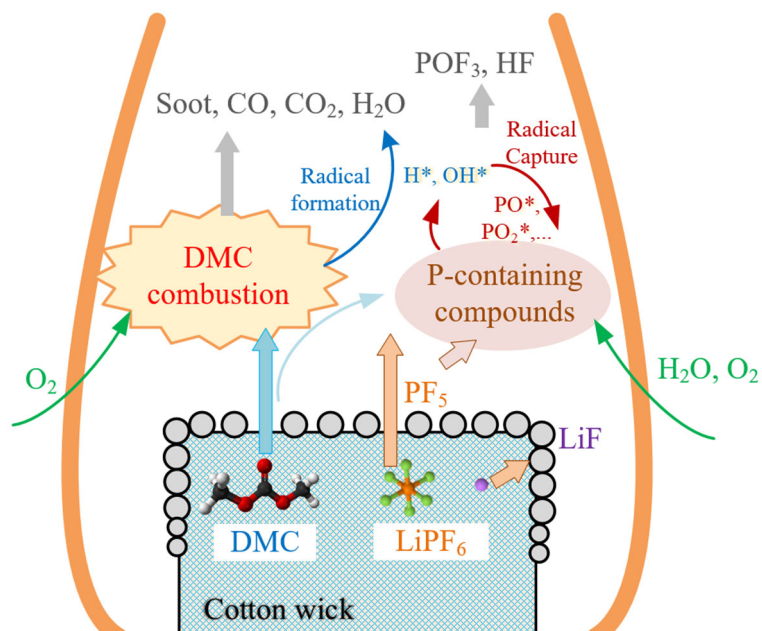


Fig. 9. Possible path of LiPF_6 involving in the DMC combustion on a wick configuration.

4. Conclusions

The combustion characteristics of DMC with lithium salts addition (LiPF_6 , LiBF_4 and LiTFSI) were investigated using the wick-LOC method, the main results are summarized below.

1. The flame behaviors of DMC-based solvents/electrolytes at 21% oxygen were observed. Differing from the stable flame of pure DMC and TMP added solvent, the flames with salts addition always showed unsteady nature leading to self-extinguishing. The unique behaviors including different flame shapes, colors and the changes of wick surface were found as well.

2. The flammability of electrolytes with lithium salts were successfully quantified by the wick-LOC method.

It showed that the electrolyte with LiPF_6 addition has a considerable flame-retardant effect; while both LiBF_4 and LiTFSI addition has limited effect on flame extinction.

3. With flame spectrum analysis, the unique flame behaviors of three electrolytes can be explained by the light emission of radicals. Combined with the LOC results, the anions of three lithium salts played different roles on the electrolyte combustion. The PF_6 anion in the solution had a quite similar role to the TMP additive in terms of the flame inhibition, but lower efficiency.

4. The combustion residues were analyzed by SEM and XRD to clarify the solid behaviors in combustion. The solid products of LiF from LiPF_6 - and LiBF_4 -added electrolytes combustion confirmed the decomposition reaction proceeded in combustion scenarios. However, in the case of LiTFSI addition, the combustion complexity like serious charring brought more concern about the potential hazard of LiTFSI .

The chemical flame inhibition in gas phase and physical suppression in solid phase of lithium salts, especially LiPF_6 , suggested a promising concept for the LIB fire protection using porous media. For the future utilization of this concept, more fundamental works are expected considering the LiF salt production and efficiency of flame suppression.

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