Thermal Conductive Materials for Lithium-Ion Batteries

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Abstract. As part of the development of energy, battery storage systems have emerged recently; however, large-scale applications of lithium-ion batteries have shown problems with heat management and safety. A high-thermal-conductivity material is added to the cooling system of the battery to extend the service life of the equipment and ensure stable, safe operation. This paper compiles available data and analyses the reasons for heat generation in lithium-ion batteries. It compares and contrasts the features of the three kinds of thermal management materials: metal-based, carbon-based and phase-change materials. Metal-based materials have good thermal conductivity and high mechanical strength, but they are relatively heavy; carbon-based materials are light and corrosion-resistant, but their thermal conductivity is anisotropic; phase-change materials absorb heat through latent heat and have the advantage of temperature regulation, but their continuous heat dissipation capacity is limited. The article introduces the current technical bottlenecks of all kinds of materials, forecasts the future development direction of thermal management materials, and concludes that future materials will be customised to some extent. This paper review and analyse battery thermal management materials to provide a basic reference for selecting materials in battery thermal management technology, promote the development of energy storage technology, and support the transition to a low-carbon energy system.

Keywords: Lithium-ion batteries, thermal conductivity materials, heat management.

1. Introduction

With the rapid development of science and technology around the world in recent years, people's living and working conditions have improved, and thus their demand for energy has been steadily rising. Fossil fuels are still used as the main source of energy in the world today, but they are finite resources. Energy and Environment Problems: To promote carbon neutrality, many countries have started to change their energy systems. Lithium-ion batteries are necessary energy-storage components that are now used widely in new-energy vehicles, electronics and grid-scale storage. At the same time, researchers have also begun to focus more and more attention on the heat dissipation and safety problems associated with large-scale applications of lithium batteries [1].

However, after multiple charge-discharge cycles, a large amount of heat is generated by the battery; thus, it will age prematurely and may be in danger of fire or explosion under certain circumstances. Therefore, the problems of safety and service life for lithium batteries need to be solved by researchers. Among them, thermal conductive materials serve as the core medium to fill the battery cells and are responsible for conducting heat transfer in the whole thermal management system. Therefore, to promote the continuous development of the new-energy era and advance society, researchers need to study the performance characteristics of these materials and optimize operating paths [2].

In recent years, many studies have been carried out by domestic and foreign scholars on thermal-conducting materials for lithium-ion batteries. Some researchers have studied carbon-based composites, such as graphene and carbon nanotubes, and enhanced their thermal conductivity by altering the microstructure [3]. A large number of studies have also been conducted to improve the performance and reduce the cost of metal-based and phase-change thermal materials for practical engineering applications in power batteries [4].

The primary research content of this paper will be thermal conductive materials for lithium-ion batteries. First, it will introduce the heat generation mechanism in lithium batteries and the working principle of interface thermal materials. Then, it will classify and analyze the definitions, advantages and disadvantages, and applications of the three main materials in recent years (metal-based materials,

carbon-based materials, and phase-change materials). Finally, it will introduce the current development bottlenecks of these materials and explore the future development direction of thermal-conductive materials.

2. Causes of Lithium Battery Heating

The heat generated during the charging and discharging of lithium batteries can be divided into three main types: reaction heat, polarization heat, and side reaction heat. The first type is electrochemical reaction heat. Heat here refers to the heat absorbed or released at the electrode interface in electrochemical systems like fuel cells or energy storage batteries due to redox reactions. It's mainly divided into two parts: reversible heat, which comes from the entropy change during the electrochemical reaction and shows up as heat absorption when charging and heat release when discharging (or vice versa), following the second law of thermodynamics; and irreversible heat, which comes from battery polarization and internal resistance, showing up as heat generation both during charging and discharging [5].

The second type is polarization heat. This is the irreversible heat generated during charging and discharging of a battery due to internal polarization that moves the system away from thermodynamic equilibrium. It's mainly caused by electrochemical polarization and concentration polarization, which can hinder the movement of ions or electrons. During the process of lithium ions passing through electrodes, electrolytes, and separators, resistance occurs, leading to concentration and electrochemical polarization. This forces the battery to produce extra polarization voltage, and the electrical energy gets dissipated as heat.

The third type falls under side reaction heat, mainly referring to the energy (heat) absorbed or released during chemical production or electrochemical energy storage when side reactions occur. It's also a major trigger for safety hazards. When the battery temperature is too high, side reactions like electrolyte decomposition, secondary growth of the SEI film, dissolution of positive electrode metal ions, and lithium plating on the negative electrode happen one after another, causing the heat release rate to rise even more. Once the heat builds up faster than it can dissipate, thermal runaway can occur, potentially leading to swelling, fires, or even explosions [6].

In order to prevent heat buildup and keep the battery operating within a safe temperature range, thermal materials are required to construct efficient heat conduction channels to transfer the heat stored in battery cells outward. This article will analyze the three main types of thermal materials currently available.

3. The Pros and Cons of Different Heat-Conducting Materials

Analysis of how heat is generated in lithium batteries and what safety problems arise from the accumulation of heat have shown that thermally conductive materials need to be added to the cooling system of the battery. Researchers have developed a large number of thermal-conductive materials to meet the demand for cooling, and the basic properties of these different kinds of materials vary significantly. First, the strengths and weaknesses of the materials are known to determine whether they are suitable for R&D and application. This paper will present them one by one in the order of metal-based materials, carbon-based materials and phase-change materials.

3.1. Metal-Based Materials

Metal-based thermal materials use base metals such as copper, aluminum or silver, or metal alloys such as aluminum alloy and copper alloy. Some are modified with ceramic fillers for performance improvement. Hard cooling components such as heat sink housings, fins, heat spreaders and heat pipes can be made from them; metal-filled thermal pads and thermal gels can also be prepared to fill small gaps in the assembly [7].

Among the many strengths of metal materials, the first is their excellent thermal conductivity. Silver, copper and aluminum are some materials with relatively high room-temperature thermal conductivities for non-metal materials, at 429, 401 and 237 W/(m·K) respectively. Metals have good mechanical properties and are not easily deformed; therefore, they can be used to conduct heat and protect against damage simultaneously. Given the current high-end metal-processing technology, it is now economically viable to meet the large-scale production requirements of assembly lines [8].

Metal materials also have some deficiencies at the same time. They generally have a relatively high density, such as copper at 8.96 g/cm³. If a considerable number are used, the total weight of the batteries will be relatively high. Metals are also highly conductive; therefore, if there is a defect in the insulation design of the packaging, a short circuit will occur. This means an insulating layer needs to be added at the top, and this will increase the workload for production. At the same time, aluminum and copper are susceptible to electrochemical corrosion in humid or salty environments, so their service life is shortened; silver has excellent thermal conductivity, but it is too expensive to be economically feasible for most small electronic devices and is therefore not widely used.

Aluminum alloy is used in many places in the upper and lower sections of power battery packs and water-cooling plates for new-energy vehicles. It can transfer heat from the battery cells to the water-cooling circuit, and at present, car manufacturers use it most often for heat conduction. Ultra-thin copper foil and heat pipes are used to cool the small built-in lithium batteries in phones and laptops in the consumer electronics industry. Aluminum alloy cooling frames are employed at the power station for energy storage to arrange large-scale energy storage battery packs. Given that the material of metals is good in all respects, it is suitable for meeting the operating requirements of many places [9].

3.2. Carbon-Based Materials

The basic material of Carbon-based thermal materials is carbon. At present, the popular types in industry and research include graphene, carbon nanotubes, natural graphite, artificial graphite and graphite films. They can be used to make flexible graphite cooling films independently or incorporated as fillers in a polymer matrix to produce thermal silicone or thermal resin composites [10].

Carbon materials are generally poor conductors of heat and exhibit strong anisotropy in heat conduction. Graphite has a thermal conductivity of less than 10 W/(m·K) perpendicular to the layers; therefore, heat transfer in the direction of thickness is relatively weak. Therefore, they are less suitable for vertical heat dissipation. Scaling up high-quality single-layer graphene or well-structured carbon nanotubes is also difficult, the finished products often have defects, and their prices fluctuate widely. Carbon itself is conductive, so if the filler content is too high, the insulation performance of the composite will be affected, and therefore insulation modification is required. Ultra-thin graphite films are also more easily scratched and worn, and damage can occur during assembly; therefore, a strict requirement has been placed on the assembly process [11].

The first applications of carbon-based materials in daily life are portable electronic devices. The surface of lithium-ion batteries in mobile phones and tablets generally has an added graphite film for heat dissipation. For power batteries of new energy vehicles, modified graphene and carbon nanotube fillers are added to thermal pads and thermal adhesives to fill the gaps between battery cells and water-cooling plates. Graphene-composite coatings can be applied to increase the heat-dissipation capability of high-end aerospace energy storage batteries. Due to the limitation of vertical thermal conductivity, carbon-based materials are generally used for planar heat dissipation and, in conjunction with metal water-cooling plates, the deficiency in heat conduction in the thickness direction can be compensated for.

3.3. Phase Change Material

Phase Change Materials (PCM) are materials that can absorb or release a large amount of latent heat during a phase transition (such as melting from solid to liquid) at a specific temperature to store

energy and then release it as heat when needed. The thermal-conducting materials are based on the latent heat of phase transition for temperature regulation. When the temperature of the battery cell reaches the start point for phase change, it will turn into a liquid and absorb excess heat to limit the rise in temperature. With a drop in temperature, the material will harden and discharge heat to keep the temperature of the battery stable. Common subcategories include paraffin-based organic phase-change materials, salt-based inorganic phase-change materials, and composite shaped phase-change materials; generally speaking, these are encapsulated and shaped with foam copper or graphite frameworks in daily life [12].

PCM is a Material with good temperature-regulation properties. Compared with the two types of traditional materials that rely on heat conduction for cooling, these can store peak heat and are therefore very suitable for temperature regulation under a short-term high-heat-load, such as fast charging or a high-temperature environment. Paraffin-type organic-phase change materials do not exhibit considerable supercooling. It has good chemical stability and low corrosion; the shaped composite phase-change material is also quite flexible and can fit the gaps in the battery module. It does not require external power components, such as pumps or fans, during operation, and a passive cooling system reduces the risk of a cooling system failure.

However, it is relatively low in terms of advantages and has a low thermal conductivity of about 0.2-0.3 W/(m·K). Paraffin alone has poor heat transfer characteristics; therefore, to enhance the rate at which accumulated heat is released, metal foams and carbon fillers are often added. Paraffin is easily melted when heated, and a loose seal will cause leakage and contamination of the battery cells. After many times of phase change, the material may have aged and its latent heat has decreased; thus, long-term stability still needs to be enhanced. Furthermore, inorganic hydrated salt phase-change materials have a relatively large degree of supercooling and are more prone to phase separation; thus, it is difficult to fine-tune their formulas. Therefore, there is a limit to how much heat it can store, and when the heating is on for a long time, the storage will become saturated, causing a significant drop in temperature control afterwards [13].

Often, in areas without air conditioning, phase-change materials are employed for portable outdoor energy storage and small-scale cold-weather battery applications to help regulate the temperature fluctuations of a day and night. Power batteries for new energy vehicles use a phase-change material and a water-cooling system to regulate a short-term temperature increase during high-speed charging or climbing. Special Energy Storage Batteries in extreme environments, such as at the poles or in deserts, also frequently employ phase-change temperature-control devices. Pure-phase change cooling is not commonly applied by itself at present. In general, a layer of phase-change material is added to a metal heat-dissipation structure to store heat and regulate the temperature by means of continuous thermal conduction.

4. Outlook and Challenges of Thermal Conductive Materials

In the future, it is expected that thermal conductive materials will be more composite and customized. The technology will be more advanced, and a larger number of materials will be available. Improve the performance of the current material to reduce costs and increase the yield of the product. Over time, thermal-conductive materials will also be used to build high-power, fast-charging batteries, thus expanding the performance range of thermal management for power batteries. Carry out composite design research by combining the longitudinal thermal conductivity of metal materials, the in-plane thermal conductivity of carbon-based materials, and the heat storage and constant-temperature characteristics of phase-change materials to build a high-efficiency heat-conducting structure. In the future, passenger car batteries will concentrate on low-cost metals, consumer electronics will focus on lightweight carbon-based thermal films, and large-scale grid storage will concentrate on corrosion-resistant alloy heat-dissipation components. At the same time, the new technologies will also consider insulation, flame retardancy and corrosion resistance, and through experiments, adapt to different climates and charging/discharging intensities. Under the initiative to

achieve carbon neutrality, the expansion of the energy storage sector will enable the large-scale production of low-carbon thermal materials and promote the development of lithium-ion battery thermal management systems.

Metal-based materials have the problem of poor light-weighting and insulation simultaneously. With increasingly stringent range targets for future cars, there is little room left to reduce the weight of high-density metals, and the production yield of ultra-thin insulated coatings still needs to be improved. Carbon-based materials are anisotropic, and there are still technical difficulties in producing high-quality oriented graphene at a low cost and scale. Uneven Distribution of the filler will result in significant fluctuations in product performance. The two problems of phase-change materials are leakage prevention and extended life; otherwise, the encapsulation layer will be damaged by continuous vibration in a car. In addition, current power batteries are becoming larger in terms of cells and modules, and a single kind of thermal conductivity material cannot meet all the working requirements. Interfacial Thermal Resistance and the thermal expansion mismatch among materials, cells, separators and packaging adhesives may lead to a decline in performance over time. At the same time, strict automotive standards for flame retardancy and environmental protection have raised the requirements for optimizing material formulations.

In the future, the two directions of development for thermal conductive materials will be composition and directional adaptation. First, there will be designs that combine multiple stages, utilizing metals' excellent longitudinal thermal conductivity, carbon-based materials' outstanding in-plane thermal properties, and phase-change materials' heat storage and temperature-stabilisation functions to create multi-layer composite thermal structures. Next, we will start the particular and detailed development. Low-cost metals and phase-change composite systems are being used for passenger car batteries. Consumer electronics are all about ultra-thin, flexible carbon-based thermal films, and large-scale grid storage focuses on corrosion-resistant alloy heat dissipation components. At the same time, nano-modification and interface-treatment technologies can reduce the interface thermal resistance by balancing insulation, flame retardancy and corrosion resistance. Set up different climates and charging/discharging strengths in advance using a simulator. With the development of the energy storage industry under carbon neutrality, thermal materials will also need to use recycling processes for low-carbon mass production and further advance the maturity of lithium-ion battery thermal management systems.

5. Conclusion

This paper will systematically study the application features of three kinds of thermal-conductive materials—metal, carbon-based and phase-change materials—in the thermal management of lithium-ion batteries. Metal thermal conductive structures have a stable heat conduction rate and controllable production cost; thus, they are suitable for large-scale energy storage and conventional vehicle battery cooling. Carbon-based materials have good in-plane thermal conductivity, are light and thin, and are thus more suitable for consumer lithium battery devices with limited space. Phase-Change Materials can store heat to reduce temperature fluctuations during fast charging or in a high-temperature environment. Therefore, each material has its own strengths in certain environments, and by forming composite thermal systems with multiple materials, these strengths can be combined to meet the demands of various demanding conditions for lithium-ion battery operation. Therefore, the materials have different suitable uses and functions. Through technology, these materials can be used to make composite materials that combine the advantages of each. Composite materials possess complementary strengths and weaknesses across different categories, making them well-suited to satisfy the operational requirements of lithium-ion batteries. It is anticipated that thermally conductive materials will keep evolving in the near future via composite modification, lightweight design and improved adaptability. This paper mainly analyzes the performance characteristics, application scenarios and matching principles of three mainstream thermally conductive materials. The findings can assist enterprises in rapid preliminary material selection, and offer references for students and

novice researchers focusing on lithium-ion battery thermal management. To address the insufficient cross-comparison in existing literature, subsequent researchers may adopt the classification framework established in this work to further explore material modification and composite structure design, so as to continuously optimize thermal management solutions for lithium-ion batteries.

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