Short communication

Allyl-substituted triazines as additives for enhancing the thermal stability of Li-ion batteries

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ABSTRACT

Triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC) are new electrolytic additives for the Li-ion battery. Both additives are structural isomers, and are found to be flame retardant. So TAC has a triallyl structure, and TAIC a triamine structure. Both molecules include unsaturated C–C bonds, which can be good building blocks for a protective film on cathode. Flame retardants that have double bonds are able to improve both the flame retardancy of the electrolyte and the thermal protection for the cathode. The unsaturated carbon materials form a good protective film, by which the exothermic oxygen evolution reaction at the cathode is suppressed very effectively. TAC is the better thermal protector. Addition of 3 wt.% TAC delays the exothermic reaction by 52 °C, i.e., from 275 to 327 °C. A 5 wt.% TAC solution suppresses 75.1% of exothermic energy from the oxygen evolution reaction.

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1. Introduction

Safety becomes more important as the size of lithium-ion batteries (LIB) becomes larger. Safer materials and smarter battery management systems are required to prevent hazardous events. For this reason, extensive research efforts on battery materials have been conducted for many years. Among the many battery components, the electrolyte has a wide impact on the safety of the battery. Electrolyte is not only flammable, but also able to make contact with all battery materials. Therefore, the properties of the electrolyte can influence performance and safety tremendously. In order to improve the safety of batteries, flame-retardant materials have been tested as additives to the electrolyte [1–6]. Many flame retardants (FRs) can, however, damage battery performance. This is because the additives are non-ionic materials [7].

Adding too much non-ionic FR to the battery is not a practical choice. It is necessary to balance performance and safety for a reliable battery by using an appropriate amount of the flame retardant. Also, manipulation of the surface reaction between the electrode and the electrolyte can provide another method for pursuing an effective outcome in terms of both safety and performance. Carbon–carbon double bonds are common functional groups in vinyl acetate (VA) [8], allyl methyl carbonate (AMC) [9] and viny-

lene carbonate (VC) [10], which can form a good solid electrolyte interphase (SEI) on graphite electrodes. A good SEI is a protective layer that prevents further electrolysis of the electrolytic elements. Also, it leads to improved cycle-life of the battery [10–13]. In contrast to the many unsaturated carbon additives for the graphite electrode, unsaturated carbon additives for the cathode have not been reported.

In this work, additives that have double bonds are studied in order to improve both the flame retardancy of the electrolyte and the thermal protection of the cathode. It is expected that double bonds on the additives can create a good thermal protective film on the cathode. Cathode material based on metal oxide can be thermally decomposed at elevated temperatures to release both oxygen and heat [14,15]. In a sealed battery, the high temperature and additional heat can trigger consecutive reactions, which can lead to fire or explosion. An additive that can delay the exothermic reaction at the cathode can prevent these rapid consecutive reactions. Electrolysis of double bonds can create a network which can shield the cathode and thereby delay the thermal reaction. S-triazine and fluorinated triazine derivatives, which are flame retardants [16,17], have been evaluated as cathode protectors [18]. Fluorination [19] and conducting polymer coatings [20] are frequently adopted to reduce the resistance on the electrode interface.

In this study, differential scanning calorimetry (DSC) is used to identify the protective film and the effects of the film on the thermal safety of the cathode. The additives are triazine derivatives that have double bonds, which are investigated as new electrolytic

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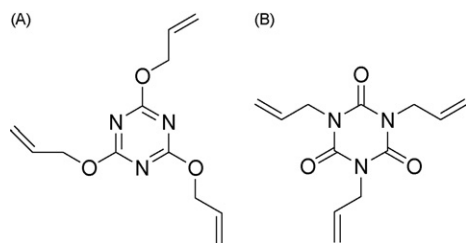E-mail address: kkim@keri.re.kr (K. Kim).

Fig. 1. Structures of unsaturated triazine additives: (A) triallyl cyanurate and (B) triallyl isocyanurate.

additives. They are isomers that have allyl ether and allyl amine groups, respectively. It is expected that double-bond substituted triazines can provide both flame retardancy and thermal protection for the cathode. Also, size effects due to the additives are minimal because they are isomers. The reinforced protective film caused by additives can be effectively in improving the cycle-life of a battery when electrodes are otherwise easily damaged at high temperature and high voltage [21,22]. Attention is paid to the means by which unsaturated carbon materials protect the cathode by forming surface films. Thermal studies show that both additives can provide better isomeric structures for cathode thermal protection.

2. Experimental

2.1. Chemicals and cell preparation

Triallyl cyanurate (TAC, Tokyo Chemical Industry), triallyl isocyanurate (TAIC, Tokyo Chemical Industry) (Fig. 1), poly(vinylidene fluoride) (PVdF, Aldrich), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC, Daejung Chemical & Metal), triallyl amine (Aldrich), allyl ether (Aldrich), and 1.0 M LiPF$_6$ in ethylene carbonate/diethyl carbonate (EC)/(DEC) = 1:1 by volume (Techno Semichem) were used.

All properties of the additives in cells were evaluated with respect to the cathode material. The properties influenced by the electrolytes were measured in 2032 type coin cells (Hohsen Corp.) for half-cell tests. The active material, NMC, was well mixed with carbon black (Super-P Black, Timcal Carbon) and PVdF at a ratio of 86:8:6, respectively, in N-methyl-2-pyrrolidone (NMP, Junsei) to make the slurry for the cathode. The slurry was spread on Al foil and dried overnight at 120 °C. The prepared electrodes were hot-roll pressed to reduce the thickness by 20%. Lithium foil served as both the reference and the counter electrode. A 15-μm thick separator (Celgard 2500) was placed between the two electrodes. All cell preparation was conducted in a dry room in which the water content was kept below 10 ppm.

2.2. Instruments and measurements

Cyclic voltammograms (CVs) of electrodes with the additives were collected by using a potentiostat (model VSP3, Princeton Applied Research). Fresh cathodes had open-circuit voltages (OCVs) between 3.3 and 3.5 V. The CVs started from OCV and were scanned between 2.5 and 4.3 V at a rate of 1 mV s^{-1}. Ten consecutive cycles were recorded from the first cycle. For comparison purposes, we have termed the electrolyte without additive the 'no-additive electrolyte'. Prior to the cycle-life tests, the cells were cycled between 2.8 and 4.3 V at the 0.1C rate (1C rate = 170 mA g^{-1} of the active material) so as to complete two formation cycles. Cycle-life tests were conducted at the 0.5C rate using a TOSCAT-2100U tester (Toyo Systems Co.). The thermal stability of the cathode was investigated with a differential scanning calorimeter (DSC, Q1000, TA Instruments). The influence of the additive on cell stability was evaluated with charged cathodes. The cells were preconditioned
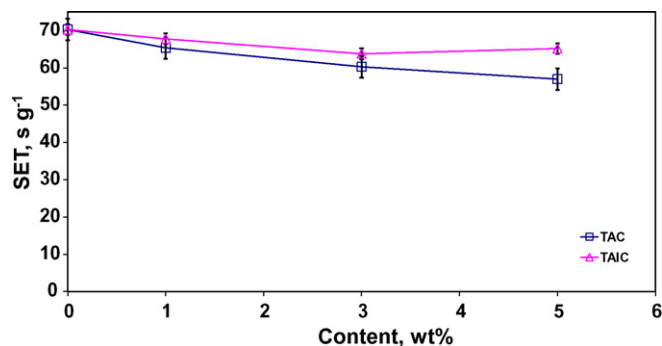

Fig. 2. Self-extinguishing time measurements on electrolytes containing additives.

with 10 charge–discharge cycles at the 0.5C rate prior to the DSC tests, which were carried out on the charged electrode materials at a heating rate of 5 °C min^{-1} from 40 to 400 °C under nitrogen. Excess solvent in the samples was removed by air-drying in the dry room. Complete removal of the solvent was avoided in order to mimic the conditions of charged electrode material in a cell. Surface films or properties created on the electrodes are often damaged by vacuum. The charged cathode samples were sealed in Al crucibles for measurements. The flame-retardant properties of additives were evaluated by measuring the self-extinguishing time (SET) normalized by the liquid mass [7]. The container for the SET tests was made of stainless steel and has a 20 mm diameter and 4 mm height. Each value was obtained from the average of three measurements.

3. Results

The flammability of the electrolytes was evaluated in terms of SET tests, as shown in Fig. 2. The electrolytes containing triazine derivatives show that both TAC and TAIC have flame-retardant properties. Increasing the concentration of either of them gradually shortens the flame time. The addition of 5 wt.% TAC to the electrolyte makes the flame time shorter by 18.9% compared with the no-additive electrolyte, from 70.3 to 57 s. By contrast, 5 wt.% TAIC reduces the flame time by only 7.3%, from 70.3 to 65.2 s, whereas 3 wt.% TAIC reduces the flame time by 9.2%. Thus, the flame retardancy of TAIC is not as strong as that of TAC. The allyl ether structure is better than allyl amine in flammability tests of the two isomers.

Double bonds can be found in some electrolyte components, such as VC, VA and AMC, which induce a good SEI film on anode. In order to utilize the film-forming ability of double bonds, it is necessary to test if the additives are oxidized. In contrast to the SEI on anode, the film on cathode is not easy to identify because the intensity of the electrolysis is very weak. CV cycles with unsaturated C–C bond additives in anodes provide clear SEI formation peaks that are easily identified [23], but the peaks on cathodes are not always separated. When film formation gradually occurs, observation of isopotential points can be expected for the cathode [18,24]. As every cycle proceeds, the surface coverage by the film is increased and a common intersection point of potential can be formed. Fig. 3(A) and (B) shows the CVs of 1 wt.% TAIC and 1 wt.% TAC solutions with NMC electrodes, respectively. Both CVs curves show isopotential points, which indicates film formation. The extent of film coverage grows on every cycle. The CV curves with TAC have a wide separation of oxidation and reduction peak in the early cycles. As cycling proceeds, the peak separation becomes narrower. The change in peak separation with TAIC is not as large as that with TAC. It is thought that the variation of peak separation in CV arises from a wetting process at the electrodes. The peak potential in the first cycle closely reflects the nature of the electrode. The effects of the surface film can be seen from the second cycle. The degree of separation is not
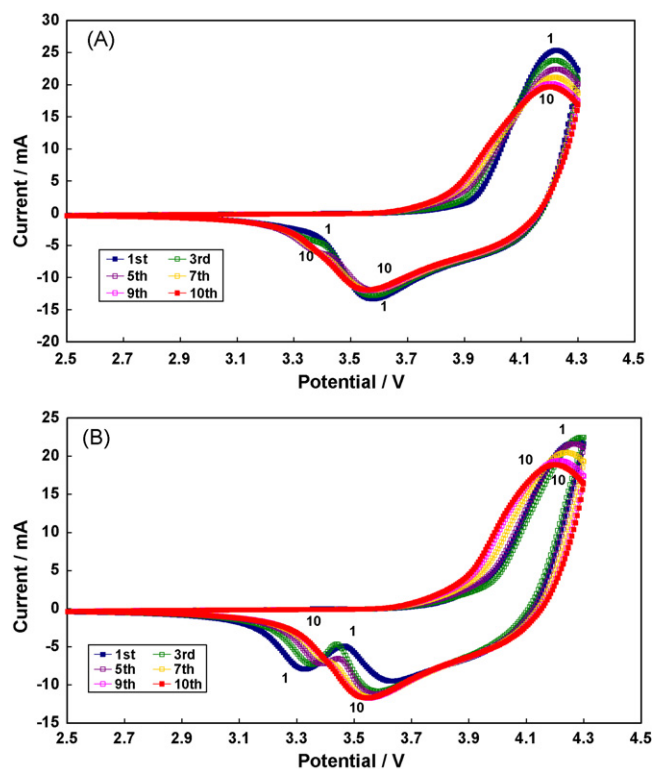
Fig. 3. Cyclic voltammograms of cathodes with 3 wt.% additive: (A) TAC 3 wt.% solution and (B) TAIC 3 wt.% solution.

Fig. 4. DSC curves of charged cathode materials to show enhanced thermal stability with different levels of (A) TAIC and (B) TAC solutions.

identical every time. The CV curves are not able to provide the thickness of the film, because full coverage of the electrode is not accomplished by the current used for the voltammetry. The charge consumed in the CV tests is not sufficient to ensure full coverage of the cathode by film formation of electrolyzed components.

Cathodes that had experienced 10 complete cycles were prepared to investigate how the additive can function as a thermal protector of the electrode. DSC measurements can provide information on the relative thickness of the film for thermal protection [25]. When the film is thicker, thermal decomposition of the cathode is either prevented or delayed further. The DSC scans of charged cathodes with TAIC, TAC and no additive are presented in Fig. 4. Peaks of surface films are detected in the area of 100 and 150 °C [18,25], which is the same as for the identification of an SEI on an anode [26]. In comparison with films with TAIC in Fig. 4(A), the films that were grown with TAC in Fig. 4(B) show much larger peaks. The exothermic heat (ΔH) that is released at film breakdown is listed in Table 1. Even though the values of ΔH are not directly proportional to the amount of an additive, TAC-containing electrolytes cause more heat release than TAIC-containing electrolytes. The larger peaks are due to a thicker film, which is a requirement for good thermal protection. In our previous study [18], it was confirmed that the film adheres to the surface by adsorption. Such a film is easily removed by rinsing it with electrolyte. The value for the SEI breakdown is proportional to the amount of adsorbates on the electrode. The endothermic reaction in the region of 240–270 °C represents the behaviour of solvent components in the electrolyte [26]. The solvent is not completely removed because a dry cathode can lose its charged condition. The very sharp exothermic peak near
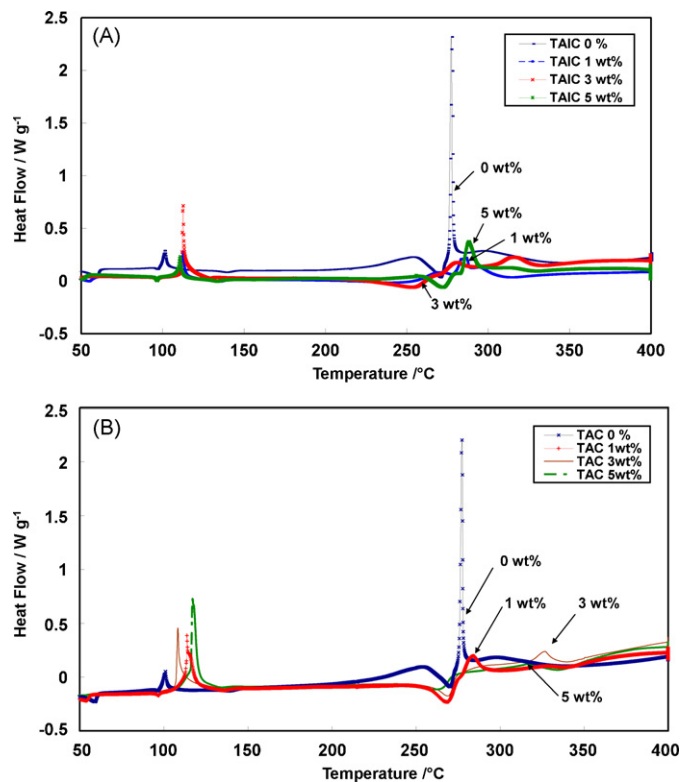
270 °C is due to the oxygen evolution reaction when NMC is thermally decomposed [14,27]. The peak temperature of the reaction is delayed, and the intensity of heat flow is very effectively suppressed by the additives and this can delay the consecutive thermal chain reactions that may trigger fire or explosion of a Li-ion battery. It seems that TAC suppresses the thermal reaction more effectively than TAIC.

Peak temperatures and heat evolved from the oxygen evolution reactions of the DSC curves are summarized in Fig. 5. Both additives delay the reaction and heat flow. The triazine additives turn the rapid exothermic reaction into a slow one. Also, the slow reaction rate diminishes the total evolution of energy. Addition of 5 wt.% TAIC reduces the exothermic energy by 43.9%, i.e., from 35.8 to 20.1 J g^{-1}. TAC at 5 wt.% suppresses 75.1% of energy evolution from 35.8 to 8.9 J g^{-1}. These data imply that reinforcement of the film by unsaturated carbon additives can shield the charged cathode from thermal impact so as not to progress to the fast thermal reaction. Addition of 5 wt.% TAC to the electrolyte deactivates 75.1% of the cathode particles from the thermal composition reaction. Examining the effectiveness of the additives in terms of peak temperature delay reveals that a 3 wt.% addition gives the best results for both additives. TAC performs better in terms of both peak temperature delay and energy release as a thermal protective additive. Addition of 3 wt.% TAC delays the exothermic reaction by 52 °C from 275 to 327 °C. By contrast, addition of 3 wt.% TAIC delays the exothermic reaction by 40 °C from 275 to 315 °C.

In order to understand the effectiveness of the functional groups that are on the triazine skeleton, two small molecules composed

Table 1
Heat release (ΔH) during surface film breakdown on electrodes for different levels of additive.

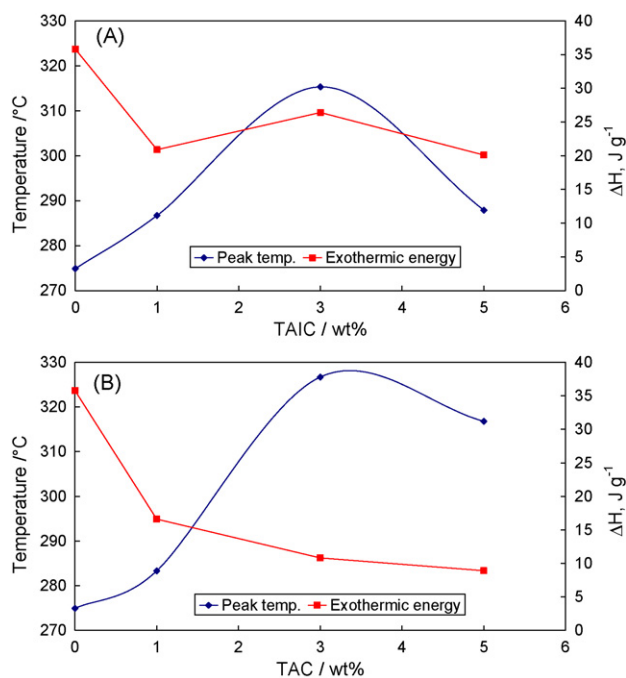| Electrolytes	No additive	TAC 1 wt.%	TAC 3 wt.%	TAC 5 wt.%	TAIC 1 wt.%	TAIC 3 wt.%	TAIC 5 wt.%
ΔH (J g^{-1})	5.19	29.34	24.21	41.22	11.63	19.02	7.24

Fig. 5. Peak temperatures and evolved energy values obtained from Fig. 4: values from (A) TAIC and (B) TAC solutions.
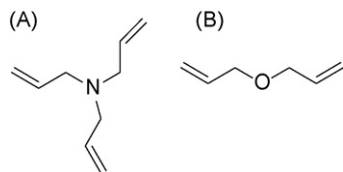

Fig. 6. Molecules that have only allyl ethers and allyl amines: (A) triallyl amine and (B) allyl ether.

of allyl amine and allyl ether, respectively, were chosen to test the thermal protection. The structures of triallyl amine (TAA) and allyl ether (AE) are in shown Fig. 6. The two additives were added separately to electrolyte to yield 3 wt.% solutions. After 10 charge–discharge cycles, rapid capacity fading caused by both additives was observed (not shown), which implies that the additives are not suitable for capacity-enhancing purposes. Charged cathode samples were prepared for DSC analysis to evaluate the materials as heat-protective additives. The DSC curves in Fig. 7 show that AE delays the thermal reaction further than TAA. The peak temperatures recorded for the AE and TAA solutions are 325 and 303 °C, respectively. Even though the number of allyl groups is different, it
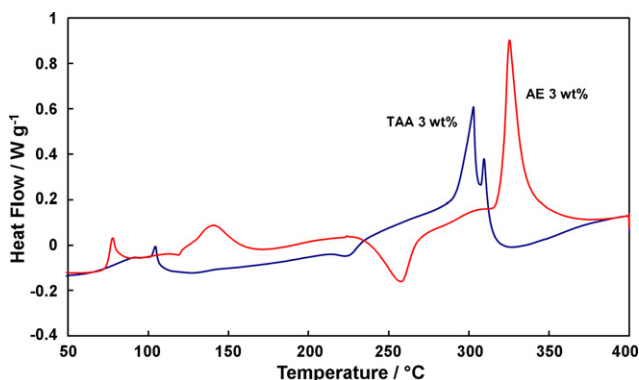

Fig. 7. DSC curves of charged cathode material with 3 wt.% TAA and AE solutions.
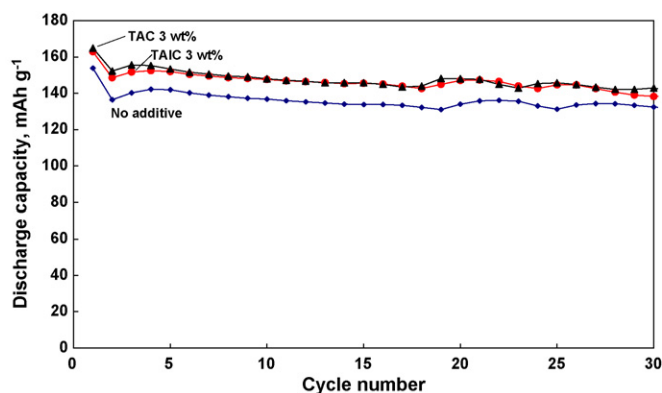

Fig. 8. Cycle-life tests of 3 wt.% TAC and TAIC solutions. A measurement with no-additive electrolyte solution is included for comparison.

is found that allyl ether is more effective than allyl amine in protecting electrodes from thermal stimulus. This result provides support for the view that allyl ether on TAC is more advantageous as a thermal protective group than allyl amine on TAIC. The energy evolution for the peaks was not compared because cells containing TAA and AE suffered rapid capacity fading. Therefore, only the comparison of peak temperature is valid information on the thermal protection capability of TAA and AE. Cycle-life tests with half-cells were performed to examine the feasibility of these materials as electrolyte additives. The data are presented in Fig. 8 and show that the capacity values from cells with additives are slightly higher throughout the tests. Additives impose no adverse effects on the capacity values compared with the sample with no additive under the given measurement conditions. Just as the unsaturated C–C bond additives for graphite electrode are effective in enhancing charge retention for long life, allyl-substituted additives can act similarly for cathode materials.

4. Discussion

The triazine derivatives TAC and TAIC not only have flame retarding properties, but also can offer thermal protection of the cathode. Unsaturated C–C bonds are able to form a good protective film through electrolysis. CV curves demonstrate that electrolysis of both electrolytes on a NMC electrode results in the formation of isopotential points that represent gradual coverage of the surface by the film on every cycle. The electrolysis of electrolytes on a cathode is not as severe as on an anode, so the charge consumed in the electrolysis is not sufficient to create the film formation peak that can be found in the CV curves of graphite electrodes. Therefore, it is difficult to analyze which additive can form the thicker protection film from the CV curves. DSC measurements can provide information on relative film thickness and the effectiveness of thermal protection by the film. The double bonds in TAIC and TAC are electrolyzed to build good protective films to change the rapid spontaneous thermal reaction of the charged cathode into a slow one. The TAC solution gives a larger surface film signal than the TAIC and delays the thermal reaction and effectively suppressed energy release from the thermal decomposition of the charged cathode. It is concluded that the larger film peak represents a thicker protective film. Between the isomers, the allyl ether group is better at thermal protection than the allyl amine. In order to prove the effectiveness of the allyl ether group as a better thermal insulator unit, TAA and AE were chosen for DSC measurements. From the DSC results, AE with the allyl ether group delays the thermal reaction further than TAA. From comparison between the values in Table 1 and Fig. 5, the thicker films generally provide better protection. Nevertheless, the thickness of the film is not always proportional

to the extent of the protection of the cathode. It is considered that the deviation is caused by different characteristics of the individual electrodes.

The structures of TAC and TAIC are quite different. TAC has an aromatic ring, which lets the allyl ether group react predominantly, but TAIC may have multiple reaction sites because it is not aromatic. For instance, double bonds and carbonyl groups are the possible reaction sites that can be reduced or oxidized. If carbonyl groups work as reaction sites, amine or amide can be created when the TAIC ring is opened. Amine and amide are rarely found in electrolyte. When TAC is electrolyzed by forming intermolecular bonds through unsaturated carbon branches, the aromatic triazine ring remains un-reacted as a part of the surface film network. Even if allyl groups lead to a thicker film for thermal protection, the increased thickness of the film is just thick enough for the protection. It does not act as a barrier against the charge–discharge cycle. It is concluded that the network formed from unsaturated carbon materials has pores that are sufficiently large to provide uninterrupted transfer of Li ions. Unsaturated C–C bonds are useful functional groups for the protection of both the anode and the cathode. If the allyl group has other performance-enhancing elements, such as fluoride [20,28], the additive could be used as a multipurpose agent.

5. Conclusions

TAC and TAIC, which are allyl-substituted triazine isomers, have been verified as flame-retardant materials. Addition of 5 wt.% TAC reduces flame time by 19%. Unsaturated C–C carbon materials have not been applied as additives for the protection of cathode. Most of the unsaturated C–C carbon materials that have been investigated have been used as additives for the anode because they can create a good SEI on this electrode. In this study, allyl-substituted materials are added to the electrolyte to form good protective films for the cathode. Charged cathodes are protected very effectively by the films reinforced by additives. The oxygen evolution reaction of charged NMC at 270 °C is well suppressed by the additives. Addition of 3 wt.% TAC delays the exothermic reaction by 52 °C from 275 to 327 °C. By contrast, addition of 3 wt.% TAIC delays the exothermic reaction by 40 °C from 275 to 315 °C. Between the two additives, TAC is a better thermal protector than TAIC. Addition of 5 wt.% TAIC reduces the exothermic energy by 43.9%, whereas 5 wt.% TAC suppresses 75.1% of the energy evolution. The unsaturated C–C bonds on the additives form a network on the cathode that is significantly protective against thermal stimulus. The additives delay the exothermic temperature and suppress the heat release from the charged cathode and thereby can improve the overall safety of batteries. Also, the flame retardancy of the additives can slow down fast fire expansion in an unavoidable situation. Cycle-life tests with half-cells demonstrate the feasibility of the additives in batteries.

Allyl ether groups offer better thermal protection. It is suggested that the allyl ether group offers good prospects in the design of electrolytic additives for cathodes.

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