Multifunction composite phase change material with inorganic flame retardant and organic form stability for improving battery thermal safety

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**GRAPHICAL ABSTRACT**

Multifunction Composite Material for Thermal Safety

- High thermal conductivity
- Flame retardant
- Excellent thermal stability

**PUBLIC SUMMARY**

- Uniform distribution of different additives within composite phase change materials is achieved.
- The total heat releasing time of multifunction composite phase change material is extended to 700 s.
- The maximum temperature in battery module can be controlled below 58.5°C at 5 C discharging rate.
Multifunction composite phase change material with inorganic flame retardant and organic form stability for improving battery thermal safety

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Phase change materials (PCMs) with superior cooling capacity and temperature equalization have great potential to mitigate thermal accumulation, benefiting the safety of electric vehicles (EVs) drivers. Although the composite phase change materials (CPCMs) with organic form stable addition can prevent leakage, they are still restricted in battery module due to easy flammable performance. Another challenge is that the inorganic flame retardants always distribute unevenly in organic CPCMs. Herein, to overcome the drawback of uneven additives dispersion within paraffin, we proposed a novel CPCM with inorganic flame-retardant and organic form stable material, composed of Paraffin/Styrene-Ethylene-Butylene-Styrene/AmmoniumPolyphosphate/Silicon dioxide/Carbon micro-nano aggregates (PS/APP/SiO2@C). The prepared material exhibits anti-leakage property with 99.5% mass retention after heating for 10 h at 70 °C, and the smoke generation rate is only 0.01 m2·s-1. The total heat releasing time is extended to 700 s, three times longer than that of PS. As for battery thermal management system, the maximum temperature and the temperature difference of battery module with PS/APP are 81.2 °C and 5.6 °C at 5 C discharge rate, respectively. In comparison, the maximum temperature and maximum temperature difference can be controlled to 58.5 °C and 1.5 °C, respectively, without heat accumulation during the twenty cycles. It indicates that the temperature is lower than the critical one to avoid thermal runaway of EVs. Therefore, this study presents CPCMs as an advanced thermal management approach that can enhance the thermal safety of battery packs, resulting in a significant impact on millions of drivers of EVs around the world.

INTRODUCTION

Electric vehicles (EVs) have developed by leaps and bounds with the rapid electrification of society in the world, with total sales volume surpassing 10 million by 2022. Lithium-ion batteries (LIBs) are the most widely utilized energy storage systems in EVs owing to their high energy/power density and long cycle life. However, LIBs are highly sensitive to the variation in temperature. Once the temperature exceeds a certain threshold, electrochemical side reactions can be triggered and make the battery uncontrollable. Moreover, a large amount of heat will be released and flammable gas will jet at high speed. It will cause severe deterioration and thermal runaway, which poses threats to the safety of passengers. Therefore, the thermal management technology in EVs is very crucially determined to prevent thermal runaway.

There are various thermal management approaches to regulate the electrochemistry of batteries and keep them within the normal range. Based on the heat transfer medium, the mainstream battery thermal management systems (BTMS) can be divided into air cooling, liquid cooling, and phase change materials (PCMs) cooling system. Intermittent spray cooling pulsing has proven effective in reducing the temperature of the battery surface after cooling, as it addresses the issue of insufficient heat transfer and the resulting large radial temperature gradient on the battery surface. However, air and liquid cooling system still exhibited some disadvantages such as extra equipment, liquid leakage and high cost, which can easily increase the energy consumption of the battery module and even result in heat hazards. In contrast, the PCMs cooling system is a passive cooling strategy that has potential in thermal management systems owing to its stable cooling capacity and temperature equalization ability. Since the quality of battery module with PCM is higher than that without PCM, it will inevitably bring about energy density loss at a certain degree. However, considering the PCM cooling system with many advantages such as compact structure, low energy consumption, and low cost, the energy density loss can be endured in practice.

Generally, the phase change in the PCMs occurs at a constant temperature, allowing for the necessary energy to be provided or stored at a steady temperature for a longer period. However, the repeated process of heat absorption/release can cause PCMs such as paraffin undergo phase change and volume change, resulting in the leakage of phase change components and failure in thermal management. To enhance the thermal stability of the PCMs and reduce the leakage of phase change components, supporting materials such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), epoxy resin (ER) are utilized to create composite phase change materials (CPCMs) and prevent phase change components leakage. Despite their ability to withstand phase transformations, these rigid composite phase change materials (RPCMs) will bring about the volume change in CPCMs. It creates an interval between the RPCMs and cooling objects, leading to noticeable contact thermal resistance at the contact interface, and it will seriously affect the thermal management performance of batteries.

To minimize the gap between batteries and CPCMs in the modules, flexible composite phase change materials (FPCMs) have been proposed to mitigate the close contact. FPCMs are suitable for the complex structure of battery modules and provide a flexible supporting skeleton for composite materials, including Olefin block copolymer (OBC), Styrene-Ethylene-Butylene-Styrene (SBS), Styrene-Ethylene-Butylene-Styrene Copolymer (SBS), Copolyester thermoplastic elastomer (TPC). While many studies have focused on optimizing the thermal stability and thermal conductivity of PCMs, there is still a need to further analyze the flame retardancy performance of PCMs, especially in preventing the thermal runaway of the battery module. Although CPCMs can meet the requirements of BTMS under normal operating conditions, the CPCMs with organic form stable additives can ignite during thermal runaway and exacerbate the severity of the fire, generating toxic smoke. To improve the flame-retardant property of CPCMs, strategies have been developed to enhance their relatively low flame retardancy. Organic halogen-free flame retardants like ammonium polyphosphate (APP) exhibit excellent flame retardant properties. APP promotes the formation of a protective coke layer on the material surface, preventing the decomposition of composite materials. What’s more, it produces gases at high temperatures and acts as a gas phase flame retardants by interfering with carbon oxidation and preventing combustion.
incorporation of APP phosphorus-containing flame-retardant toughening agents into PA is a suitable method to improve the fire safety of CPCMs. However, the inorganic APP has defects such as poor compatibility and is vulnerable to migration of small-molecular flame retardants within the CPCMs that have an organic form stable addition. Besides, the high amount of APP additives can reduce the thermal stability of CPCMs. While most studies have adopted organic molecules to reduce the flammability of CPCMs, few researchers pay attention to using inorganic fillers to improve the flame-retardant property of CPCMs. In addition, although the battery module with CPCMs can delay thermal runaway and prolong the thermal runway time to adjacent batteries at a certain degree, it still needs to explore multifunctional CPCMs to restrict the thermal runaway.

Considering the aforementioned analysis, silicon-based inorganic flame retardants offer synergistic and harmless advantages by increasing the oxidation resistance of the carbon layer, thereby protecting the inner materials. Through the incorporation of micro or nano-sized inorganic fillers, the mechanical properties, thermal stability, and heat resistance of CPCMs can be improved, effectively inhibiting heat propagation after batteries undergo thermal runaway. In this study, a multifunction composite flexible phase change material with organic form stable additives and inorganic flame-retardant has been successfully developed and applied in the battery module. This material integrates both carbon-coated silicon dioxide (SiO$_2@C$) and APP micro-nano aggregates to achieve prominent flame-retardant property and thermal stability. It is also compatible with organic form stable additives, improving the integrity performance of CPCMs. Despite being a passive cooling system don’t need any power supply, advanced CPCMs are still required to overcome thermal safety concerns between thermal management and thermal runaway in battery pack. The designed flame-retardant PS/APP/SiO$_2@C$ CPCM can provide comprehensive life-cycle protection from thermal management to inhibiting the thermal runaway propagation for the battery module. Considering these advantages of this innovative CPCM design, the novel multifunction flame-retardant composite material can improve the thermal safety of battery pack in EVs, which will increase consumer’s confidence in EVs.

**RESULTS AND DISCUSSION**

**Microscopic characterization**

Initially, the form of SiO$_2$ and SiO$_2@C$ and APP are observed by SEM, as shown in Figure 1. The pure APP appears a micron-scale loose edge particle, as indicated by the presence of the P element (Figure 1A,D&G). The prepared SiO$_2$ sphere is about 20 µm in diameter with a smooth surface (Figure S2). As shown in Figure 1B&E, following the carbonization of SiO$_2@RF$ sphere particles at high temperatures, a carbon layer was formed on the surface of the SiO$_2$ sphere, resulting in the formation of SiO$_2@C$ sphere. At the same time, the element analysis shows that the SiO$_2$ sphere can be restrained by the carbon layer effectively. The carbon layer of SiO$_2@C$ facilitates the uniform adhesion of SiO$_2@C$ to the surface of APP and forms micro-nano aggregates. Consequently, when the APP and SiO$_2@C$ spheres are agglomerated in solution, the sizes of the aggregates increase until the SiO$_2@C$ spheres layer is closely attached to the surface of APP particles (Figure 1C&F).

**Chemical composition and thermal properties**

The chemical compatibility of five FPCMs is analyzed by XRD, as shown in Figure 2A. Two diffraction peaks of PA are observed at 23.57° and 25.08°, corresponding to the crystal planes diffractions of (110) and (200), respectively (Figure S4). Besides, two typical characteristic diffraction peaks with different intensities are observed at 14° and 16°, as well as the corresponding diffraction peaks at 26°, 29°, and 31°, which consistent with crystalline form II type APP. Thus, the crystalline form II type APP is an orthorhombic material with a compact structure difficult to be permeated. The low crystallinity of SiO$_2@C$ spheres and the block copolymer nature of SEBS result in no observable diffraction peaks in the XRD analysis for both components. Besides, the FT-IR analysis of five samples is presented in Figure 2B. As for the PA, the peaks at 2850 cm$^{-1}$ and 2920 cm$^{-1}$ represent the -CH$_2$ symmetrical and asymmetrical stretching vibration. Compared with the individual peak of the three components displayed in Figure 2J, it is evident that the corresponding characteristic peaks are retained in the APP/SiO$_2@C$, PA/SEBS/APP and PA/SEBS/APP/SiO$_2@C$ samples. This indicates that no chemical reaction occurs when preparing FPCMs.

The latent heat value is also an important parameter of PCMs. As shown in Figure 2C, the phase transition temperature ($T_p$) of pure PA is 53 °C, with a corresponding latent heat value of 197 J·g$^{-1}$. As the mass fraction of PA in FPCMs reduces, the latent heat value of the FPCMs decreases correspondingly. Interestingly, the addition of APP does not affect the latent heat value of FPCMs, but it does cause an increase in the phase transition temperature to about 50 °C. The phase transition temperatures of PS/APP/SiO$_2@C$ further
The thermal conductivity of PS is only 0.2 W/mK, while that of PS/APP increases to 0.85 W/mK. The APP surface coated with SiO$_2$@C can obtain a better dispersion in CPCMs, while the APP/SiO$_2$@C micro-nano aggregates further improve the thermal conductivity of FPCM, with the values of PS/APP/SiO$_2$@C and PS/APP/SiO$_2$@C3 and PS/APP/SiO$_2$@C5 are 0.91, 1.02, and 1.11 W/mK, respectively. Thus, it indicates that APP/SiO$_2$@C micro-nano aggregates can establish sufficient thermal conduction paths within the FPCM, resulting in higher thermal conductivity compared to FPCM without APP/SiO$_2$@C micro-nano aggregates. Thus, it can be concluded that APP/SiO$_2$@C micro-nano aggregates can not only dissolve with PA effectively but also reduce the precipitation and gasification of PA.

The anti-leakage performance of FPCMs is crucial for improving the thermal stability of battery module. As shown in Figure S5-A, pure PA melts quickly and collapses on the heating table within an hour at 70 °C. In contrast, although some leakage occurs with PS, the quality retention rate remains over 95.5 % after continuously heating for 10 hours at 70 °C. As for PS/APP, its quality retention rate increases to 97.8 %, as the APP helps restrict the leakage of PA. Notably, the quality retention rate of PS/APP/SiO$_2$@C3 reaches 99.5 % after heating for 10 hours. To clearly characterize the microstructures of samples, SEM analysis of the microstructures reveals that pure PA has a continuous sheet structure (Figure 3C). When it is exposed to high electron beam focusing temperature, it melts and PS is effectively wrapped by SEBS, maintaining a stable and continuous structure (Figure 3D-E). In case of PS/APP/SiO$_2$@C, the surface of FPCMs exhibits a granular sensation (Figure 3F). This is primarily due to better compatibility between APP/SiO$_2$@C micro-nano aggregates and SBS/PA, resulting in uniform dispersion of each component and effective prevention of PA leakage. Moreover, different FPCMs are placed on heating tables at various temperatures for 1 h, and the corresponding leakage is recorded. The pure PA completely melted after heating at 50 °C for 1 h, while PS exhibited obvious leakage over 100 °C owing to the oxidation. Besides, although the addition of APP to PS helps to restrict leakage, there is still noticeable leakage over 100 °C, and APP powder may also leak along with PA in PS/APP. However, for PS/APP/SiO$_2$@C3, the leakage temperature is delayed to 150 °C, which is significantly later than PS/APP. Thus, this indicates that PS/APP/SiO$_2$@C3 exhibits excellent thermal stability (Figure S5 and Figure S6). Besides, according to the Figure S7, the tensile strength of flexible PS is 0.81 MPa. The addition of APP enhances the mechanical strength, increasing the tensile strength of PS/APP to 1.22 MPa. Similarly, the tensile strength of PS/APP/SiO$_2$@C1, PS/APP/SiO$_2$@C3 and PS/APP/SiO$_2$@C5 are 1.38, 1.56, and 1.51 MPa, respectively. Thus, it can be concluded that APP/SiO$_2$@C micro-nano aggregates can form a continu-
Combustion characteristic and flame-retardant performance

The schematic diagram of the combustion process of PS, PS/APP, PS/APP/SiO$_2$@C is shown in Figure 4A. The components of PA/SEBS are combustible materials, so PA and SEBS will volatilize during combustion, and the residual carbon is unable to form a stable carbon layer, causing the rapid spread of combustion throughout PA/SEBS. With the addition of APP, the PCMs act as a carbon source, leading to the formation of an expanded carbon layer after combustion. However, the structure of the carbon layer is thin and loose, which can be easily destroyed due to the volatilization of PA and the gas generated by adding APP. Therefore, pure APP can only achieve partial isolation of oxygen and heat. In contrast, during the formation of the carbon layer, PS/APP/SiO$_2$@C can withstand the impact of gas without being destroyed, thereby effectively improving the layer density and achieving desirable flame-retardant performance.

Considering that EG is an expansive flame retardant, the flame-retardant performances of FPCMs with APP, APP/SiO$_2$@C and PS/EG are compared. As shown in Figure 4A-C, under the 35 kW testing condition, pure PA releases a large amount of heat rapidly within 190 s with the heat release rate (HRR) of 1688 W·m$^{-2}$. The concentrated heat release of PS is significantly improved.
when it is combined with SEBS, with the HRR of PS reaching 970 W·m\(^{-2}\) in 200 s. Furthermore, due to the flame retardancy of APP, the HRR of PS/APP reaches 898 W·m\(^{-2}\) in 379 s, while the PS/EG achieves 877 W·m\(^{-2}\) in 350 s, respectively. Notably, the APP/SiO\(_2\)@C micro-nano aggregates demonstrate desirable flame retardancy. The peak heat release rates of PS/APP/SiO\(_2\)@C, PS/APP/SiO\(_2\)@C3 and PS/APP/SiO\(_2\)@C5 are 621 W·m\(^{-2}\), 305 W·m\(^{-2}\), and...
Besides, the PA and PS reach the total heat release (THR) platform at 125 MJ·m$^{-2}$ and 141 MJ·m$^{-2}$ before 200 s, respectively. In contrast, the PS/APP/SiO$_2$@C micro-nano aggregates with the mass of SiO$_2$@C increase show a better pronounced effect in delaying heat release, and the THR platform of PS/APP/SiO$_2$@C3 (148 MJ·m$^{-2}$) is extended to 700 s.

Besides, smoke production is also an important monitoring parameter to describe flame-retardant performance, as it not only increases the risk of secondary combustion but also seriously threaten the safety of driver and passengers. As displayed in Figure 4D-E, the centralized heat release time of CPCMs corresponds with the smoke production rate. The APP can decrease the SPR of PS/APP (0.06 m$^2$·s$^{-1}$) in 350 s rather than reducing the total amount of smoke produced (14 m$^2$). Furthermore, APP can generate nitrogen (N$_2$) and ammonia gas (NH$_3$) during the combustion. However, the SPR of PS/APP/SiO$_2$@C composite material decreases when the APP/SiO$_2$@C micro-nano aggregates are incorporated. The maximum SPR values of PS/APP/SiO$_2$@C1, PS/APP/SiO$_2$@C3 and PS/APP/SiO$_2$@C5 reach 0.04 m$^2$·s$^{-1}$, 0.01 m$^2$·s$^{-1}$ and 0.02 m$^2$·s$^{-1}$, respectively. The total smoke production (TSP) of PS/APP/SiO$_2$@C3 reaches 8 m$^2$ in 700 s, which indicates that the SiO$_2$@C sphere layer is attached to the surface of APP, and it can effectively reduce gas releasement and isolate gas.

Additionally, the limiting oxygen index (LOI) value and total duration of the residual flame of PA reach 15.4 % and 35.6 s, respectively, with the droplet after burning easy to rekindle. The total duration of the residual flame of PS still reaches 33.4 s, and it receives a UL-94 grade of V2. The LOI value and UL-94 grade of CPCMs is improved significantly by adding the APP, and the LOI value of CPCMs significantly improves to 24.2 % and the total duration of the residual flame is reduced to 15.1 s. Importantly, the flame retardancy of CPCMs is further enhanced by adding the flame retardant of APP/SiO$_2$@C micro-nano aggregates, especially PS/APP/SiO$_2$@C3 and PS/APP/SiO$_2$@C5, the LOI values are 35.9 % and 34.7 %, respectively, and their total duration of residual flame decreases to 5.3 s and 6.7 s, respectively. Compared with 20 wt% flame retardant, the flame retardant effect of FPCM with 15 wt% flame retardant is greatly reduced. The sample continues to burn for the first 10 s, and after extinguishing the flame at 15 s, the sample strip length is maintained at 90 %, which is shown in Figure S8, with LOI value of 26.3 %. Conversely, increasing the flame retardant to 25 wt%, the vertical combustion of FPCM is similar to that of 20 wt% CPCM, and the LOI value is 36.1 %, as listed in Table S5. In conclusion, the SiO$_2$@C sphere can be attached to the expanded carbon layer generated by APP endothermic decomposition, and it will improve the instability of the expanded carbon layer and obtain an excellent isolating oxygen.

To intuitively reflect the combustion of FPCMs and the flame retardancy in the thermal runaway of battery module, the flame spread and HRR of seven FPCMs strips and blocks are compared. In case of vertical combustion, the corresponding properties of PS, PS/APP and PS/APP/SiO$_2$@C3 are displayed in Figure 4F, and PS burns seriously after being ignited by a candle. When the fire source is removed, the flame of PS strip accelerates and continues until it
It can also be observed that PS/APP exhibits a certain level of flame-retardant effect. After removing the ignition source, the PS/APP strip extinguishes only after 5 s, and the sample strip preserving approximately 80% of its length. However, the drippage of PS/APP/SiO$_2$@C3 does not appear during continuous combustion. Even after burning for 15 s, PS/APP/SiO$_2$@C3 immediately stops burning when the ignition source is removed, and the length of sample retention rate stays within 99%. Besides, as for FPCMs block combustion (Figure 4G), when the PS block is ignited in the center, the flame spreads quickly and develop into a violent and uncontrollable condition in the surrounding modules. From the infrared thermal imaging of PS/APP block during combustion, it is observed that the temperature of the middle flame quickly transfers to the surrounding area of PS/APP FPCMs, thus avoiding the high temperature. The PS/APP/SiO$_2$@C3 demonstrates the optimum flame-retardant effect in the block burning test. During combustion, the steady burning time of PS/APP/SiO$_2$@C3 block is significantly extended, and no flame propagation occurs. As depicted in Figure 4G, when the flame is burned from the center of the modules, it will keep combusted stably in the area and a little slight flame diffusion will occur. Similarly, the combustion of three FPCMs blocks at the edges is also compared, which is shown in Figure S9. PS/APP/SiO$_2$@C3 exhibits better fire retardancy than PS and PS/APP. Therefore, it can be indicated that PS/APP/SiO$_2$@C3 exhibits excellent flame-retardant performance. FPCMs not only maintain a stable structure at high temperature but also inhibit flame expansion and realize automatic fire extinguishment with the liquefied residues flowing back to the flame.

Although EG has been used as an inflatable flame-retardant material, it fails to form an inflatable carbon layer after combustion. The char residue of PS/EG exhibits numerous cracks and has a discontinuous structure, as shown in Figure S11. Besides, Figure 4H demonstrates that the PS/EG residue presents a flake-like structure EG with a discontinuous construction and traces of PS on the EG surface. It indicates that EG is unable to effectively isolate combustion, so an extra material should be deposited on the surface of FPCMs before EG plays a role in oxygen isolation. Notably, the PS/APP/SiO$_2$@C3 can form a dense and expandable carbon layer without cracks on the surface, and SEM images also indicate that the carbon layer has multiple layers and is covered with SiO$_2$@C spheres. The performance comparison of this study with other studies of flame-retardant PCMs is listed in Table S6. The FPCMs with APP/SiO$_2$@C micro-nano aggregates exhibit a higher limiting oxygen index and a lower HRR value to achieve better flame retardancy.

**Figure 6.** Thermal management capability and thermal runaway protection (A) Electric heating rod module and serial number; (B) Maximum temperature curves and (C) Temperature differences of PS/APP, PS/EG, and PS/APP/SiO$_2$@C3 battery modules at three discharge rates (1 C, 3 C and 5 C); (D) Thermal runaway control factors of PS/APP, PS/EG, and PS/APP/SiO$_2$@C3 module at center position (#5). (E) Temperature curves of twenty cycles charge-discharge test of PS/APP, PS/APP/SiO$_2$@C3, and PS/EG battery modules at 5 C discharge rates; (F) Temperature changes of the heating rod at two positions of PS/APP/SiO$_2$@C3 module when thermal runaway is triggered at center position (#5).
Battery thermal management system performance

The power LIBs battery packs offer numerous advantages such as high energy density, long driving range, fast charge and shape diversity in application, as energy supply for the electric vehicles, which is depicted in Figure S5A. However, the thermal runaway incidents in EVs caused by overcharge, over-discharge, internal short circuit, and heat accumulation within battery pack during long operating process, which severely affect the million people and their safety (Figure 6B). The battery module with FPCMs can effectively prevent thermal propagation of power battery module, reducing traffic accidents and fire accidents caused by LIBs batteries (Figure 5C).

In order to restrain the heat propagating spread, the flame-retardant FPCMs should also meet the requirements of maintaining uniform temperature and the temperature control performance of battery module. The battery module is welded by ten 18650-type NCM batteries in the form of 10 parallel, and the parameters of the battery and battery module are listed in Table S2. CPCMs are used to absorb and transfer the heat generated by batteries. PS/APP, PS/APP/SiO$_2$@C3 and PS/EG are selected to construct passive thermal management systems for battery module (Figure 6A), and the temperature changes at discharge rates such as 1 C, 3 C, and 5 C are investigated, and the testing planform is shown in Figure S1. In Figure 6B, the maximum temperature of PS/APP module at 1 C, 3 C and 5 C reaches 47.2 °C, 71.4 °C and 81.2 °C, respectively, which are higher than those of PS/APP/SiO$_2$@C3 module and PS/EG module. The maximum temperature curves of PS/APP/SiO$_2$@C3 module closely resemble those of the PS/EG module. Even at 5 C discharge rate, the temperature difference between the maximum temperature and minimum temperature of PS/APP/SiO$_2$@C3 remains below 3 °C (Figure 6C). Thus, it reveals that PS/APP/SiO$_2$@C3 module not only exhibits temperature control ability but also provides temperature equalization. The main reason is that APP/SiO$_2$ micro-nano aggregates can sufficiently construct more thermal conduction paths than pure APP, which improves the heat absorption rate of FPCMs, thus achieving a prominent thermal management effect.

In addition, the battery module endures multicycles in application, so battery modules with PS/EG, PS/APP, PS/APP/SiO$_2$@C3 are all subjected twenty cycles of charge-discharge tests at discharge rates of 1 C, 3 C and 5 C. Specifically, at a 5 C discharge rate, the heat accumulation of PS/APP module begins after the ten cycles process, with the final temperature reaching 85 °C. The PS/APP/SiO$_2$@C3 module and PS/EG module are capable of maintaining the temperature of the battery below 60 °C throughout the twenty cycles of charge-discharge test. Thus, it demonstrates that the PS/APP/SiO$_2$@C3 and PS/EG modules can meet the requirements of battery thermal management for long-term use, which will provide stable temperature control capacity to ensure batteries within normal operating temperature ranges (Figure S12). Furthermore, the battery modules undergo fast charge testing (Figure S12). The battery module with PS/APP carried out 20 cycles of 3 C-3 C process, and the maximum temperature increased to 74 °C. However, the temperature of the PS/APP Module is obviously dropped after 17th 3 C-3 C cycle. The main reason is probably that the internal structure damage of the electrodes inside the lithium-ion battery, resulting in a decrease in battery capacity and subsequently lower temperatures due to reduced heat generation during charging and discharging processes. In contrast, PS/APP/SiO$_2$@C3 Module exhibits a lower maximum temperature than PS/EG Module. Even during 3 C-5 C charge and discharge rate after 20 cycles, the maximum temperature of the battery module with PS/APP/SiO$_2$@C3 reaches only 62 °C, which indicates that the battery module with PS/APP/SiO$_2$@C3 can exhibit optimum thermal management capability.

Thermal runaway spread analysis of battery module

However, in cases of thermal abuse in batteries, the battery module is inevitably exposed to thermal runaway hazards. Therefore, it is crucial to investigate FPCMs with flame-retardant function for battery module (Figure S10). In this study, the edge (#1) and center (#5) positions of battery module with FPCMs are studied in this triangular area. Additionally, in the experiment, the transfer stage of thermal runaway heat is divided (Stage $n$, $n = I, II, III, IV$) based on the number of battery modules involved.

When thermal runaway is triggered in the center position (#5), the stay time of PS/APP module at Stage I is extended to 910 s. The temperature drop of the thermal runaway trigger (No. 5) rod of PS/EG module is more noticeable, with temperature decreasing to 170 °C at the end of Stage I. Compared with PS/APP and PS/EG modules when thermal runaway is triggered in the center position, the temperature rising gradient is reduced in the module with PS/APP/SiO$_2$@C3. The No. 2 position in PS/APP/SiO$_2$@C3 module shows a gradual temperature rise in Stage I, with the end time postponed to 570 s. The No. 4 and No. 5 positions exhibit a more moderate temperature increase throughout the process, eventually reaching 97 °C and 82 °C, respectively (Figure S16). On the other hand, the No. 8 and No. 7 positions display a gentle temperature increase, eventually falling below 60 °C, which is significantly lower than the dangerous temperature. The main reason is that PS/APP/SiO$_2$@C3 enjoys prominent thermal stability and thermal conductivity, which can effectively absorb and transfer heat even at high temperatures. When thermal runaway spreads rapidly in the rest of the module, PS/APP/SiO$_2$@C3 can effectively restrain the influence of high temperature caused by the thermal runaway of each battery. There is a time difference during the propagation of thermal runaway when it is triggered at the edge position (#1), as displayed in Figure S13. Thus, it can be concluded that heat is absorbed in the transfer process through the FPCMs, and then transfers to the next layer.
Besides, considering the inconsistency of thermal runaway triggered by batteries at two positions of the module, the proportion of heat accumulation at different stages of the thermal runaway process in the battery module is analyzed (Eq. 1-3) to further analyze its potential dangers, and the proportion of heat accumulation is presented in Figure S14.

\[ \phi_n = \int_{t_n;start}^{t_n;end} T_{Stage;ndt} \cdot r \cdot 3600 \cdot dt \]  

(1)

\[ Q_n = C_p \cdot \Delta T_n = \int_{t_n;start}^{t_n;end} T_{Stage;ndt} \cdot w \cdot dt \]  

(2)

\[ Q_n = C_p \cdot \Delta T_{total} = \int_{0}^{T_{total}} T_{total} \cdot dt \]  

(3)

where \( \phi_n \) is the proportion of heat at different stages, \( n = i, II, III, IV \), \( i \) is the temperature of different heating rods, \( i = 1, 2, 4, 5, 7, 8 \).

An approach has been proposed to evaluate the performance of FPCMs in relation to the number of batteries in the module, aiming to prevent heat accumulation and thermal runaway. The accumulation time is closely related to the thermal conductivity. At the same time, the thermal runaway process is accompanied by flame generation, and the HRR value of CPCMs reflects the speed of flame propagation. Therefore, a thermal runaway controlled factor (TRCF, \( n_i \)) for battery module with FPCMs is very necessary in defining the relationship between CPCMs and batteries. The TRCF represents the area that thermal runaway spreads for every degree of temperature increase per unit mass (unit: \( m \cdot K^{-1} \cdot g^{-1} \)), and serves to describe the possibility of thermal runaway of battery module. The correlation Eq. 4 can be summarized as follows:

\[ n_i = \frac{\lambda_{FL} \cdot \Delta H \cdot N_{Supp} \cdot D}{V_{FL,PCM}} \cdot \frac{\sum_{i=1}^{N_{Supp}} f(x_i) \cdot dt}{V_{FL,PCM}} \]  

(4)

where \( N_{Supp} \) is the number of batteries in different stages, \( \lambda_{FL} \) represents the thermal conductivity of FPCMs, and the test value in this experiment is used in calculation; \( N_{Supp} \) is the number of the battery in different stages, \( D \) is the distance between batteries (thickness of CPCMs) and \( V_{FL,PCM} \) is the HRR value of the FPCMs.

The TRCFs of three FPCMs battery modules are calculated when thermal runaway are triggered on the edge and in the center. As shown in Figure 6D-F, the TRCF increases gradually with the spread time of the thermal runaway stage of the three battery modules. When thermal runaway is triggered in the center position (#5), the heat is evenly dispersed to the six surrounding batteries, significantly reducing the amount of heat carried by each cell and enhancing the control capability of thermal runaway. Stage II is a critical monitoring phase as it affects the largest number of batteries when thermal runaway is triggered in the central position. However, the TRCF of PS/APP module in Stage II only reaches \( 0.77 \times 10^{-4} \ m^2 \cdot K^{-1} \cdot g^{-1} \), indicating insufficient thermal runaway control capability. On the contrary, the TRCF of PS/APP/SiO\(_2\)@C module is 4.89 \( \times 10^{-4} \ m^2 \cdot K^{-1} \cdot g^{-1} \) in Stage II, approximately six times larger than that of PS/APP module, significantly improving the control degree of thermal runaway. However, the TRCF of PS/EG module just reaches \( 2.01 \times 10^{-4} \ m^2 \cdot K^{-1} \cdot g^{-1} \) at this stage. At Stage III, the TRCF of PS/APP/SiO\(_2\)@C grows to 10.05 \( \times 10^{-4} \ m^2 \cdot K^{-1} \cdot g^{-1} \). Besides, the TRCF of three battery modules at the edge position (#1) is presented in Figure S15.

Although PS/APP/SiO\(_2\)@C module has lower thermal conductivity than the PS/EG module, it still effectively controls the thermal runaway of battery module. Additionally, to inhibit thermal runaway of the battery module, the designed FPCMs with flame-retardant property can not only suppress the propagation of flame at the macro level, but also exhibit high thermal conductivity to meet the requirements of equilibrium temperature and heat dissipation when thermal runaway heat bursts. As a result, it can be concluded that the battery module with dual-effect barrier of flame-retardant FPCMs can successfully control the maximum temperature below 61 °C even at 5 C discharge rate after twenty cycles.

CONCLUSION

The thermal safety of battery pack is essential to the safety of drivers and passengers. Passive cooling systems utilizing phase change materials (PCMs) have been widely implemented in battery modules to improve thermal management. However, the drawbacks of poor thermal stability and high flammability restrict the large-scale utilization of PCMs in thermal management systems, particularly in preventing the thermal runaway of battery module. In this study, to overcome the aggregating problem of different additions after long-term usage, we have developed a novel multifunctional composite flexible phase change materials with inorganic flame-retardant and organic form stable additives for the battery module. The inorganic flame-retardant can achieve stable flame-retardant effect and sufficient heat conduction paths in FPCMs. The APP/SiO\(_2\)@C flame-retardant micro-nano aggregates exhibit higher compatibility with PA than pure APP, which can effectively ensure long-term usage during the phase change process. It forms the expanded carbon layer, serving as a uniformly heat-resisting layer, effectively preventing thermal propagation after FPCMs combustion. Meanwhile, the battery module with PS/APP/SiO\(_2\)@C demonstrates excellent battery thermal management and restrains thermal propagation performance, especially at 3 C discharge rate, the maximum temperature and maximum temperature difference can be controlled within 61 °C and 3 °C, respectively. Thus, the PS/APP/SiO\(_2\)@C module FPCMs accomplish uniform temperature distribution and effective control of the maximum temperature within safety range, protecting the battery module under high discharge rate and long cycling conditions. Furthermore, it enables rapid heat transfer and mitigates flame spread in the thermal runaway process, preventing the thermal runaway propagation of thermal runaway. Overall, this research provides an efficient solution to improve the thermal safety of battery packs in practical applications, which can protect the tens of millions lives and property of drivers and passengers of the EVs in the world.

MATERIALS AND METHODS

Synthesis

Figure 7A-B describe the synthesis process of APP/SiO\(_2\)@C micro-nano aggregates and the preparation of flame-retardant FPCMs. As shown in Figure 7A, APP/SiO\(_2\)@C micro-nano aggregates are synthesized using the chemical template method and melt blending methods. APP/SiO\(_2\)@C micro-nano aggregates have a core-shell structure to enhance the structure stability. The synthesis process of SiO\(_2\) spheres and SiO\(_2\)@C spheres is illustrated in Supplementary Information in detail. During the combusting process, the APP generates a carbon layer and SiO\(_2\)@C sphere attach to the surface of the carbon layer. This composite structure serves as a secondary heat insulation and oxygen insulation, and enhances the stability of the carbon layer.

A typical physical mixing method is utilized to prepare the flame-retardant FPCMs (Figure 7B). Initially, the PA blocks and SEBS particles are melted in an oil bath at 150 °C and the mixture is stirred evenly by an electronic mixer (300 rad·min\(^{-1}\)). In the next step, as listed in Table 1S, the additives are added into the PA/SEBS mixture one by one and stirred evenly, and the mixture is then poured into the mold and solidified at 25 °C. Further details of the preparation can be found in our previous research.\(^{21}\)

Chemical characterization

The chemical structures of FPCMs and their components are analyzed by X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR). Different crystalline phases of FPCMs are determined by the XRD (D/MAX-Ultima III) with the scanning rate of 8 °·min\(^{-1}\) (2 theta) ranging from 10° to 80°. Besides, the chemical structures of FPCMs are characterized by the FTIR (Bruker Tensor-27) with spectra ranging from 400 to 4000 cm\(^{-1}\) with 2 cm\(^{-1}\) resolutions using KBr disk.

Thermal physical properties of flame-retardant flexible CPCMs

The phase change performance of FPCMs is tested by differential scanning calorimetry (DSC, Q 0, TA Instruments, Inc.), which is set with a temperature range of 0 °C to 80 °C. Meanwhile, the thermal stability of CPCMs is analyzed by a thermal gravimetric analyzer instrument (TGA, STD 2960, Texas Instrument Inc, USA), and the operating temperature range is set at 20-800 °C with a temperature rise rate of 20 °C·min\(^{-1}\). Besides, the quality change and leakage

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of samples of FPCMs samples are analyzed, which are placed on the heating table heating for 10 hours at 70 °C and recorded every 2 hours.

**Flame-retardant property of FPCMs**

Flame-retardant property of different FPCMs is analyzed by an oxygen index meter (J-007, Jiangsu) following EN45545-2:2013+A1:2015 (Requirements for fire behavior of materials and components) and vertical combustion instrument (J-001, Jiangsu) following UL 94:2016. To analyze the flame-retardant effect of FPCMs for battery module, LOI and CONE analysis have been used to compare the fire retardance of PA, PS, PS/APP, PS/SiO, SiO/C1, PS/APP/SiO/C3, PS/APP/SiO/C5 and PS/EG. The flame-retardant FPCMs sizes of LOI and UL-94 measurements are designed as 130 mm × 6.5 mm × 3.2 mm and 130 mm × 13 mm × 3.2 mm, respectively. The LOI value of each flame-retardant FPCMs is the average value of fifteen parallel tests. Furthermore, the CONE tests including HRR, THR, SPR and TSP are measured, and the combustion behaviors of flame-retardant flexible CPCMs are investigated by an FFT CONE calorimeter instrument following ISO 5660. The flame-retardant FPCMs with the sizes of 100 mm × 100 mm × 3.2 mm are also exposed to heat radiation with the heat flux of 35 kW/m², and each result is an average of two parallel tests. Besides, the microstructures of the flame-retardant FPCMs and their char residues are observed via SEM (Hitachi S-3400 N, Tokyo, Japan) equipment with an accelerating voltage of 20 kV, respectively.

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