

# Preparation and Application of Composite Phase Change Materials

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**Abstract.** With the popularity of lithium-ion batteries, thermal runaway accidents occur frequently. The importance of thermal management was becoming increasingly prominent. In this paper, a new composite phase change material (CPCM) was developed and applied to the thermal management of lithium-ion batteries. The chemical and microstructure of the material were deeply analyzed by scanning XRD and SEM. The thermal stability of the material was tested by using DSC and TG techniques. The thermal conductivity was exhaustively analyzed. The experimental results showed that CPCM containing 9% Aluminum phenylphosphinate exhibits optimal thermal storage performance and flame retardant efficiency, which effectively delayed and reduced the risk of thermal runaway in lithium batteries.

**Keywords:** Thermal runaway; Composite phase change materials; Thermal management; Thermal runaway

## 1. Introduction

Batteries were exposed to complex working conditions in the actual use of vehicles. Because of the limited capacity of the battery. To enhance the range, more batteries need to be installed in the limited space. Lithium-ion batteries generate a large number heat when they work [1]. If the heat can't be released quickly, it was easy to cause the temperature of the battery pack to thermal runaway [2]. Therefore, it was necessary to build an effective battery thermal management system (BTMS) to inhibit excessive temperature rise and prevent the spread of thermal runaway [3]. BTMS was critical to modern battery technology, ensuring that the battery pack maintains the appropriate temperature and optimizes operation in a variety of environments [4]. According to the cooling medium, BTMS can be classified into air-cooling, liquid-cooling, phase change material and combined heat dissipation [5]. The efficiency of air cooling was low and difficult to meet the demand for high-power charging and discharging of lithium batteries. Liquid cooling had superior performance, but there was a risk of liquid leakage, high weight and high maintenance costs. Phase change material (PCM) cooling had no external energy consumption and was easy to assemble and maintain, which was receiving extensive attention and research. Al-Hallaj et al. proposed a novel thermal management system for electric vehicle applications that integrates phase change materials (PCM), which significantly improved the temperature distribution uniformity of the battery at different discharge rates [1]. Javani et al. investigated the passive thermal management of PCM in conjunction with lithium-ion batteries and found that the use of a 3-mm-thick PCM resulted in a more uniform temperature distribution of the battery, with a reduction in the maximum temperature and the temperature excursion [1]. Zeng et al. prepared organic PCM/silver nanoparticle composites and showed that the increase of silver nanoparticles enhanced the thermal conductivity of the composites, which was important for thermal management systems in electric vehicles [1]. In this paper, the variation of properties after adding different proportions of aluminium phenyl hypophosphite to PCM was thoroughly investigated, and the effect of its application in lithium-ion batteries was discussed.

## 2. Materials and Methods

### 2.1 Materials

Phase change paraffin (PA) was purchased from Jiangsu Yijia Plasticizing Technology Co., Ltd. Expanded graphite (EG) was provided by Anhui Zesheng Technology Co., Ltd. Aluminum phenylphosphinate (PADP) was prepared in the laboratory.

### 2.2 Preparation of CPCM

PA 4.5 g solid was placed in a beaker and heated to melt, after melting 10% EG was added and stirred well. Add aluminium phenylphosphate powder to the mixture of PA and EG and mix well to prevent lumping. After standing for half an hour, a uniformly dispersed powdered PA/EG/PADP CPCM was obtained. The powder was poured into a mold and allowed to cool. In making the composite phase change materials, different contents of aluminium phenylphosphonate were produced by controlling the mass fraction of aluminium phenylphosphonate as 3%, 6%, 9% and 12%. 3% PA/EG/PADP CPCM was named CPCMb, 6% PA/EG/PADP CPCM was named CPCMc, 9% PA/EG/PADP CPCM was named CPCMc, 12% PA/EG/PADP CPCM was named CPCMd.

### 2.3 Characterization

The CPCM was characterized by X-ray diffraction (XRD, Shimadzu Co.) using XRD-6100 in the range of 5 ° to 80 °. The microstructure of the CPCM was investigated by scanning electron microscopy (SEM, Thermo Fisher Instrument Co.) using Nicolet IS 5 under the spectra range of 500-4000 cm<sup>-1</sup>. The Phase transition properties of CPCM were analyzed by HP DSC 1 differential scanning calorimeter (DSC, Mettler Toledo Co.) and the latent heat value was calculated. The thermal stability of the CPCM was analyzed by thermogravimetric analysis (TGA, Mettler Toledo Co.) using TGA-101 in a nitrogen (N<sub>2</sub>) atmosphere over a temperature range of 30-500 °C at a temperature increase rate of 20 °C/minute. The thermal conductivity of CPCM was measured by a DER-III thermal conductivity meter (Xiangtan Instrumentation Co., Ltd.). To study whether CPCM had a positive effect on the suppression of thermal runaway of lithium-ion batteries, a lithium-ion battery with 90% SOH was selected to pass the arc insulation test.

## 3. Results analysis

### 3.1 XRD analysis

Fig.1 showed the XRD of PA and CPCM. It can be seen from the figure that the XRD spectrum of PA had three significant diffraction peaks at 6.64 °, 21.52 ° and 23.6 °. In the XRD spectra of PA/EG PCM, due to the crystal structure of EG, strong diffraction peaks appeared at 26.7 ° and 35.84 °. The XRD spectra of CPCMa, CPCMb, CPCMc and CPCMd showed two PADP diffraction peaks at 8.94 ° and 18.34 °, which increased with the increase of PADP content in CPCM. There was no additional diffraction peak in the figure, indicating that PA, EG and PADP were physically combined.

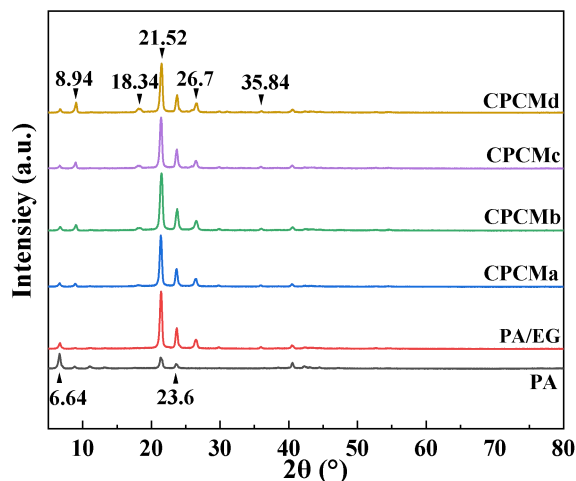


Fig.1 XRD profiles of PA, PA/EG PCM, CPCMa, CPCMb, CPCMc and CPCMd.

### 3.2 SEM analysis

SEM images of PA/EG PCM, PADP, CPCMa, CPCMb, CPCMc, and CPCMd were shown in Fig.2. PA/EG PCM presented a smooth surface as shown in Fig.2(a). It could be seen that PADP was in the form of uniform fine particles in Fig.2(b). The surface of the CPCMa surface showed irregularly shaped wrinkles on the surface and a few PADP aggregated in Fig.2(c), which suggested that PADP was mixed into the PA/EG PCM. The SEM image of CPCMb had more folds on the surface and more PADP aggregates as shown in Fig.2(d). On the surface of CPCMc, irregular surface folds can still be seen and the amount of aggregated PADP was increased as shown in Fig.2(e). It could be seen that the surface of CPCMd was covered with fine and dense granular PADP in Fig.2(f).

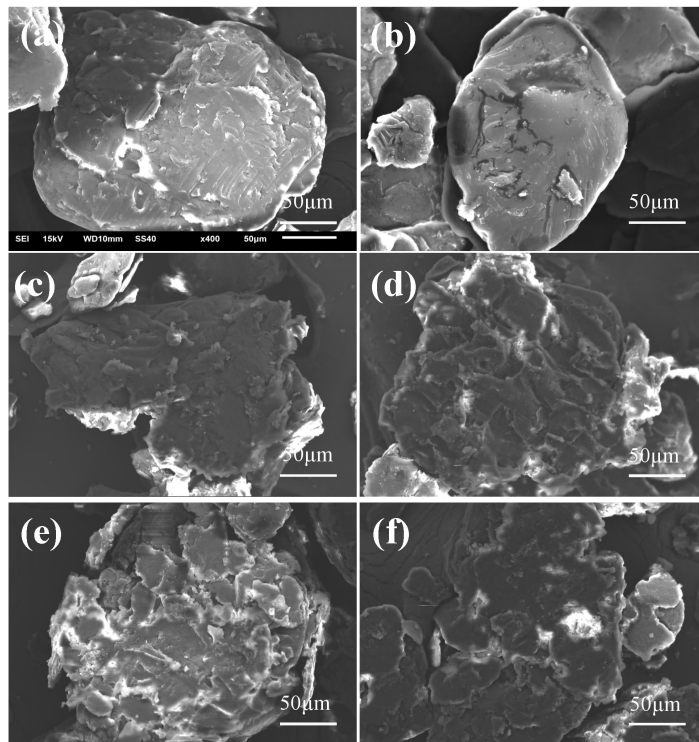


Fig.2 SEM images of (a) PA/EG PCM, (b) PADP, (c) CPCMa, (d) CPCMb, (e) CPCMc, (f) CPCMd.

### 3.3 DSC analysis

The DSC profiles of PA/EG, CPCMa, CPCMb, CPCMc and CPCMd were shown in Fig.3 and the specific data were shown in Table 1. The latent heat value of PA/EG was 122.1 J/g. The latent

heat value of CPCMa was 134.5 J/g. The latent heat value of CPCMb was 138.8 J/g. The latent heat value of CPCMc was the highest, 146.9 J/g. The latent heat value of CPCMd was 146.3 J/g. With the increasing content of PADP, the latent heat value of CPCM increased gradually. When the content of added PADP reaches 9%, the latent heat value was the largest and continued to be added, the latent heat value decreased. Therefore, the CPCM with 9% PADP content was the optimal ratio and had good heat storage performance.

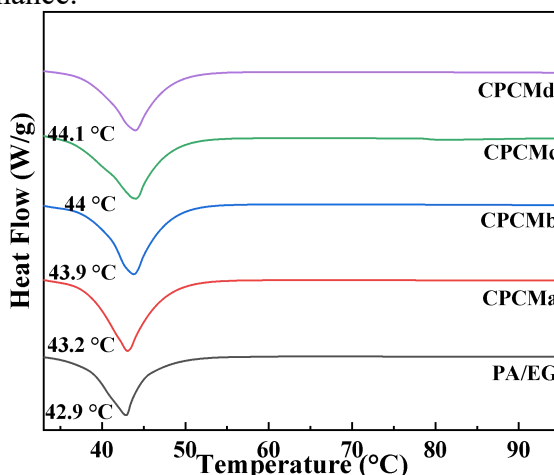


Fig.3 DSC curves of (a) PA/EG, CPCMa, CPCMb, CPCMc, CPCMd.

### 3.4 TG analysis

The TG profiles of PA/EG, CPCMa, CPCMb, CPCM and CPCMd were as shown in Fig. 4. The degradation of PA started at 200 °C and completely decomposed at 370 °C. The PA/EG PCM curve corresponded to the degradation stage around 200 °C-356 °C, which was mainly due to the pyrolysis of PA adsorbed in PA/EG PCM. The TGA curves corresponding to CPCMa, CPCMb, CPCMc and CPCMd corresponded to the degradation stage around 200 °C-378 °C, which was mainly due to the pyrolysis of PA in CPCM. The residual mass of PA/EG, CPCMa, CPCMb, CPCM and CPCMd were 9.1%, 9.07%, 12.65%, 16.47% and 20.88%. The reason could be attributed to the decomposition residues of PADP. The results showed that the PADP flame retardant additive improved the thermal stability of CPCM.

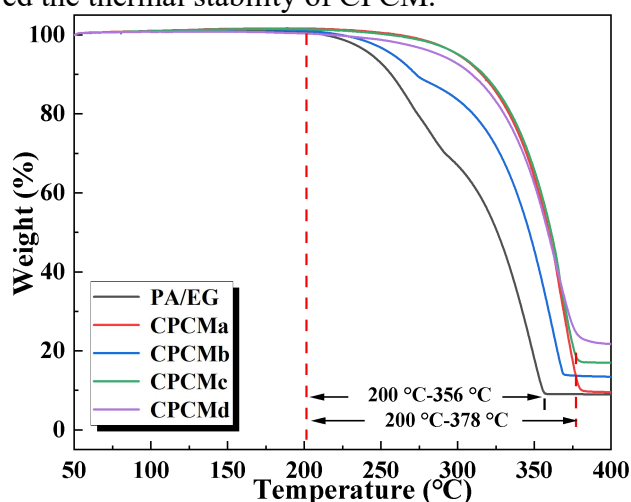


Fig. 4 TGA analysis of PA/EG PCM, CPCMa, CPCMb, CPCMc and CPCMd.

### 3.5 Thermal conductivity analysis

The thermal conductivity of CPCM was shown in Table 3. It could be seen from the figure that the thermal conductivity of PA/EG was 0.345 W/(m·K), which increased when the content of PADP gradually increased. The highest thermal conductivity was observed at 9% PADP. The continued addition of PADP decreased the thermal conductivity.

Table 1. Thermal Conductivity of PA/EG, CPCMa, CPCMb, CPCMc and CPCMd.					
Samples	PA/EG	3%	6%	9%	12%
Thermal conductivity/ W/(m·K)	0.345	0.380	0.394	0.423	0.364

### 3.6 Thermal runaway study of lithium-ion batteries by CPCM

The thermal runaway process of air-cooling (empty) lithium-ion battery and lithium-ion battery wrapped with CPCMc as shown in Fig.5. For the air-cooling lithium-ion battery,  $T_0$  was 147.07 °C,  $t_0$  was 647.14 min,  $T_1$  was 200.18 °C,  $t_1$  was 697.87 min,  $T_2$  was 390.60 °C,  $t_2$  was 701.28 min. For the lithium-ion battery wrapped with CPCMc,  $T_0$  was 174.21 °C,  $t_0$  was 1104.87 min,  $T_1$  was 228.79 °C,  $t_1$  was 1257.87 min,  $T_2$  was 394.40 °C,  $t_2$  was 1284.40 min. It could be seen that the self-heating reaction temperature increased by 27.14 °C and the time was delayed by 407 min with CPCMc. The TR triggering temperature was increased from 200.18 °C to 228.79 °C, which was a 28.61 °C increase and the time was delayed from 697.87 min to 1257.87 min. The TR trigger temperature was increased from 200.18 °C to 228.79 °C with an increase of 28.61 °C and the time was delayed from 697.87 min to 1257.87 min with a time delay of 560 min. The results verified that the CPCMc had a good latent heat cooling performance, which had a positive effect on the delay of the TR and the reduction of the TR occurrence.

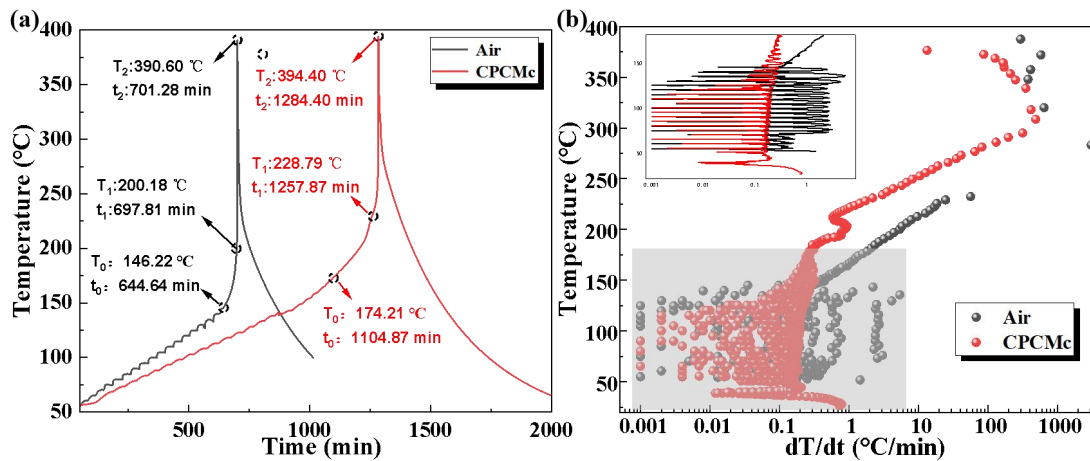


Fig. 5 Adiabatic thermal runaway test data results for single wrapped with CPCMc and unwrapped lithium-ion battery with 90% SOC: (a) The temperature vs time, (b) Temperature vs temperature rise rate.

## 4. Summary

High latent paraffin (PA) was used as the phase change material, expanded graphite (EG) as the thermal conductivity enhancement material and aluminum phenylphosphinate (PADP) as the flame retardant material to prepare the composite phase change material, which was applied in lithium-ion batteries, and analyzed in terms of chemical structure, microstructure, and thermal stability. The results showed that the physical combination of PA, EG and PADP did not produce new substances. The DSC test showed that the thermal conductivity of PA/EG/PADP CPCM reached up to 146.9 J/g when the content of phenylaluminium hypophosphite was 9%. The TGA test showed that the product had good thermal and shape stability, which mitigated the phase change process of PA leakage and is suitable for battery thermal management applications. The thermal runaway test showed that the self-heating reaction temperature of the lithium-ion battery in CPCMc increased by 27.14 °C, and the time was delayed by 407 min. TR trigger temperature increased from 200.18 °C to 228.79 °C, which was an increase of 28.61 °C, and the time was delayed from 697.87 min to 1,257.87 min, and the time was delayed by 560 min.

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