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Experimental study on flammability limits of electrolyte solvents in Lithium-ion Batteries using a wick combustion method

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Abstract

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. 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 flameretardant 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. The results of this work provided valuable information about the flammability limits of single and mixed electrolyte solvents, and it may be useful for designing electrolyte balanced in both performance and safety.

Keywords

Flammability limit; Wick combustion; Electrolyte solvent; Lithium-ion battery; Organophosphorus compound; Flame-retardant

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are widely used in a range of consumer electronics and industrial products due to their high energy density and relative maturity in production. However, since some fire and explosion accidents associated with LIBs reported frequently in this decade, the safety issues are raised to be one of the most important concerns in the design of LIBs.

The electrolyte solvents used in commercial LIBs are mostly linear and cyclic alkyl carbonates and their combinations [1,2]. The flammable organic electrolyte brings quite higher combustion energy than electrochemical energy of the LIB, which causes the potential fire risk especially during battery failure [3]. In the current stage, using flame-retardant additives to inhibit the flammability effect is an effective strategy without changing the structure of the battery cell [4,5]. The organophosphorus compounds (OPCs) are promising candidates with low environmental impact [6–9] and excellent flame-retardant effectiveness [10,11] in comparison with halogenated flame retardants. The OPC additives reduce the flammability of LIB effectively, but most of them degrade the battery performance in terms of electrochemical cycling stability, capacitance and/or lifetime [12,13]. Therefore, improvements are being sought which requires higher flame retardancy with less OPC addition. To meet such balance, the flammability of electrolyte mixtures should be quantified, and the flame-retardant effectiveness of OPC additives should be evaluated as well.

Due to the complexity of lithium-ion battery fire safety issues, a series of comprehensive evaluation methods need to be developed involving with different levels like system level, cell level, and component level. To solve the fire safety issues fundamentally, safer materials for the battery components are required, especially for electrolytes. Take a glance at literature, that various methods have been used for the flammability evaluation of electrolyte at a component level. For the preliminary screening of single component used for electrolyte solvent, several flammability characteristics are referred including flammable limits (explosive limits), flash points, the auto-ignition temperature, the heat of combustion and so on [5,14]. While the liquid electrolyte in LIB always comprises several chemical components (solvents, additives, and lithium salts) with a specific ratio, it is difficult to characterize the flammability of electrolyte mixtures just using the above characteristics. Another indicator in terms of burning behavior, self-extinguishing time (SET), are most frequently used for electrolyte mixtures. SET describes the duration or the rate of burning for an ignited electrolyte sample, but the test method varies in different publications. Most of the SET tests use open flame method to ignite the solvent directly [5] or through a porous media soaking with electrolyte [14–19], in which the results are strongly affected by the ignition source and the liquid volatilization. Besides the SET tests, two common methods were reported, the linear flame propagation tests [16,19] modified from ASTM D5306 [20] and the test of flame extinction probability [21-23]. However, due to the considerable errors caused by the uncertain experimental conditions, SET and other two methods often give a qualitative classification of flammability ("flammable", "flame-retarded" and "nonflammable"). They can hardly provide quantitative evaluations of the improvement in flame retardancy following the modification of the liquid electrolyte composition, especially by changing the type or quantity of fire-retardant additives. Along with the breakthroughs of safer electrolytes in LIB research [24], the improvements of flammability evaluation method for electrolytes is also expected, which requires a quantitative indicator and scientific understanding of electrolyte combustion.

For the quantitative material screening, the limiting concentrations of oxidizers for ignition or flame extinction are widely used for evaluating the flammability of gaseous fuels, volatile solvents and solid materials [25].

Comparing with the flash point, the flammable limits in terms of oxidizer are more related to the chemical properties in the combustion reaction of fuels. If the oxygen can be controlled below such limits, the burning of the fuels can be prevented. The limiting oxygen concentration (LOC) of the premixed combustion is a typical indicator to evaluate the flammability of gases and vapors like lower and upper flammability limits (LFL, UFL). Utilizing a spherical premixed chamber, Zabetakis have measured the premixed-LOC of many volatile liquid fuels [26]. Osterberg also tested nine organic solvents in the pharmaceutical industry to prevent explosion hazard [27]. However, the electrolytes in commercial LIB always use low vapor pressure components like propylene carbonate or ethylene carbonate mixing with other solvents, additives, and lithium salts. It is difficult to vaporize such mixed electrolytes for the premixed combustion tests. Thus, a simpler diffusion flame configuration might be more suitable for electrolyte combustion involving evaporation and decomposition of multi-component fuel. The limiting oxygen index (LOI) in a candle-like diffusion flame has been widely accepted as an index of the fire-retardant characteristics of solid materials in ISO 4589-2 [28]. LOI is the oxygen concentration at extinction in a defined axial flow velocity under specific test conditions. The term of limiting oxygen index (LOI) or limiting oxygen concentration (LOC) of a wire, rod, and wick flame has been widely reported in the combustion and fire researches [29–37]. Some modifications for electrolyte solutions are reported using a small cup burner [16,38,39]. When the electrolyte burned in such small cup (typically a pool fire configuration), the concentration of high boiling point component can be increased by distillation effect, which may overrate the flame-retardant effectiveness.

In the present work, therefore, we introduced a wick combustion system to measure the limiting oxygen concentration of the wick flame (called wick-LOC) for electrolyte mixtures and try to solve the drawback of

above existing test methods. By using the wick combustion method, the LOCs of some single components were determined experimentally; and then the flammability of mixed solvents and effectiveness of fire-retardant additives used for LIBs were evaluated by the method.

2. Experimental methodology

2.1 Experimental setup

The schematic of the experimental system used to determine the wick-LOC value is shown in Fig. 1. The system generated a diffusion flame on a wick placed along the centerline of the cylindric combustion chamber. The wick complying with the quality standards specified in ASTM D1322 [40] 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 selftrimming (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 paper. 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%. 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 crosssectional 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.



Fig. 1. Schematic of experimental setup.

2.2 Experimental procedure

Based on the traditional LOI tests [41], the experimental procedure of wick-LOC method was specified. At the beginning of the experiment for a new solvent, the wick tip was ignited to generate a stabilized flame at a higher oxygen concentration (above 20 vol%). The oxygen was then reduced step by step under the constant flow velocity until flame extinction, where the approximate value of LOC can be found in this preliminary test. Subsequently, repeated tests (at least four times) were conducted for a precise and reliable wick-LOC by averaging the repeated results. The minimum decrement of oxygen concentration was 0.1 vol%. According to the replacement time (less than 20s) of the new gas mixture in the gas supply system, the test duration at a given condition was at least one minute. If the flame kept burning more than 1 min, it was judged as "sustained

combustion" state which required further oxygen decrease. Otherwise, it was judged as "extinction" state when the flame was extinguished within one minute. The wick-LOC value was determined between the closest two states above. In the experiment, each wick was only used in the same solvent or solution. The wick was refreshed by cutting the used head in each test to avoid the aging effect of the wick.

2.3 Selection of solvents

In the present work, seven kinds of typical solvents used in LIB electrolyte were tested by wick-LOC method, including linear carbonates, cyclic carbonates, and ether-based solvents. For the validation of wick-LOC results, three common solvents (Ethanol, methanol, and Acetone) were also tested as references. Table 1 shows the chemical formulas and some properties like boiling point (BP), flash point (FP) and auto-ignition temperature (AIT) of solvents obtained from Material Safety Data Sheets (MSDS). Furthermore, the wick-LOC of mixed solvents were evaluated depending on the mixing ratio of carbonate solvents and addition of OPCs, respectively.

Full name	Abbreviation	Formula	BP [°C]	FP [°C]	AIT [°C]
Dimethyl carbonate	DMC	$C_3H_6O_3$	90	18	458
Ethyl methyl carbonate	EMC	$C_4H_8O_3$	109	23	446
Diethyl carbonate	DEC	$C_{5}H_{10}O_{3}$	126	33	445
Ethylene carbonate	EC	$C_3H_4O_3$	248	160	465
Propylene carbonate	PC	$C_4H_6O_3$	242	132	455
Tetraethylene glycol dimethyl ether	TEGDME	$C_{10}H_{22}O_5$	276	140	265.56
1,2-dimethoxyethane	DME	$C_4H_{10}O_2$	84	-2	202
Methanol		CH ₃ OH	64.7	12	470
Ethanol		C ₂ H ₅ OH	78.28	14	363
Acetone		CH ₃ COCH ₃	56.05	-18	561
Trimethyl phosphate	TMP	$C_3H_9O_4P$	197	107	391

Table 1 Chemical formula and properties of electrolyte solvents, reference solvents and OPCs (MSDS)

Triethyl phosphate	TEP	$C_6H_{15}O_4P$	216	111	454
Dimethyl methyl phosphonate	DMMP	$C_3H_9O_3P$	181	69	
Trimethyl phosphite	TMP(i)	$C_3H_9O_3P$	110	28	250

3. Results and discussion

3.1. LOC with experimental condition variation

To analyze the effects of experimental conditions on the wick-LOC results, three aspects were considered: the axial flow velocity, the exposed wick length and the elapsed time after ignition. The experimental conditions specified in the previous section were validated and applied to the flammability comparison of single-component solvent and mixtures.

3.1.1. Axial flow velocity effect

The flow velocity is one of the environmental variables that may affect the material flammability and fire dynamics in an opposed flow diffusion flame configuration [30,42]. According to the blow-off mechanism of a wire or candle-like flame [43,44], the increased axial flow velocity can shorten the fluidic residence time and lead to an earlier extinction (corresponding to a higher LOC). The axial flow velocity of the wick-LOC method should also be specified properly for the flammability comparison of solvents. The wick-LOC results of pure DMC and pure EMC in different axial flow velocities were measured experimentally, shown in Fig. 2. The plot indicates the relation between wick-LOC values and axial flow velocities from 4 cm/s to 18 cm/s. The flame images show the stabilized flames near flame extinction (LOC+0.2 vol%). Overall, the LOC of each solvent climbed gradually with the increase of axial flow velocity, and the DMC was less flammable than EMC with around 1 vol% difference of LOC. The velocity dependence of LOC could be explained as the change of

residence time in Damköhler under the blow-off mechanism as mentioned above. While in a low external flow from 4 cm/s and 18 cm/s, the wick-LOC seemed to be not sensitive to the axial flow velocity. Referring to some researches [45,46], the 10 cm/s was selected as a standard value of the axial flow velocity in the following tests.



Fig. 2. The wick-LOC of pure DMC and EMC solvents under different axial flow velocities.

3.1.2. Exposed wick length effect

The wick length exposed out of the stainless tube should be proper to supply sufficient fuel to the wick tip and provide reproducible LOC results. As the geometry of exposed wick may affect the capillary action of the liquid fuel [47] and the wick flame shapes [35], a fixed exposed wick length should be specified for reliable flammability comparison in this work. Thus, the wick-LOC change of pure DMC flame under the 10cm/s axial flow velocity were measured experimentally by varying exposed wick length from 2mm to 15mm, shown in Fig. 3. The flame images indicate the near limit stabilized flames (LOC+0.2 vol%). As the local flow velocity around the boundary layer decreases along with the downstream, the LOC of 15mm exposed wick length

showed lower (flame is more stable) than that of 2 mm. However, it shows that the exposed length of wick in the range of 4 to 10 mm had limited effects on the wick-LOC results. In this paper, the exposed wick length of 7mm was chosen as a standard value because of ease of wick handling.



Fig. 3. The wick-LOC of DMC with the change of exposed wick length at a constant axial flow.

3.1.3. The effect of elapsed time after ignition

To quantify the flame-retardant effectiveness of OPC-added solution, one of the concerns is the effect of distillation (solution composition might change during combustion due to the boiling point difference). For example, the boiling points of DMC, TMP, and TEP are 90 °C, 197 °C, and 216 °C, respectively, as shown in Table 1. If in a pool fire configuration of DMC with addition OPC, the OPC concentration may increase during continuous burning, which would overrate the flame-retardant efficiency of OPC addition. To clarify such potential effect on wick-LOC results, the elapsed time after the ignition was varied from 0 to 30 mins, and the wick-LOCs of DMC with 10 wt% addition of TMP and TEP were measured, as shown in Fig. 4. The elapsed

time in the experiments was the burning time at the axial flow velocity (u_a) of 10 cm/s and the oxygen concentration of 20%. The wick-LOC results had a small fluctuation range (within 0.4%) which was close to error range of a single experiment. It indicated that the wick-LOC was almost independent of the elapsed time after ignition. Due to the continuous fresh fuel supplement from the tank to the wick, the OPC organic solvents can be supplied to the flame zone simultaneously with negligible distillation effect.



Fig. 4. Wick-LOC dependence of elapsed time after ignition.

3.2. Correlations to other flammability properties

As modified from LOI method, the wick-LOC reflects the extinction limit of a candle-like diffusion flame, where the lower wick-LOC obtained means more flammable the solvent is. To validate the wick-LOC method for the flammability evaluation of LIB electrolyte solvents, the correlation study of wick-LOC with other flammability properties was conducted, as shown in Fig. 5. The wick-LOCs of typical electrolyte solvents and reference solvents in Table 1 were tested and compared with their flash points, auto-ignition temperatures, the heats of combustion and other types of LOC available. The flash point of EC:EMC/1:1 is referred from Hess

[5]; the heat of combustion values were referred from databases [48,49]; and the wick-LOC of pure EC was estimated in Fig. 6 in next section.



In Fig. 5(a), the wick-LOCs showed a rough positive correlation to the flash points of most solvents but excluding Acetone and TEGDME. The wick-LOC would be controlled by the burning velocity of the fuel-air mixture due to insufficient oxygen for combustion; while the flash point is more related to the evaporation

process to generate flammable mixture. Therefore, Acetone gave the lowest flash point but medium LOC value; while TEGDME was very flammable in low oxygen level even with a high flash point. The wick-LOC had broad correlations to auto-ignition temperature and heat of combustion corresponding to Fig. 5(b) and (c), because these properties are more related to the chemical aspect of combustion. In comparison with other recognized LOC methods in Fig. 5(d), the wick-LOC of reference solvents showed a good consistency with LOCs for premixed flame [26] and counterflow diffusion flame [50], respectively. Being different from premixed-LOC and counterflow-LOC focusing on the gaseous fuel or volatile liquid, wick-LOC method involves processes of liquid-phase transport in the wick, phase change and gas-phased combustion, which is applicable for both high- and low-volatile solvents. Based on the above comparisons, the wick-LOC method is competent to quantify the flammability of liquid solvents for LIB electrolyte.

3.3. Applications in mixed solvents

Most electrolytes are combined with different types of solvents such as cyclic carbonates, linear carbonates or ethers to balance the pros and cons of each solvent in practical applications [14]. Cyclic carbonates like EC and PC have both high dielectric constant and viscosity. However, the poor cycling efficiency of PC and the high melting point of EC make them difficult to be used alone. Linear alkyl carbonates and some ethers have low melting points and viscosities; they can provide higher ionic conductivity and better low-temperature performance when mixing with cyclic carbonates. For a balanced electrolyte formulation in both performance and safety aspects, not only electrochemical performances but also flammability of such mixed solvents should also be quantified.

As shown in Fig. 6, the wick-LOCs of the mixed solvents of linear and cyclic carbonates with different ratios

were plotted. The LOC values were determined at an axial flow velocity (u_a) of 10 cm/s. The horizontal axis shows the mass fraction of EC or PC in the mixtures. The wick-LOC of pure EMC was measured around 14.85 vol%. The LOC increased linearly with the additions of both EC and PC, but the growth gradient of LOC is higher with EC addition. The mass fraction of EC was varied from 0 to 66 wt% due to the EC solubility limit in EMC [51]. The pure EC is a crystalline solid in the room temperature, so its LOC was estimated as 17.3 vol% by extrapolating the linear fitting (solid circle point in Fig. 6). Comparatively, the pure PC (liquid in the room temperature) with a measured LOC of 16.3% was more flammable. Being different from the binary carbonates, carbonate-ether mixed solvents had non-linear changes of LOC with ratio variation, as shown in Fig. 7. The DME and TEGDME with LOC of 12.9 vol% and 13.45 vol%, respectively were more flammable than the carbonates tested. The nonlinear change of LOC in Fig. 7 showed that a small amount of ether addition in carbonates can decrease the LOC significantly. The LOC values of carbonate-ether solutions with equal ratio were always lower than the mean LOC values of two pure solvents.



Fig. 6. Wick-LOC of mixture of linear and cyclic carbonates in different mixing ratios.



Fig. 7. Wick-LOC of mixtures of carbonates and ether-based solvents in different mixing ratios.

3.4. Flame-retardant effectiveness of OPC additives

As mentioned in the previous sections, OPCs are effective flame-retardant additives used in electrolytes of Liion batteries. To quantify the flame-retardant effectiveness of OPC additives in electrolyte solvents, the wick-LOCs of different OPC-added solvents were measured in this section.



Fig. 8. Wick-LOC change with addition of OPC in DMC-based solvents.

The effect of different OPC additions on the flammability of DMC-based solvent was shown in Fig. 8. In this figure, the vertical axis is the wick-LOC (in vol%) and the horizontal axis is the amount of OPC (TMP or TEP) added (in wt%). The flame images in the figure are stabilized flames of DMC with different TMP addition near extinction conditions (0.2 vol% above LOC). Small amounts of added OPC had a significant impact on the LOC of DMC solvent, and the LOC growth rate was quite large within 2 wt% OPC addition. However, the gradient of LOC increase became smaller as the amount of OPC continuously added. In the comparison of two OPCs, TMP showed better flame-retardant effectiveness than TEP with the same addition into DMC, but both had diminished effectiveness in a higher OPC addition. Such marginal effect on flammability was also found in cupburner tests by Bouvet and Babushok using DMMP as a fire suppressant [11,41]. It was explained as the fuel effect of OPC and the loss of active phosphorus compound. As shown in Fig. 8, the size and luminance of the near-limit flames increased with the addition of TMP, the fact of increased particle formation (condensation of active phosphorus compound) was consistent with such explanations.



Fig. 9. Wick-LOC change with different OPC additions in EMC-based solvents.

Similarly, the flame-retardant effectiveness of different OPC in EMC-based solvents was compared in Fig. 9. Four kinds of typical OPC additives, TMP, TEP, DMMP and TMP(i), were tested with 0, 5 and 10 wt% additions. The wick-LOC increased significantly with additions of all types of OPCs, but the growth rate decreased slightly. The flame-retardant effectiveness of TEP was the lowest among the four OPC, while DMMP showed the best performance. The effect of OPC addition on flammability was explained as the radical capture in the combustion of carbonate solvents. The effective phosphorus compounds capture H and OH radicals to form H₂O without being consumed [52].The combustion reaction rate can be decreased by the reduction of chain carriers. Since the intensity of this inhibition mechanism is dominated by the number of phosphorus atoms added to the system, the different flame-retardant effectiveness of the four OPCs (in Fig. 9) can be explained as the different amount phosphorus atoms in the same weight of OPCs.



Fig. 10. Measured temperature distribution along the centerline of flames given by pure EMC and

EMC+TMP 10 wt%.

Besides the flame inhibition of OPC in the gas-phase chemical reaction, the potential physical effect of OPC addition should be concerned as well. As reported by Korobeinichev in his chemical calculations [53], OPCs have promotion effect leading to a temperature rise of hydrogen flames. Here, to check such double-edged effect experimentally, the wick diffusion flame temperatures were measured with and without adding OPC. The temperature profiles of the stable flames at 20% oxygen given by pure EMC and EMC + 10 wt% TMP were shown in Fig. 10. The vertical axis shows the axial flame temperature along the centerline of the flame, and the horizontal axis is the distance from the top of the wick. The curves were the averaged values under at least 3 times measurements, and the shaded areas represented the ranges of error. The R-type thermocouple with 0.3mm thickness was shaped and utilized for the temperature measurement. Even without the compensation of radiation effect on the temperature, the potential temperature discrepancy can be controlled up to 40K under 1400K. The addition of OPC to EMC (EMC + TMP 10 wt%) produced a higher temperature distribution in the flame. Because of the exothermic radical-capture reaction by phosphorus compound, temperature increases in the main body of the flame $(0 \sim 45 \text{ mm})$ with OPC addition. While the high luminosity due to the particle formation of EMC + TMP 10wt% flame causes a large amount of radiant heat loss in the tail of the flame (\geq 45 mm), which leads to a lower temperature distribution in the downstream than the case of pure EMC. The difference in flame luminosity and temperature accounts for different heat feedback from the flame to the wick. Such additional heat feedback could accelerate the evaporation of the fuel, which led to a larger flame size near extinction, as shown in Fig. 8. It could be a potential explanation for the marginal effect of high OPC additions on the LOC increase.

4. Conclusions

The flammability limits of electrolyte solvents in lithium-ion batteries were studied experimentally using the wick-LOC method, a wick combustion system in conjunction with the limiting oxygen concentration method under a candle-like burning configuration. The results were summarized as follows:

- The wick-LOC of electrolyte solvents were determined under well specified the experimental conditions.
 The effect of various experimental conditions like the axial flow velocity, the exposed wick length and the elapsed time after ignition on wick-LOC were investigated to provide reproducible results.
- 2. The correlations of wick-LOC to other flammability properties (flash points, auto-ignition temperatures, the heat of combustion and other types of LOC) were analyzed among several solvents. According to the correlations, the quantification of solvents flammability can be provided by the wick-LOC method with reliable results.
- 3. With the application for mixed electrolyte solvents, the effects of different mixing ratios on wick-LOC were studied. The linear change of LOC in binary carbonates solvents and non-linear change of LOC in carbonate-ether mixed solvents were found experimentally.
- 4. The flame-retardant effectiveness of different types and amounts of OPC additions in carbonates solvents were quantified. The wick-LOC 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 were rated as DMMP > TMP(i) ≈ TMP > TEP. Besides the flame inhibition, the potential promotion effect of OPC addition was discussed using flame temperature measurements.

By using the wick-LOC method, not only the flammability of single solvents, but also the role of mixing and

OPC additions on solvents combustion can be quantified. For the further application to real electrolytes, the

fundamental study of lithium salts effects on electrolyte combustion are expected in the future work.

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