

Thermal Management of Lithium-ion Batteries at Low Temperature Based on Composite Phase Change Material

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ABSTRACT

The operating performance of lithium-ion batteries will degrade in extremely cold environments. A thermal management system for cold temperatures to make the lithium-ion batteries work in a reasonable temperature range is significant. This paper proposes a low-temperature battery thermal management system based on composite phase change material that preheats batteries quickly under cold environments with heating effect. The chosen CPCM of paraffin (82 wt%), graphite (15 wt%) and electrolytic copper powder (3 wt%) has the leakage rate of 4.43 %, the thermal conductivity of 6.256 W/(m·k), the latent heat of solidification of 152.68 J/g, the latent heat of melting of 164.77 J/g, and at -30 °C the electrical conductivity of 0.357 S/cm. Under the preheating effect of the CPCM, Lithium-ion battery can discharge at -30 °C with a small current. Furthermore, the CPCM rapidly heats up the single battery from -20 °C to 10 °C after the current flows through it, a process that consumed only 258 s (1 C) and 189 s (2 C), and the maximum temperature difference between the various parts of the battery is 4.2 °C and 4.8 °C, respectively. The results of the battery preheating test show that the chosen CPCM has good heating capacity, thermal uniformity and thermal conversion efficiency.

Keywords: lithium-ion battery, composite phase change material, self-preheating, thermal conversion efficiency, low-temperature battery thermal management

NONMENCLATURE

Abbreviations

LIBs	Lithium-ion Batteries
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BTMS	Battery Thermal Management System
CPCM	Composite Phase Change Material
EG	Expanded Graphite
<i>Symbols</i>	
s	Second

1. INTRODUCTION

With the advantages of high energy density, long lifespan, low self-discharge rate, and good cycle stability, lithium-ion batteries (LIBs) have taken over as the primary power source for electric vehicles and energy storage devices [1]. However, in order to function with excellent performance and maximum safety, the temperature-sensitive LIBs need a precise thermal temperature between 15 and 40 °C [2]. Operating lithium-ion batteries outside of this temperature range will damage batteries, especially at temperatures below 5 °C [3]. Low temperature conditions not only affect battery performance, such as discharge failure and decreasing lifespan [4]. Therefore, establishing a well-designed battery thermal management system (BTMs) at low temperatures is crucial for improving battery performance and preventing the occurrence of risky accidents.

Low-temperature preheating strategies include internal and external heating methods. Among them, internal heating is a heating method that preheats the battery by generating heat directly from inside the battery through a series of operations. Wang et al [5] proposed a self-heating lithium-ion battery structure. A nickel foil with two lugs is embedded into the Li-ion battery to generate ohmic heat for battery heating. Zhang et al [6] proposed a lumped energy conservation

model to predict the temperature rise rate of the AC preheating method. Zhu et al [7] found that the rate of temperature rise of the battery is determined by the combination of current amplitude, frequency and limiting voltage when pulse heating method is used. The internal heating method can quickly and uniformly heat from inside the battery with a higher rate of warming. however, internal heating accelerates battery aging which increases the safety risk of the battery pack. Therefore, research on low-temperature heating strategies mainly focuses on safer external heating methods [8]. Jin et al [9] found that the temperature rise rate could reach 0.35 °C/min when using PTC to preheat the battery. Song et al [10] analysed the economics of battery heating operation of a hybrid energy storage system (HESS) at low temperatures. The traditional external heating method often requires a additional heat source to bring the battery temperature back to the appropriate operating temperature zone, which makes the structure of the external heating system more complex and results in higher energy consumption [11]. Recently, the external heating method using phase change materials has attracted much attention due to the lack of extra energy input and simple structure. However, the high leakage rate and low thermal conductivity of phase change materials have hindered the promotion and application of this method. In this study, a low-temperature battery thermal management system based on composite phase change material of paraffin (82 wt%), graphite (15 wt%) and electrolytic copper powder (3 wt%) was proposed. The system leverages the current released by the battery for preheating without requiring an extra energy supply. The low-cost and simple structure design not only maintains the temperature of the battery within a reasonable range, but also improves the environmental adaptability and application scenarios of BTMS.

2. EXPERIMENTAL SECTION

2.1 Preparation of CPCMs

The CPCM was prepared via the melt-blending method. First, pure paraffin (Henan Shenyu Star Sky Technology Co., Ltd., China) was melted into a liquid state in an 80 °C water bath. Then the liquid paraffin was decanted into a beaker containing electrolytic copper powder (Shenzhen Tianpu Biotechnology Co., Ltd., China), and a magnetic stirrer (MSH-R-03P, Hangzhou Qiulai Technology Co., Ltd., China) was used at 80 °C and 800 rad/min for 30 min to ensure an even mixing of the

two fractions. The molten mixture was added to expanded graphite (EG, Qingdao Yanhai Carbon Materials Co., Ltd., China), followed by stirring manually for 10 min. EG skeleton and electrolytic copper powder ensure that the CPCM has a low leakage rate, good thermal and electrical conductivity. When the CPCM was cooled down, it was reheated in a vacuum oven for 30 min at 80 °C to melt the CPCM, and then stirred for another 10 min. This procedure was repeated six times, and finally the CPCM was poured into the mould to cool. In order to study the influence of additives on the properties of phase change materials, and to find a preheating medium with better performance, different CPCMs were obtained by adjusting the amount of EG and electrolytic copper powder added, as shown in Table 1. The CPCM used in the preheating experiment of LIBs is sample 8 with a total weight of 40 kg.

Table 1 Mass Fractions of Components in CPCMs

Sample	Paraffin (wt%)	EG (wt%)	Electrolytic Copper powder (wt%)
1	90	10	0
2	89	10	1
3	88	10	2
4	87	10	3
5	85	15	0
6	84	15	1
7	83	15	2
8	82	15	3
9	80	20	0
10	79	20	1
11	78	20	2
12	77	20	3

2.2 Characterization of CPCMs

2.2.1 Leakage testing of CPCMs

Each sample (0.2 mg) was moulded in the grinding tool of a powder tablet press (BJ-15, Tianjin powder tablet press, China) at 5 MPa pressure for 5 minutes. After weighing each sample with an electronic balance (FA1004EN, Changzhou Lucky Electronic Equipment Co., Ltd., China), they were placed on different weighing papers one after another and dried for 3 hours in a vacuum drying oven (DZF-6020AF, Shanghai Qixin Scientific Instrument Co., Ltd., China) at 60 °C. Then, each sample was weighed again. The poor quality of the sample before and after drying is the leakage of the CPCM [12]. The leakage rate is determined via

$$S = \frac{M - M_1}{M} \quad (1)$$

Where S is leakage rate, M is the original mass, and M_1 is mass of sample remaining after leakage.

2.2.2 Thermal properties of CPCM

The diameter and height of each sample were obtained through using a vernier caliper (DL91150, Ningbo Deli Tool Co., Ltd., China). The thermal properties of each sample, including the phase transition point, latent heat and specific heat were measured by a low-temperature differential scanning calorimeter. a laser thermal conductivity analyzer (LFA467HT, Netzsch. Ltd, China) was applied to each sample for obtaining its thermal diffusion coefficient. The thermal conductivity of each sample is determined via

$$\lambda = a\rho c \quad (2)$$

Where λ is thermal conductivity, a is thermal diffusion coefficient and c is specific heat.

2.2.3 Electrical conductivity of CPCM

An appropriate amount of CPCM was ground into a cylindrical shape. The diameter and height of each sample were measured with a vernier caliper, and two 40×30 mm rectangular copper plates were adhered to the upper and lower surfaces of the cylindrical CPCM by copper conductive adhesive (DB2011, Hubei Shuangjian Fine Chemical Co., Ltd., China). Thermocouples were sequentially inserted in the cylinders of CPCM. The two copper electrode plates were connected to the charge and discharge tester through wires to provide a constant current, and then the cylinders of CPCM were placed in a constant temperature box (TX-3T-125F, Dongguan Giant Pressure Testing Equipm-ent Co., Ltd., China) to obtain the electrical conductivity of each sample within the temperature range of 5 °C interval from -30 °C to 20 °C, and the electrical conductivity is calculated via

$$\sigma = \frac{IL}{US} \quad (3)$$

Where σ is electrical conductivity of CPCM, I is the input current value, L is height of the cylindrical CPCM, U is input voltage and S is cross-sectional area of the cylindrical CPCM.

2.3 Experimental designs of the battery with CPCM

2.3.1 Construction of battery experimental system

The parameters of the 18650 battery (NCR18650B, Panasonic) used in the battery preheating experimental system are shown in Table 2.

Table 2 Specific Parameters of 18650 Battery

Parameters	Value
Size (mm)	18x65
Weight (g)	47.3
Nominal capacity (mA · h)	3400
Charging cut-off voltage (V)	4.2
Discharge cut-off voltage (V)	2.5
Charging temperature (°C)	10-45
Discharge temperature (°C)	-20-60

The battery experimental system consists of two groups: One is the experimental group wrapped in phase change materials (Figure 1 (a)), and the other is the control group directly exposed to the environment (Figure 1 (b)). Three thermocouples were distributed radially on the surfaces of two sets of batteries. The experimental group was sealed in a cylindrical container, with a height of 6.2 cm and a diameter of 4 cm. The container was filled with CPCM, and the gaps at the external connections of the container were sealed with high thermal conductive silicone. The experimental group and control group batteries were placed on a 4-wire battery bracket in a constant temperature box, and they were respectively connected to the Xinwei charging and discharging tester (5V100A-NTFA, Shenzhen Xinwei Electronics Co., Ltd., China). The battery experimental system, including experimental group and control group is shown in Figure 1 (c).

2.3.2 Preheating experiment of LIBs

To study the preheating performance of CPCM, low-temperature preheating experiment of LIBs were conducted under different operating conditions. The preheating target was set at 10 °C, with initial ambient temperatures of -30 °C and -20 °C, and discharge rates of 1 C and 2 C, respectively. The physical diagram of the circuit connection is shown in Figure 2 (a), equivalent circuit is shown in Figure 2(b).

The positive wire of the charging and discharging tester is connected to the positive pole of the battery, the negative wire of the battery is connected to one of the two copper strips inserted into the CPCM, and the circuit is led out from the other copper strip and connected back to the negative pole of the charging and discharging tester. A switch is added between the two copper strips.

In the preparation stage, the charge and discharge tester is set to the charging mode, the switch is closed, experimental group battery is charged to full capacity.

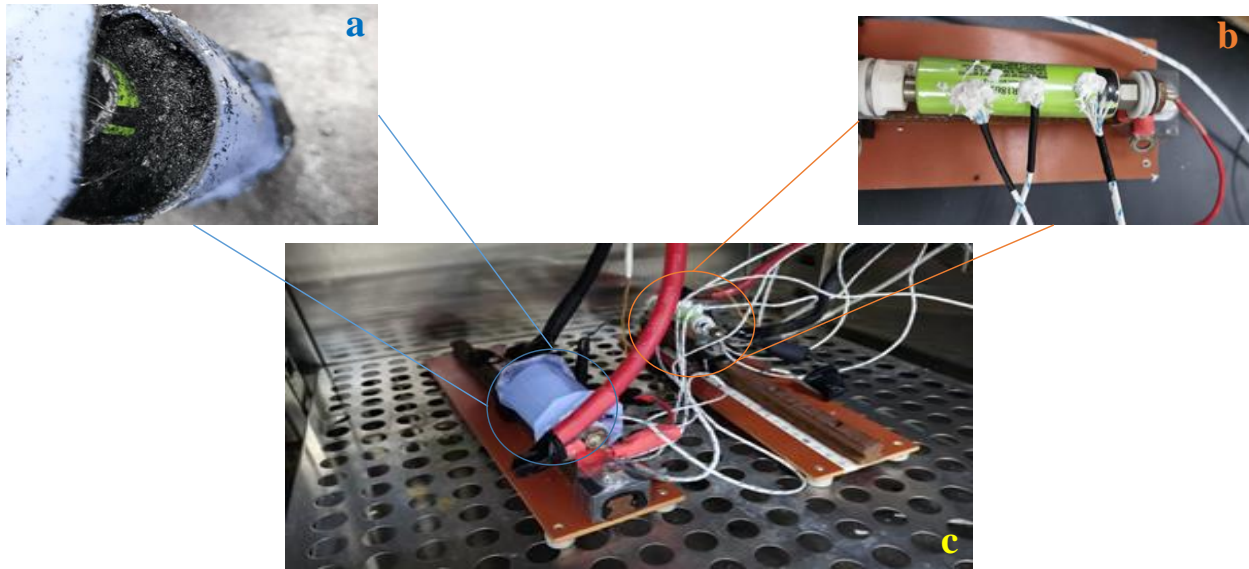


Fig. 1. Electrical conductivity test of the CPCM

The ambient temperature is adjusted to the low-temperature test condition and the battery and CPCM are sufficiently cooled. During the test phase, the charge and discharge tester is set to discharge mode, the switch is opened, the battery current flows through the CPCM to generate Joule heat, so that the battery is rapidly warmed up to the appropriate temperature range, when the battery temperature reaches 10 °C, the switch is closed, and the battery continues to discharge until the end of the preheating experiment. The temperature of the batteries was recorded. Battery retention capacity is defined as the gap between total battery capacity and the capacity battery used in the preheating process of the CPCM. Total battery capacity is characterized as

$$C = I \cdot t \quad (4)$$

Where C is total battery capacity, I is discharge current, t is discharge time.

3. RESULTS AND DISCUSSION

3.1 Characterization analysis of the CPCM

3.1.1 Leakage resistance of the CPCM

As shown in Figure 3, EG and electrolytic copper powder have a significant inhibitory effect on the leakage rate of CPCM. This is due to the excellent supporting effect of graphite. Meanwhile, due to the inability of copper powder to melt at 80 °C, the flowability of the CPCM is further reduced, resulting in the inability of paraffin to flow out of the CPCM even if it melts. When the mass fraction of graphite is 15% and the mass

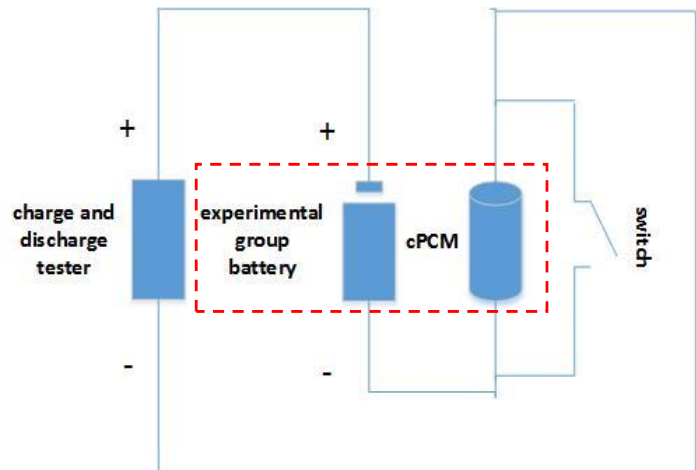
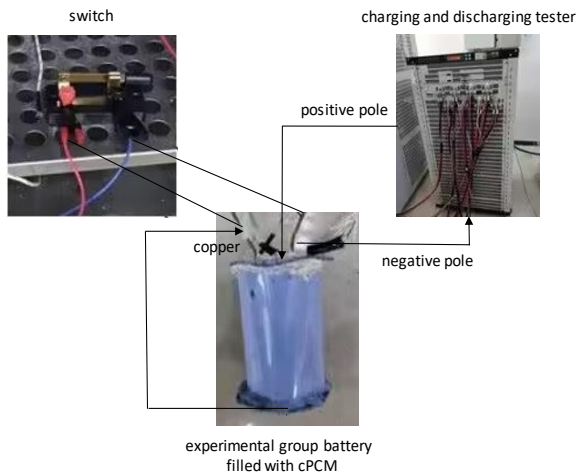


Fig. 2. Low temperature preheating experiment circuit diagram

fraction of electrolytic copper powder is 3 %, that is, starting from group 8, the leakage rate of the material starts to be lower than 5%. Therefore, the CPCMs from sample 8 to sample 12 can be considered that the material is basically fixed.

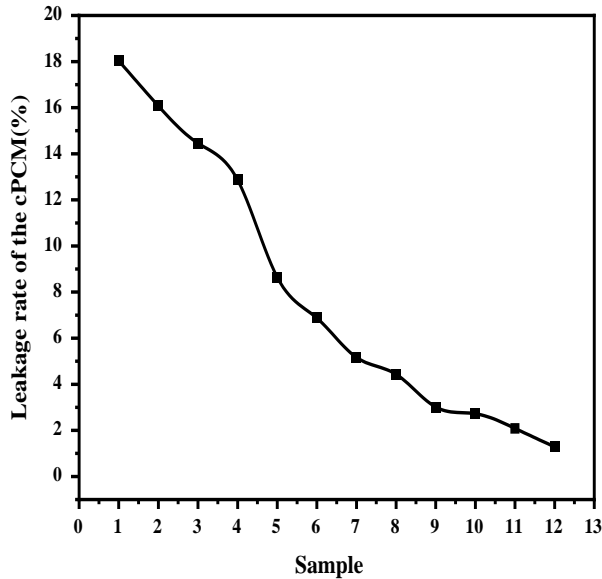


Fig.3. Leakage rate trend of CPCMs

3.1.2 Thermal properties of the CPCMs

As shown in Table 3, the thermal properties of each sample, including phase change temperature, melting point, and thermal conductivity that are significant to the working performance of battery thermal management were compared.

When the mass fraction of EG is 10%, paraffin cannot fully enter the porous structure of EG. The addition of electrolytic copper powder further reduces the uniformity of the CPCMs. During the pressing process, some paraffin is squeezed to the periphery of the sample, and the thermal conductivity decreases with the increase of the mass fraction of electrolytic copper powder. When the mass fraction of EG is 15%, paraffin, EG and electrolytic copper powder can be mixed evenly. The addition of electrolytic copper powder increases the thermal conductivity of the CPCMs. When the mass fraction of EG is 20%, due to the high mass fraction of EG, there are many voids formed in the process of moulding. Air enters the voids, resulting in a decrease in the thermal conductivity of CPCMs. The CPCMs with thermal conductivity exceeding 5.4 W/m·K are sample 5, sample 7 and sample 8. Additionally, the latent heat of solidification decreases with the reduction of paraffin content.

Table 3 Thermal Properties of the CPCMs with different additive

Smample	Thermal conductivity (W/m·k)	Melting point (°C)	Latent heat (J/g)
1	3.034	34.94	178.95
2	2.773	35.02	174.33
3	2.409	35.02	172.54
4	2.421	34.89	171.66
5	5.337	34.81	168.77
6	5.509	34.75	167.66
7	5.73	34.76	165.48
8	6.256	34.81	164.77
9	5.32	34.65	155.89
10	4.985	34.72	152.82
11	4.696	34.71	153.09
12	5.102	34.67	150.99
13*	0.208	35.43	203.84

Note: sample 13* was pure paraffin.

3.1.3 Electrical properties of the CPCMs

As shown in Figure 4, the electrical conductivity of each sample was compared. Based on the experimental result that the voltage applied to the paraffin reaches around 6.5V and there is still no obvious current, the paraffin can be approximately regarded as an insulator. The addition of graphite can not only serve as a support material, but also increase the thermal and electrical conductivity of paraffin. The presence of electrolytic copper powder makes the overall conductivity of the CPCMs even better.

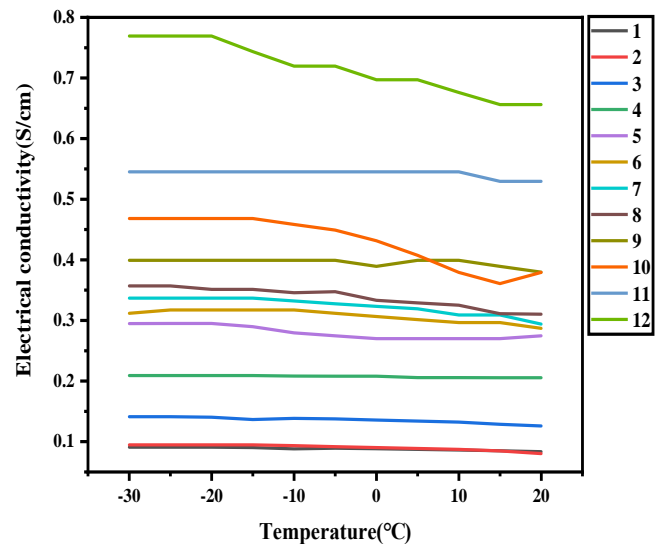


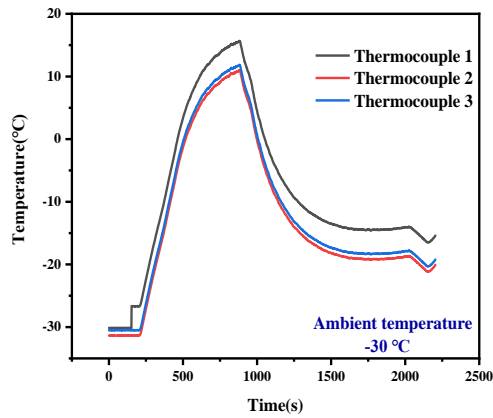
Fig.4. Electrical conductivity trend of CPCMs

3.2 Preheating performance of CPCMs toward battery

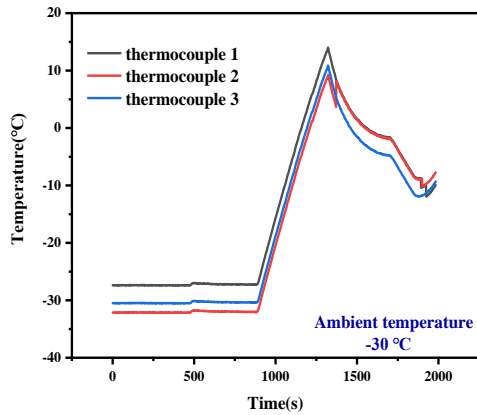
3.2.1 Preheating effect of CPCM at -30 °C

It is difficult to maintain the discharge process of the control group battery at both 1 C and 2 C discharge rates in an environment of -30 °C, and experimental data of the control group battery under -30 °C operating conditions cannot be obtained. The initial current of experimental group battery cannot reach the set current value at both 1 C and 2 C discharge rates. After the temperature of the CPCM rises, it in turn heats the battery. After the working temperature of the battery rises, it allows the battery to discharge with set current value until the remaining capacity of the battery approaches zero. The experimental group battery has a discharge time of about 30 minutes at 1 C discharge rate and about 17 minutes at 2 C discharge rate.

As shown in Figure 5 (a) and Figure 5 (b), during preheating process from -30 °C to 20 °C, the maximum temperature difference of battery parts is 4.7 °C (1 C) and 3.6 °C (2 C). At a discharge rate of 1C, it takes 458 s for the battery to reach the preset temperature (10 °C). At a discharge rate of 2 C, the preheating time is 409 s.



(a) Experimental group battery (1 C)



(b) Experimental group battery (2 C)

Fig. 5. The trend of battery temperature over time at -30 °C

3.2.2 Preheating effect of CPCM at -20 °C

The total battery capacity is closely related to temperature, the lower the temperature, the less the total capacity of battery. By comparing the total battery capacity of the control group under different discharge rates at -20 °C, it is shown that the discharge rate will affect the total battery capacity deeply under low temperature, and the discharge rate is negatively correlated with the total battery capacity. Meanwhile, although part of the battery energy is used for preheating at -20 °C, the battery retention capacity of the experimental group is still higher than that of the control group, just as shown in Table 4. Therefore, the existence of CPCM can not only help the battery to warm up quickly and reach the appropriate working temperature to protect the battery, but also make the battery work longer.

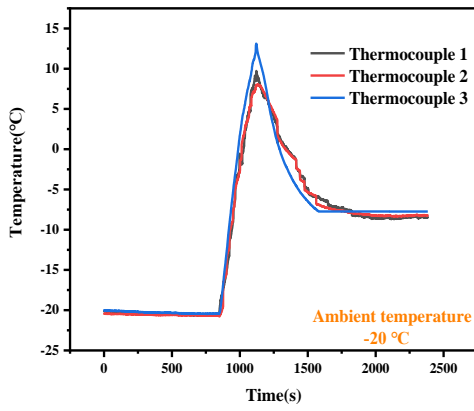
Table 4 Comparison of battery capacity

Group	discharging rate(C)	total battery capacity(A·h)	battery retention capacity (A·h)
control group	1	1.9006	—
	2	1.2712	—
experimental group	1	2.1070	1.9074
	2	1.4395	1.2853

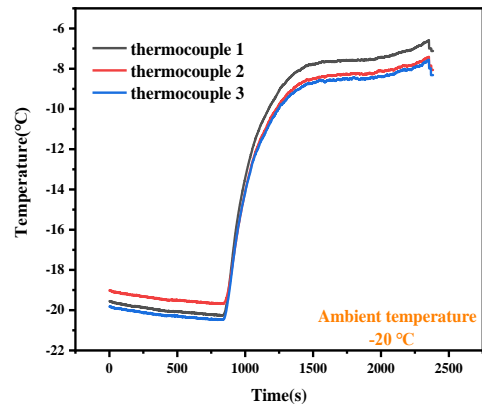
As shown in Figure 6 (b) and Figure 6 (d), at the ambient temperature of -20 °C, the control group battery is difficult to heat up to the optimal temperature range at both 1 C and 2 C discharge rates. On the contrary, as shown in Figure 6 (a) and Figure 6 (c), the CPCM rapidly heats up the experimental group battery to a suitable operating temperature after the current flows through it, a process that consumed only 258 s (1 C) and 189 s (2 C). And the maximum temperature difference of battery parts is 4.2 °C (1 C) and 4.8 °C (2 C), which are not more than 5 °C. This indicates that the CPCM has high efficiency of electrothermal conversion and good thermal uniformity.

4. CONCLUSION

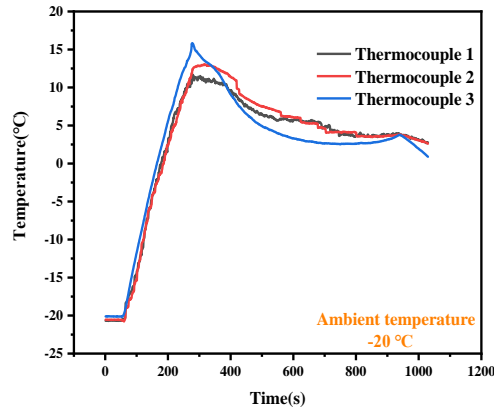
A low-temperature thermal management system for LIBs based on CPCM was proposed. CPCM consisting of different mass fractions of paraffin, EG and electrolytic copper powder were prepared. The effects of component content on the leakage rate, thermal conductivity, latent heat and electrical conductivity of CPCM were studied, and the preheating effect of the



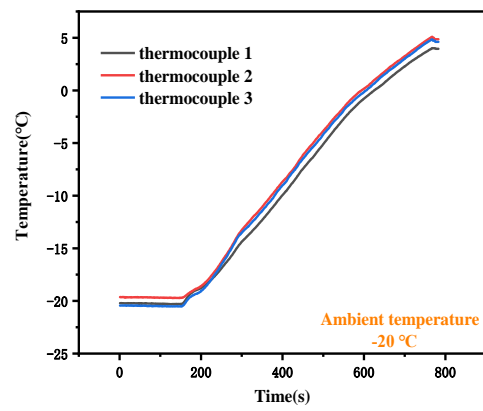
(a) Experimental group battery (1 C)



(b) Control group battery (1 C)



(c) Experimental group battery (2 C)



(d) Control group battery (2 C)

Fig. 6. The trend of battery temperature over time at -20 °C

CPCMs on LIBs in a cold environment was investigated. The results show that the selected CPCMs of 82 wt% paraffin, 15 wt% graphite and 3 wt% electrolytic copper powder have a leakage rate of 4.43%, thermal conductivity of 6.256 W/(m·k), latent heat of 152.68 J/g, latent heat of melting of 164.77 J/g, and at -30 °C electrical conductivity of 0.357 S/cm. Under the heating effect of the CPCMs, the battery that could not operate at -30 °C can discharge with a small current, and when the temperature of the CPCMs rises, the battery can discharge normally. At an ambient temperature of -20 °C, the temperature rise rate of experimental batteries was much higher than that of control batteries. Although part of the battery energy flows into the CPCMs, the battery retention capacity of experimental group is higher than the total battery capacity of control group after the preheating process stops. The presence of the CPCMs not only brings the battery to the appropriate operating temperature quickly, but also prolongs the operating time of the batteries.

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