



A novel nanosilica-enhanced phase change material with anti-leakage and anti-volume-changes properties for battery thermal management

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ABSTRACT

As an advanced battery thermal management method, phase change material (PCM) cooling technology is highly desirable but remains significant challenges, considering the instability of the PCM module, including PCM leakage, volume changes and inhomogeneity of the whole module during the repeated melting/solidifying processes. Herein, we develop a kind of nanosilica (NS)-enhanced composite PCM (CPCM-NS) with outstanding anti-leakage and anti-volume-change performances for power battery thermal management. The NS presents numerous nanoscale pores ranging from 30 to 100 nm, which can adsorb liquid phase paraffin (PA) intensively, thus preventing the migration and leakage of liquid PA, increasing the homogeneity and relieving the volume change phenomenon of the module to a great extent. As a result, these enhanced properties of CPCM-NS endow the obtained battery module with much better cooling efficiency and durability. For instance, the maximum temperatures of CPCM-NS with 5.5 wt% of NS are 1.6, 2.4, 4.5, 5.3 and 5.9 °C lower than those of CPCM without NS at the 1st, 2nd, 4th, 6th and 8th cycle charge/discharge cycle, respectively, and this temperature difference remains stable at 6.22 ± 0.05 °C during the subsequent cycles.

1. Introduction

Fossil-fuel-free Electric vehicles (EVs) are believed to substitute traditional internal combustion engine vehicles in the next decade due to the increasingly serious issues of fossil fuel energy consumption [1] and global climate change [2]. However, the safety of the power battery pack in EVs has always been one of the most important bottlenecks, especially which derived from the overheating [3] and/or non-uniform temperature distribution [4]. It is well known that the best working temperature range of the batteries is 25–50 °C [5], and the maximum temperature difference of the whole battery module should be strictly maintained below 5 °C [6]. Thus, a concept of battery thermal management (BTM), with the aim of controlling the temperature and temperature uniformity of the power battery module in EVs, has been proposed, and many efforts are devoted to developing advanced BTM technologies, including focus air cooling [7], liquid cooling [8] and phase change materials cooling [9]. Among them, phase change materials (PCM)-based cooling has been considered as the one of the most potential alternatives to conventional BTM technology because of its high cooling efficiency [10], low cost and simple installation [11]. It is based on the principle that PCM can absorb/release tremendous latent heat during the phase change process, thus giving rise to a relatively stable temperature of the power battery system [12].

PCM can be classified into inorganic PCM (IPCM) [13–15] and organic PCM (OPCM) [16–18]. Although IPCMs possess wider phase change temperature and lower volume changes, considering their obvious limitations of high replacement costs [19], super-cooling [20] and metal-corrosion capability [21], most studies are focusing on the development of OPCMs because of their negligible super-cooling [21] and low cost [22]. At the same time, additional components such as expanded graphite (EG) [23,24] and metal foam [25,26] are usually added, forming composite PCM (CPCM), to overcome the low thermal conductivity and/or poor shape stability of pure PCM [27,28]. A. Trigui et al. [29] reported the fabrication of a low density polyethylene (LDPE)/paraffin (PA) CPCM and found that LDPE acted as the supporting matrix to enhance the shape stability during the phase change process. Bahraseman et al. [30] reported that a CPCM with 20 wt% of EG showed much faster temperature response rate compared to that with 10 wt% of EG. Li et al. [31] prepared a microencapsulated PCM (MEPCM)/metal foam CPCM, and found that it presented excellent temperature uniformity performance compared to the pure MEPCM. Recently, we developed a kind of ternary LDPE/EG/PA-based CPCM and confirmed its preliminary feasibility for using in BTM, including the basic requirements of mechanical property, forming capability, and especially the cooling and temperature-uniform efficiency [32]. After coupling with low fins, the as-constructed CPCM-based battery module

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presents excellent heat dissipation and temperature uniform performance, keeping the battery module working under the safety temperature of 50 °C and temperature difference of 5 °C, even at an extremely high discharge rate of 3.5 C.

However, although the formability and the cooling/temperature-uniform performance of the module have been proven applicable, there remain several self-security problems of CPCPM that couldn't meet the requirements for a battery module yet in practical application. For example, the migration of the PCM component at liquid phase is still bothering both the academia and industry so far, which leads to the PCM leakage and decreasing homogeneity of the whole module during the repeated phase change processes. What's worse, safety risk rises exponentially as the leaked PCM builds up because most PCMs are combustible. Although the microencapsulation wrapped strategy has been proven effective to prevent PCM leakage [33], the tedious procedure [34], relatively high cost [35,36] and inevitable microcapsule rupture restrict its practical application seriously. In addition, another neglected issue is the volume changes of the CPCPM during the heating/cooling process [28]. This becomes another major barrier for the practical application of PCM cooling technology owing to the following reasons: (1) instable power output and safety problems arisen from the vibration of the loose batteries under serious road condition or even car crash; (2) sharp increase of the thermal resistance resulting from the gaps between the batteries and PCM during volume changes. Therefore, exploring new or modified CPCPMs and/or strategies to relieve or even address the PCM migration and volume change phenomena is urgently needed, but remains a formidable challenge.

To overcome these issues, in the present work, we develop a class of PA-based CPCPM with great anti-leakage and anti-volume-change performances for the thermal management of the power batteries. This is realized by adding a small amount of nanosilica (NS) into the CPCPM. Benefiting from the intensive adsorbability provided by the nanoscale pores and the rigid nano-skeleton, NS dispersed in the EG pores can fix liquid phase PA and restrict the expansion of EG, thus preventing PA leakage, increasing the homogeneity and reducing the volume changes of the module to a great extent. These outstanding anti-leakage and anti-volume-change performances of the NS-enhanced CPCPM endow the corresponding battery module with excellent cooling efficiency and durability.

2. Materials preparation and characterization

2.1. Materials

Industrial grade PA (RT45) from Petro China Co., Ltd. was used as the PCM. Expandable graphite (average particle size: 150 μm, expansion ratio: 220 cm³g⁻¹) was heated at 760 °C for 180 s in a muffle furnace to obtain EG. NS with a specific surface area of 160 m²g⁻¹ was purchased from Aladdin®. LDPE with a density of 0.925 g cm⁻³ was purchased from Sinopec Shanghai petrochemical Co., Ltd.

2.2. Preparation of the CPCPMs

NS-enhanced CPCPMs were obtained through a physical mixing method based on our previous work [32] with some modifications (Fig. 1). First, PA was melted using a low-speed mixer (DC-100 W, Changzhou Wanhe instrument manufacture Co., Ltd.) at 85 °C in an oil bath for 1 h. Secondly, predetermined amount of NS (Table 1) was added to the PA with continuous stirring to adsorb PA until completely gelatinous. Thirdly, EG with a percentage of 7 wt% was added to the resultant PA/NS composite with continuous stirring. Finally, 30 wt% of LDPE was added to the mixture and the temperature of the oil bath was increased to 145 °C for 2 h. The mass ratio of PA/EG/NS/LDPE composites is shown in Table 1. After that, the resultant mixture was gradually cooled to room temperature. The obtained NS-enhanced CPCPMs were denoted as CPCPM-NS_x, where x represented the mass percentage

of the NS. For comparison, another sample without adding NS was prepared at a PA/EG/LDPE mass ratio of 63:7:30, and denoted as CPCPM-NS0 (Table 1).

2.3. Homogeneity, thermal conductivity and PA leakage tests

The CPCPM-NS0 and CPCPM-NS5.5 samples were processed into cylindrical shapes with 43.5 mm in diameter and 25 mm in height. Then the samples were put into an oven (Dongguan A-PEX Test Equipment Co., Ltd.) at 60 °C for 2.5 h, and carried out at room temperature (25 °C) for 2.5 h repeatedly for 10 cycles. Subsequently, in order to evaluate their homogeneity, some powders were scratched off from the top, middle and bottom parts of the cylinders to compare their mass loss in thermal gravimetric analysis (TGA) at 600 °C with a heating rate of 10 °C min⁻¹. In addition, the thermal conductivity of the samples was measured by a short light pulse flash method [37]. In brief, the sample was processed into 10 × 10 × 1 mm and kept at an established constant temperature until thermal equilibrium. Then an energy pulse was passed at one side of the sample using a Hyperflash analyzer (LFA 447), and the temperature rise on the other side was measured with the help of a mercury cadmium telluride (HgCdTe) IR detector.

The PA leakage phenomenon was evaluated by a mass loss test as follows: An oven (Dongguan A-PEX Test Equipment Co., Ltd.) was used to simulate the working temperature of 55 and 60 °C, respectively. Then all CPCPM-NS_x samples were processed into round cake shapes with a diameter of 43.5 mm and 5 mm high, and placed into the oven for 20 h. Filter paper was placed under the sample surface to adsorb the leaked PA. The mass losses of the samples were measured by a BSM320.3 electronic balance (Shanghai ZhuoJing Electronic Technology Co., Ltd., accuracy ± 0.001 g) at every 1.5 h.

3. Experimental setup

3.1. Preparation of the battery module and the connection of the experimental system

Fig. 2a shows the preparation of the CPCPM-NS_x based battery module as well as the schematic diagram of the experimental system. First, 6 holes with a diameter of 18.5 mm were drilled on the CPCPM-NS_x using a milling machine, in which 6 commercial 18,650 Lithium-ion power batteries with a capacity of 2 Ah were placed. Then, all of the cells were connected in 1S × 6P configuration (one cell in series and six strings in parallel) by a laser spot welding machine (Fig. 2b). Finally, the battery module was charged/discharged using a BTS-5V30A-NTF battery testing system (Shenzhen Neware Electronic Co., Ltd. China) with an accuracy of ± 0.01%. 2 T-type thermocouples (TC-TFF of 2 × 0.25 × 1000 mm, accuracy of ± 0.1 °C, USA) were mounted on the surface center of two cells in the battery module and connected to an Agilent 34970A Data Acquisition (Keysight Technologies, Inc.).

3.2. Design of the experimental platform for volume changes phenomenon

Volume changes are inevitable phenomenon for most materials during temperature and phase change. Here we propose an experimental setup utilizing the optical diffraction principle to demonstrate the volumetric expansion visually. The schematic diagram of the experimental platform is shown in Fig. 3. A torch (BK-D09-5W-LED, Ningbo Sunlight Electronics Co., Ltd) was used as the light source and placed 80 mm from the top surface of the modules. A cardboard was placed 60 mm from the bottom surface of the modules. The diffractive aperture from the gap between the batteries and CPCPMs is presented on the cardboard while volumetric expansion occurs. In order to simulate the actual application environment, the tests were performed at different temperatures of 25, 35, 45 and 50 °C, respectively.

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