Short communication

Thermal stability and flammability of electrolytes for lithium-ion batteries

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ABSTRACT

Safety is the key-feature of large-size lithium-ion batteries and thermal stability of the electrolytes is crucial. We investigated the thermal and flammability properties of mixed electrolytes based on the conventional ethylene carbonate–dimethyl carbonate (1:1 wt/wt)–1 M $LiPF_6$ and the hydrophobic ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$). The results of thermogravimetric analyses and flammability tests of mixed electrolytes of different compositions are reported and discussed. An important finding is that though the mixtures with high contents of ionic liquid are more difficult to ignite, they burn for a longer time, once they are ignited.

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1. Introduction

Much effort has been expended in the last few years to improve the safety of lithium-ion batteries given that safety is a key requisite for large-size batteries for stationary applications and sustainable transportation, including electric vehicles [1–6]. The thermal properties of the electrolyte are crucial for lithium-ion battery safety. In fact, the organic carbonate-based electrolytes, which are used in the lithium-ion batteries on the market, have a poor thermal stability even at temperatures below 100 °C. Unsought reactions among the battery components and the electrolyte sparked by unforeseen local overheating or short circuits can produce a rapid increase in battery temperature and, eventually, trigger a fire or explosion. The main strategies that have been investigated to increase safety include changing lithium-ion battery chemistry and electrolyte [6,7] as well as the addition of fire retardants [8–10]. Ionic liquid (IL)-based electrolytes have been proposed for Li-ion batteries for the favorable combination of IL physicochemical properties such as low vapor pressure, high thermal stability, good ionic conductivity and a wide electrochemical stability window [11]. They are often classified as non-flammable materials, even if a more appropriate description of many ILs would be non-volatile (up to the decomposition temperature) class IIIB combustible materials given that their flashpoint is above 200 °C [12,13]. This is an important point because the definition "non flammable" does not mean "non combustible" and does not imply a safe use near heat sources or fire.

Another approach may be the use of IL-organic carbonate mixed electrolytes with the aim to decrease the amount of flammable components [5,14]. The replacement of part of the organic electrolyte with ILs could reduce the risk of thermal runaway and, to this purpose, the advantage of the use of mixed electrolytes instead of pure ILs in term of cost is evident.

We investigated the thermal and inflammation properties of mixtures based on ethylene carbonate–dimethyl carbonate (EC–DMC 1:1 wt/wt)–1 M $LiPF_6$, one of the most widespread organic electrolytes for lithium-ion batteries [15], and N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$), which has already been investigated with the addition of a lithium salt as a electrolyte for such batteries, and the results are reported and discussed.

2. Experimental

Mixtures of EC–DMC–1 M $LiPF_6$ (Merck, LP30, used as received), with 0, 10, 30, 50, 70 and 100 wt% of $Pyr_{14}TFSI$ (solvent innovation 98%, dried under vacuum 80 °C overnight, 20 ppm water content after drying) were prepared for thermal stability and flammability tests. The molecules are reported in Scheme 1.

Conductivity measurements of the mixtures of EC–DMC–1 M $LiPF_6$ with 50 and 100 wt% of $Pyr_{14}TFSI$, and of $Pyr_{14}TFSI$–0.4 M LiTFSI were carried out with a Radiometer Analytical CDM210 Conductivity meter. The electrochemical stability window of $Pyr_{14}TFSI$ was evaluated by linear sweep voltammetry (LSV) on a glassy carbon electrode (GC, 0.07 cm^2) with a Perkin Elmer VMP potentiostat. An Ag/AgTFSI–$Pyr_{14}TFSI$ (+3.50 V vs. Li/Li$^+$) was used as reference electrode.

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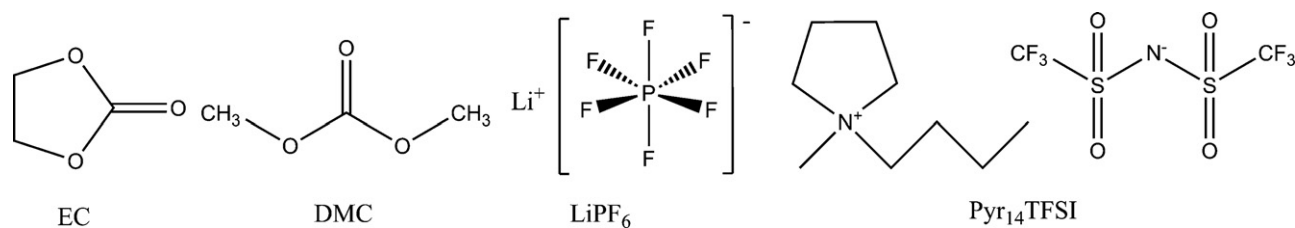
Scheme 1.

Thermogravimetric analyses (TGAs) of mixed electrolyte solutions were carried out with a Mettler Toledo TGA/STD A851 under N_2 or N_2/O_2 (80:20 mol ratio) flux at 5° min^{-1} between 28 and 550 $^\circ$C. The inner diameter of the crucible and the volume of the electrolyte samples were 5 mm and ca. 30 μL, respectively. The flammability tests were performed with an electronic Bunsen burner (Electrofor, Flame control Poligas) fed with controlled butane/air flux that produces an oxidant blue flame. An 8 mm × 20 mm piece of glass fiber mat (Whatman, GF/F) was soaked with the electrolyte and then firmly placed at a distance of 123 mm from the top of the burner tube so that the flame did not lick the glass fiber mat and ignition was only due to temperature increase. This distance was set so that all the 100% IL-soaked samples did not ignite and all the 100% EC–DMC-soaked ones caught fire after exposure to the flame for 5 s. The meaning of "exposed to the flame" herein is "placed at the fixed distance from the flame, but not in contact". Each electrolyte was tested six times: the burner was switched on under the sample for 5 s and then switched off. The time it took for the flame to extinguish was normalized against liquid mass (0.09–0.13 g) to give the self-extinguishing time (SET) in s g^{-1}.

The temperature reached at the bottom of the samples was recorded with an Impact IN 5 plus infratherm pyrometer by substituting the glass fiber mat with Nefalit®, which has a high temperature resistance. The temperature at the bottom of the glass fiber mats that were soaked with 100 wt% Pyr$_{14}$TFSI or 100 wt% EC–DMC–1 M LiPF$_6$ was also measured.

3. Results and discussion

The use of pyrrolidinium- or piperidinium-based electrolytes for lithium-ion batteries has been reported by several authors [16–20]. Particularly, Pyr$_{14}$TFSI displays, as shown in Fig. 1a, a wide potential range of electrochemical stability useful for many lithium-ion battery chemistries. The conductivity of the pure ILs is usually lower than that of organic conventional electrolytes for lithium batteries and the addition of a Li salt further decrease the conductivity. The use of mixtures of Pyr$_{14}$TFSI and EC–DMC–1 M LiPF$_6$ may be a good compromise to maintain a high conductivity as shown in Fig. 1b. The lowering of the amount of IL percentage in the mixture is an advantage in terms of costs; however, too low percentage of IL can result ineffective in terms of thermal stability of the electrolyte.

The TGAs in N_2 flux of the pure carbonate-based organic electrolyte, of the pure Pyr$_{14}$TFSI and of the solutions with IL contents of 10, 30, 50 and 70% are reported in Fig. 2a. While the pure organic electrolyte showed a 27% weight loss when heated to 100 $^\circ$C and a 77% loss at 250 $^\circ$C, the solutions containing 10, 30, 50 and 70% of Pyr$_{14}$TFSI displayed a weight loss of 15, 10, 11 and 5% at 100 $^\circ$C.

The curves show that DMC and EC evaporated at different stages depending on their boiling temperature (89 $^\circ$C and 260 $^\circ$C). In addition, LiPF$_6$ started to decompose with the formation of LiF and PF$_5$ at relatively low temperature (<100 $^\circ$C) [21,22]. By contrast, pure Pyr$_{14}$TFSI did not show any weight loss up to 350 $^\circ$C and at 400 $^\circ$C

the loss was only 3%, thus demonstrating that volatile decomposition products were scarce.

TGAs were also carried in N_2/O_2 to simulate air composition and Fig. 2b displays the curves of EC–DMC–1 M LiPF$_6$, of the solution with 10% Pyr$_{14}$TFSI and of Pyr$_{14}$TFSI; the TGA curve of the latter in N_2 flux is also reported for comparison. The curves of Pyr$_{14}$TFSI in N_2 and in N_2/O_2 did not show substantial differences, nor did those of the mixed electrolytes. In the presence of O_2, the Pyr$_{14}$TFSI curve did not show almost any weight loss up to 350 $^\circ$C and a 3% weight loss occurred at 375 $^\circ$C; the slope change at 450 $^\circ$C was probably due to the decomposition of the oxidation products. The 10% Pyr$_{14}$TFSI solution shows a 13% weight loss at 100 $^\circ$C (comparable value to that found in N_2) against a 35% loss of EC–DMC–1 M LiPF$_6$ at the same temperature.

The TGA curves provide useful information regarding the stability of the electrolyte under heating with or without oxygen. However, a battery may be placed in more hazardous conditions, such as in the presence of fire or sparks. So we also carried out flammability tests and, given the lack of specific international norms or procedures for our samples, we chose the most suitable
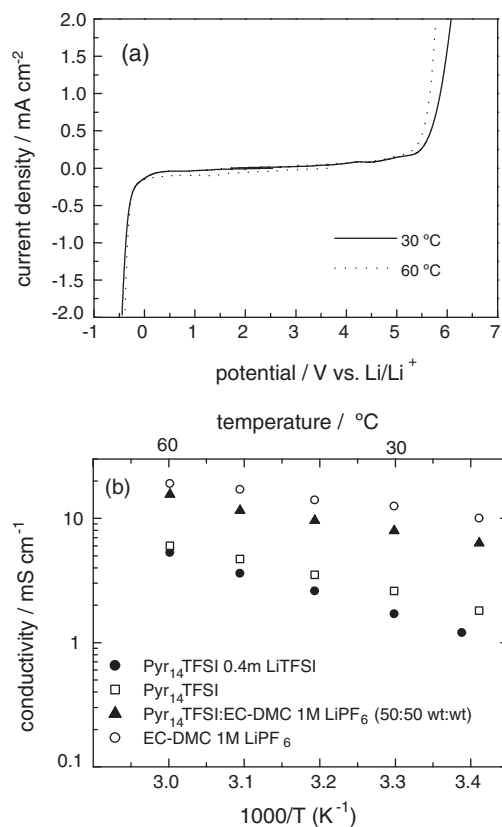

Fig. 1. (a) LSVs at 20 mV/s of Pyr$_{14}$TFSI at 30 and 60 $^\circ$C with the potential reported vs. Li/Li$^+$ and (b) conductivity data of EC–DMC–1 M LiPF$_6$ from Ref. [15], of the mixture with 50 wt% of Pyr$_{14}$TFSI, of Pyr$_{14}$TFSI and of Pyr$_{14}$TFSI–0.4 M LiTFSI.
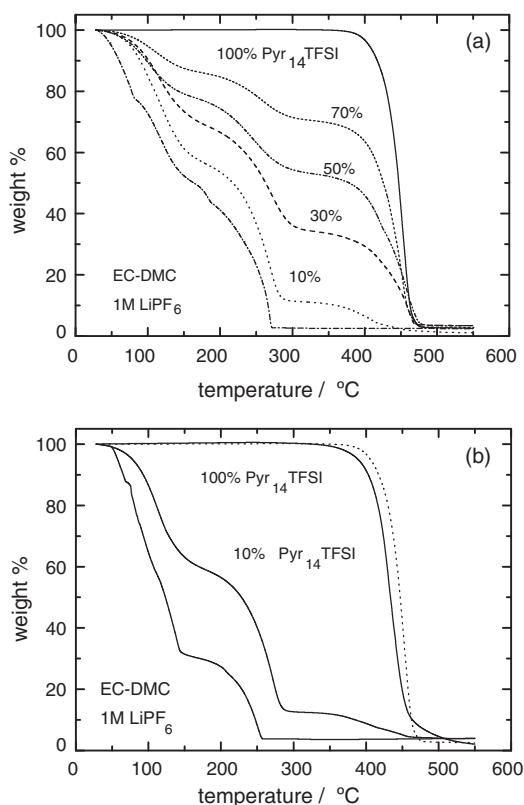
Fig. 2. TGA curves of (a) EC–DMC–1 M LiPF$_6$, Pyr$_{14}$TFSI and solutions with different wt% of Pyr$_{14}$TFSI in N$_2$ flux and (b) EC–DMC–1 M LiPF$_6$, Pyr$_{14}$TFSI and a solution with 10% Pyr$_{14}$TFSI in N$_2$/O$_2$; for comparison the curve of Pyr$_{14}$TFSI in N$_2$ flux (dotted line) is also reported.

(see description in Section 2) among those reported in literature [2,5,9,10,13,23].

Fig. 3a and b shows the glass fiber mat and the experimental set up for flammability tests, and Fig. 3c–f the samples with EC–DMC–1 M LiPF$_6$ (c and d) and with Pyr$_{14}$TFSI (e and f), when the flame was lasted for 5 s and when it was switched off. Table 1 reports the occurrence of ignition (each sample was tested 6 times) and the average value (ca. 10% error) of the self-extinguishing time of the mixed electrolytes containing organic solvent and Pyr$_{14}$TFSI.

Fig. 3c and d shows that EC–DMC–1 M LiPF$_6$ burned very brightly and Fig. 3e and f shows that during the exposure to the burner Pyr$_{14}$TFSI produced only small flare-ups that promptly extinguished after burner switch off, so this phenomenon was not considered as ignition. Ignition occurrence in Table 1 gives an indication of the flame inhibition effect induced by the addition of IL: all 6 samples containing 10% of IL ignited, but only 2 samples out of 6 containing 50% and 70% did. The lower amount of Pyr$_{14}$TFSI needed to observe the flame-inhibition effect was 30 wt%, whereas at 50 wt% the tendency to ignite was significantly reduced. By contrast, the SET values have the opposite trend: the greater the IL content in the sample, the greater the time it took for the flame
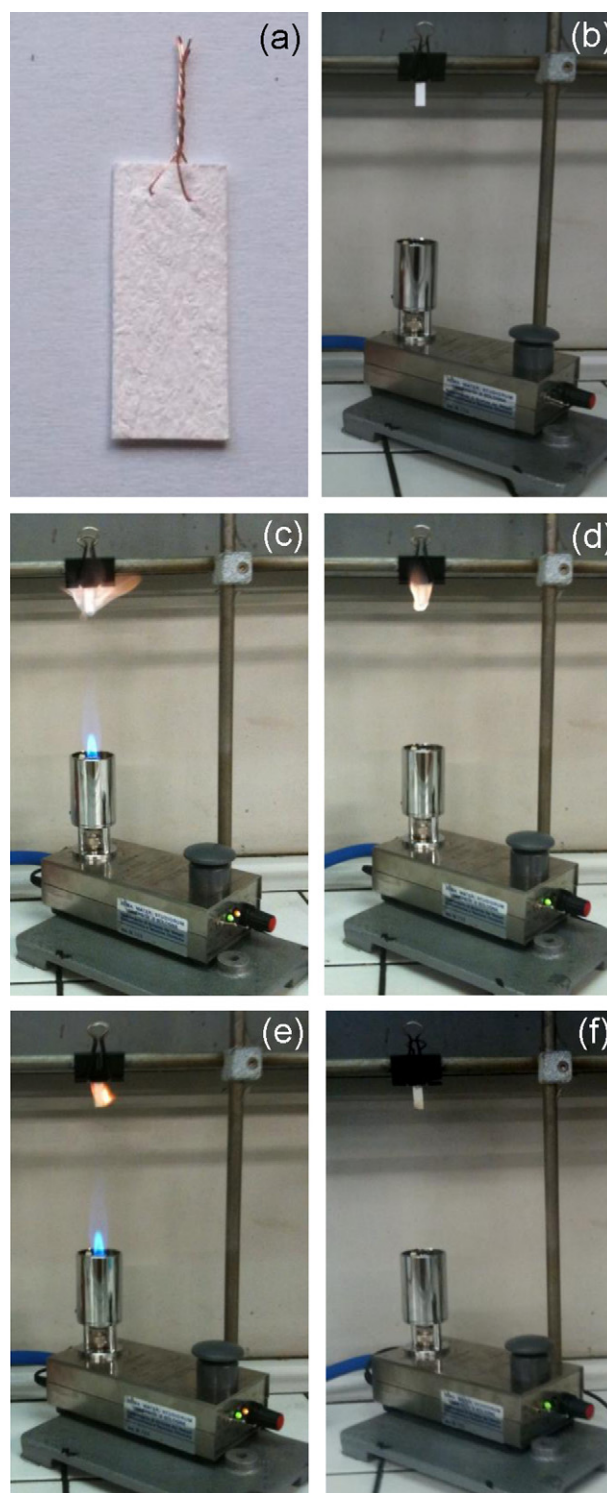
Table 1
Ignition occurrence and the mean values of the self-extinguishing time of several mixtures of Pyr$_{14}$TFSI and EC–DMC–1 M LiPF$_6$.

Pyr$_{14}$TFSI (wt%)	Ignition occurrence	SET (s g^{-1})
0	6/6	55
10	6/6	67
30	4/6	109
50	2/6	125
70	2/6	127
100	0/6	–

Fig. 3. (a) Glass fiber mat, (b) experimental set up for flammability tests, (c and d) EC–DMC–1 M LiPF$_6$ and (e and f) Pyr$_{14}$TFSI during exposure to flame and after flame switch off.

to extinguish (normalized against liquid mass). The samples with 10% Pyr$_{14}$TFSI ignited with a SET of 67 s g^{-1}, which was higher than that (55 s g^{-1}) of pure EC–DMC–1 M LiPF$_6$. Though the mixtures with high amounts of ionic liquids are more difficult to ignite, they burn for a longer time once they are ignited. This is a worth noting point, especially for the overall estimation of the safety behavior of IL-based mixed electrolytes.
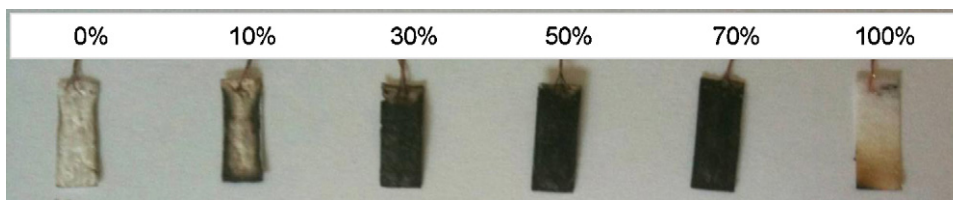
Fig. 4. Glass fiber mat after flammability tests of the mixed solutions at different wt% of $Pyr_{14}TFSI$ content in EC–DMC–1 M $LiPF_6$.

The most logical explanation seems to be that ignited EC–DMC vapors triggered the combustion of IL. The evidence of IL combustion is the state of the glass fiber mats after the flammability tests displayed in Fig. 4. The oxidizing flame completely burned the EC–DMC vapors without leaving a layer of carbon as the reducing yellow flame of a lighter does. This can be seen by the first sample in the figure: after total EC–DMC–1 M $LiPF_6$ combustion, it remained quite intact and white. Similarly, the support with pure $Pyr_{14}TFSI$ after exposure to flame at the fixed distance as shown in Fig. 3b showed no carbon trace but a yellow spot, probably due to impurities or decomposition products. By contrast, the samples soaked with the solutions containing $Pyr_{14}TFSI$ in different percentages displayed carbonaceous deposit due to a slow, oxygen-poor combustion of the IL triggered by the organic electrolyte: the more IL in the mixture, the more carbon was formed. The low volatility of IL determined oxygen-poor combustion of IL that burned on and inside the glass fiber mat that was soaked with the mixed electrolytes. While a yellow reducing flame reaches temperatures near 400–500 °C, the blue oxidizing flame we used can well exceed these temperatures. At the bottom of the sample, indeed, a piece of dry Nefalit® reached 350 °C in 2 s and 600 °C in 5 s, as Fig. 5 shows, so that at these high temperatures most of the organic electrolyte evaporates and the vapors ignite and continue to burn even after the Bunsen burner was switched off.

Fig. 6a shows that the temperature recorded at the bottom of our IL-soaked samples (the part nearest to the flame) reached 500 °C after 5 s and then decreased immediately when the burner was switched off; reproducibility was good for the samples of $Pyr_{14}TFSI$, which did not ignite. When flame-exposure time of the IL was extended to 7 s, 3 of 6 samples started to ignite and continued after the flame was turned off; then when the flame, in the burning sample, moved toward the top of the glass fiber mat, the temperature decreased abruptly as shown in Fig. 6b, which also displays the temperature pattern of EC–DMC–1 M $LiPF_6$. This means that the risk of igniting the vapors due to IL degradation increases when the exposure time to a heat source is extended.

Fig. 6. Temperature plot vs. time of samples of (a) $Pyr_{14}TFSI$ during 5 s flame-on tests and (b) $Pyr_{14}TFSI$ during 7 s flame-on tests and EC–DMC–1 M $LiPF_6$ during 5 s flame-on tests.

The binary organic electrolyte ignited after less than 2 s and reached higher temperatures than IL; after 5 s, when the burner was switched off and the sample continued to burn in the upper part of the glass fiber mat, the temperature decreased abruptly as in the case of the ignited IL.

These tests indicate that, in the mixed electrolytes exposed to relatively high temperatures, the binary organic electrolyte ignites and the high temperatures reached can trigger the formation of IL degradation products and their combustion, with self-extinguishing times proportional to the amount of IL in the mixture.

4. Conclusions

$Pyr_{14}TFSI$ is a thermally stable IL, with high degradation temperature even in N_2/O_2, and the mixtures of conventional organic electrolyte EC–DMC–1 M $LiPF_6$ with $Pyr_{14}TFSI$ proved less volatile than the pure organic electrolyte, an effect that was more evident the more IL was added. The lower amount of $Pyr_{14}TFSI$ needed to observe flame inhibition was 30 wt%, and with 50 wt% of IL the tendency to ignite was significantly reduced. However, the mixtures containing $Pyr_{14}TFSI$ that ignite because of the presence of the organic solvent continued to burn with self-extinguishing times proportional to the amount of IL, which acted as a retar-
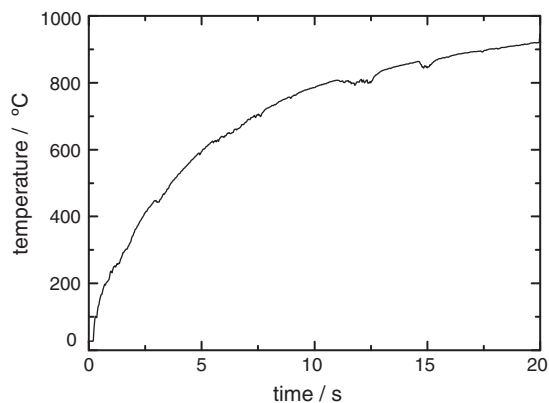

Fig. 5. Temperature plot vs. time of a dry Nefalit® sample placed at 123 mm from the top of a Bunsen burner tube when an oxidizing flame was burning.
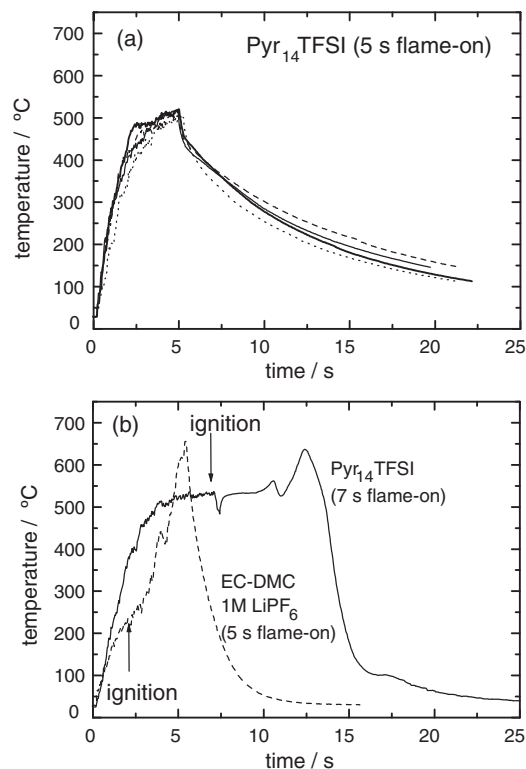
dant rather than a flame-inhibitor. The fact that the mixtures with high amounts of ionic liquids are more difficult to ignite and burn for a longer time once they are ignited is worth noting especially for the overall estimation of the safety behavior of IL-based mixed electrolytes.

Acknowledgement

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