# Recent advances in energy storage materials: A nanoscale review

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## Abstract

The demand for scientific experts and entrepreneurs who can create novel materials with advanced properties - addressing important issues from energy to healthcare - and bring scientific discoveries to the commercial world is growing as a result of global challenges in climate, environment, healthcare, and the economy. Energy Storage Materials is an interdisciplinary field of materials and their devices for advanced energy storage and relevant energy conversion. This field is quite the need of the hour keeping in mind the depletion of fossil fuel reserves due to increase in demand for energy. This over utilisation of fossil fuels is threat to the environment causing global warming. The discontinuous supply of renewable sources like solar energy also necessitates the use of energy storage systems. Nanotechnology and material scientists have come forward to contribute to the field of energy storage. Phase change materials (PCMs) are the future when it comes to energy storage. Nanotechnology comes into play to develop energy storage materials of better energy storage density with improved thermophysical properties, and cycle life. When it comes to improve the properties of PCMs like thermal conductivity, leakage issue, enhancing melting and freezing rates, adding nanoparticles is the most widely accepted approach. Of all the type of nanoparticles, researchers are mostly interested in metal nanoparticles also evident from the huge amount of work that has already been carried out. This chapter discusses the different nanoparticles for the purpose and reviews some of the recent works on developing novel or improved energy storage materials.

**Keywords- PCM, energy storage, nanoparticles, thermal conductivity**

## 1. Introduction

The discovery, production, characterisation, modelling, and use of nanoscale materials are all included in the discipline of nanoscience and nanotechnology, which is a subfield of materials science. The ability of materials to change their characteristics as the size scale of their dimensions approaches the nanoscale is one of the most intriguing aspects of nanotechnology. The goal of the work done by materials scientists is to comprehend, manipulate, and develop novel uses for the nanostructures of well-known materials. Imagine assembling construction materials with the required composition and structure, atom by atom, layer by layer. We already do this using nanotechnology and materials science. Nanotechnology and materials science also can serve as a betterment for human society, one such growing interest for researchers is the field of phase change materials. One such field of increasing interest is a combination of nanotechnology and material science in the field of energy storage. Oil, natural gas, and other resources are becoming less plentiful; therefore, it is crucial to understand how to use resources wisely and effectively, and the need for fresh energy is the need of then hour. We need to employ renewable resources wisely to avoid an imbalance in the entire energy system, such as solar and wind energy.

Thermal energy storage technology is crucial in the face of a challenge during imbalance of supply and demand of energy at various times of the day. We might be able to solve the issue of significant energy variations using energy storage. When demand is less, it may store energy and when the demand is high it may give off the stored energy. Thermal energy storage may be compared to a regulator that keeps the energy equation in balance [1,2]. Latent heat storage, sensible heat storage, and reversible thermochemical reaction heat storage are the three types of heat storage. The usage of PCMs is crucial for this work's latent heat storage since it allows for the best utilisation of their capacity to absorb or release energy during phase changes. Compared to sensible heat storage materials, PCMs have a greater latent heat storage density. The phase change method, which has applications in a variety of industries, does not cause the temperature of PCMs to alter. The need for high-energy density or high-power density energy storage materials is always increasing, from mobile devices to the electrical grid. Materials with at least one nanometre-scale dimension have possibilities for improved energy storage, but there are also difficulties in terms of production and stability. Fatty acids and paraffin are two organic PCMs that are frequently employed to store latent heat. Additionally, organic PCMs offer a few benefits over inorganic ones, notably the fact that the impacts of corrosion and supercooling are minimal in the case of organic PCMs. However, the low heat conductivity of often employed organic PCMs prevents their widespread usage in Thermal energy Storage system (TES) applications. PCMs suffer from leakage as a result of the liquid phase's fluidity. Integrating and containing the liquid phase of PCM while maintaining system performance and reliability is a difficult design problem. This is when nanotechnology and materials science come in handy to tackle such problems. The reduction of organic PCM leakage and enhancement of thermal conductivity have previously been the subject of several investigations. The innovative form-stable PCMs (FSPCMs) have been prepared using a variety of approaches, including the melt impregnation method [3,4], vacuum impregnation method [5,6], melt adsorption compression method [7,8], etc., to avoid the leaking of molten PCMs. In recent years, a plethora of evaluations on the development of composite PCMs' research have been carried out. A thorough overview of the impact of porous media on the composite phase change behaviour and heat storage properties of composite PCMs was provided by Liu et al. [9]. The architectural synergy of structurally enhanced hybrid support composite PCMs was studied by Atinafu et al. [10]. The characteristics impacting the thermophysical performance of metal foam-based composite PCMs for thermal energy storage were reviewed by Aramesh and Shabani [11] This chapter reviews some of the works carried out by researchers in the nano level in the field of energy storage with the applications in some allied field.

## 2. Phase change material (PCM)

Phase change material (PCM) was first discovered in the early 1900s through the continued efforts of Alan Tower Waterman of Yale University. Waterman discovered several irregularities in the conductivity of molybdenite (MoS2) when researching the thermionic emission of various hot salts. It was discovered that the chalcogenide's conductivity may be gradually changed. Proper definition of

PCM may be “Phase change materials (PCMs) are substances that, while changing from a solid to a liquid or vice versa, absorb or release significant amounts of so-called latent heat.” When the PCMs transition from solid to liquid or from liquid to solid, respectively, heat is stored and retrieved. The temperature of PCMs first increases when heat is absorbed. In contrast to sensitive storage materials, the temperature of PCMs during heat absorption and release is nearly constant. The storage of heat and melting of the PCM is known as the charging process, while the release of heat and solidification of the PCM is known as the discharging phase since the PCMs are equivalent to a battery for a TES system. Compared to typical sensible storage materials, PCMs have 4–15 times the capacity to store heat per unit volume. PCMs are popular options for thermal energy storage due to their large latent heat capacity. From the literature, PCMs are of mainly three types, namely, organic, inorganic, and eutectic [12].

**Organic-**Without phase segregation, organic PCMs can undergo several cycles of melting and freezing. They do not corrode. Their latent melting heat degradation causes minimal supercooling throughout their crystallisation process. Organic PCM mostly come in two varieties:

1. **Paraffin wax-**The majority of paraffin waxes are mixers of straight n-alkane chains (CnH2n+2). The n-alkanes chain crystallisation releases a significant quantity of latent heat. Both the melting temperature and the latent heat of fusion rise as the chain length grows. Economic considerations, however, simply restrict the use of technical grade paraffin in Latent Heat Storage Systems (LHS). The benefits of paraffin include its dependability, predictability, affordability, non-corrosiveness, safety, and accessibility in a broader range of temperatures [12].
2. **Non-paraffin-**These PCMs come in a variety of types and have a wide range of different characteristics. Glycols, esters, alcohols, and several fatty acids are potential non-paraffin PCMs. High heat of fusion, low flashpoints, low stability at high temperatures, and limited thermal conductivity are all characteristics of these mater [12].

**Inorganic-**For solar applications requiring high temperatures, inorganic PCMs are preferable. However, they are difficult to maintain since they freeze at low temperatures and become difficult to handle at high temperature ranges. Their super-cooling is negligible, and cycling has little effect on the deterioration of melting enthalpies. They are mainly of the following two types:

1. **Salt hydrates-**They typically have the crystal structure ABnH2O, in which the salt undergoes a phase change by being alternately hydrated and dehydrated. Either a lower salt hydrate or anhydrous form of the substance melts. At the melting point, salt hydrate dissociates into anhydrous salt and water. All salt hydrates struggle with incongruent melting, which is brought on by the crystallization's inadequate water release, which does not completely dissolve all of the existing solid phases. Due to the difference in densities, the lower salt hydrate or its anhydrous form settles towards the bottom of the container.
2. **Metallic-**This category includes low melting-point metals and their alloys. They are seldom used in applications for heat storage because of their poor melting enthalpies. Low specific heat, low vapour pressure, high thermal conductivity, high volumetric heat of fusion, and low gravimetric heat of fusion are shared properties of metallic PCMs. They can meet the needs of power plants with greater capacities.

**Eutectic-**Eutectics are composites with two or more components. Organic-organic, inorganic-inorganic, or organic-inorganic are the three categories that they fall under. Each component undergoes a consistent phase transition, and a mixture of the component crystals is created during crystallisation. They have a higher latent heat capacity per volume than organic PCMs. The component is not separated since their melting and freezing are consistent.

## 3. Types of nonadditives/nanoparticles as supporting for commercially available PCMs

Nanoparticles are tiny (between 1 to 100 nm) and have a vast surface area. The performance of the phase-change material is enhanced by adding nano-scale additives to the phase-change material, which interact with the phase-change material and work in concert with the base liquid to alter its initial thermal characteristics. The physical characteristics of various nanoparticles and their proportions for performance enhancement vary. These sorts of nano-additives are the most common ones utilised to enhance phase change materials, namely, Metal nanomaterials, Metal oxide nanomaterials, Carbon-based nanomaterials [13]. Demirbas [14], Kenisarin ansd Mahakov [15], as well as other researchers have examined the thermophysical characteristics of various PCMs and associated topics. These investigations have demonstrated that a weakness of PCMs is their poor heat conductivity. Charging and discharge rates are impacted by low thermal conductivity. Incorporating highly conductive elements into the PCM to create a composite is a reasonable answer to this issue.

### 3.1 Metal nanoparticles

Metal nanoparticles thrive in the domains of thermodynamics, kinetics, magnetism, and other fields in addition to their remarkable thermal, magnetic, or optical properties as reported by authors [16-18]. N-eicosane-Fe3O4/SiO2/Cu (50 nm) microencapsulated PCMs were created by Do et al. [19]. PCMs are made from n-eicosane, Fe3O4 is useful for recovering PCMs that have leaked from microencapsulated PCMs, SiO2 serves as an encapsulating shell to stop PCM leakage, and Cu nanoparticles were used as thermal conductivity boosters. According to the test findings, n-eicosane has a thermal conductivity of 0.4716 W/(mK), n-eicosane-Fe3O4/SiO2 has a thermal conductivity of 0.7598 W/(mK), and n-eicane-Fe3O4/SiO2/Cu (50 nm) has a thermal conductivity of 1.3926 W/(mK). The thermal conductivity of the PCMs that are microencapsulated is significantly improved by the inclusion of Cu nanoparticles. Cu nanoparticles with a concentration of 5% of the phase change material, according to Said [20], increased the value of air conditioning energy savings to 6.09% and 7.41%. Composite PCMs (CPCMs) were created using the melt eutectic approach by Gupta et al. [21]. By dispersing Fe and Cu nanoparticles in inorganic nitrate hexahydrate, the impact of metal nanoparticles on the thermal conductivity of PCMs was examined. The thermal conductivity of nitrate hexahydrate is 0.4 W/(mK), and it increases to 0.61 W/(mK) and 0.63 W/(mK) with the addition of 0.5 wt% Fe and Cu nanoparticles, respectively. Cu nanoparticles have a better impact on the thermal conductivity of nitrate hexahydrate than Fe nanoparticles do. This is because copper has a higher heat conductivity than iron does. Copper powder was employed by Cheng et al. [22] to improve the titanol/expanded perlite's thermal conductivity. To create the CPCMs, titanol and copper powder were completely combined before being added to expanded perlite. The thermal conductivity of CPCMs rises in direct proportion to the amount of copper powder present. As a result, the amount of copper powder in CPCMs may be changed to achieve the desired thermal conductivity. The thermal conductivity of CPCMs rises from 0.42 W/(mK) to 1.3 W/(mK) when the mass fraction of copper powder reaches 4 wt%. Yuan et al. [23] developed microcapsule PCMs with encapsulation ratios of 15.6, 34.3, and 64.7% (designated as P1, P2, and P3, respectively) using palmitic acid as the PCM and Ag as the shell. The best thermal performance is demonstrated by P3, according to experiments. P3 has a thermal conductivity of 0.447 W/(mK), which is 1.978 times more than that of palmitic acid (0.226 W/(mK)). P3 has a latent heat of 107.87 kJ/kg upon melting.

Thermal cycle tests revealed that P3 has good thermal stability. Utilising solar energy and conserving energy in buildings are two applications for this microcapsule PCM. The experiment by Parameshwaran et al. [24] showed that the thermal conductivity enhanced from 0.284 W/m/k to 0.765 W/m/k by the addition of 0.1-1.5% wt% by weight of nano silver particles to organic ester phase transition materials. Many researchers have utilised metal foams as well for their lightweight. Cetyl palmitate was created by Wang et al. [25] by combining binary 1-hexadecanol with palmitic acid in nitrogen. Cetyl palmitate has a low thermal conductivity of 0.3432 W/(mK), however this thermal conductivity can be increased by impregnating nickel foam with varying pore densities with cetyl palmitate. Nickel foam had pore densities of 70, 90, and 110 PPI, respectively. The thermal conductivity of CPCMs is 1.6687 W/(mK) when the pore density of nickel foam is 110 PPI. The obtained thermal conductivity data leads to the conclusion that the thermal conductivity of CPCMs increases with nickel foam pore size. Using metal foam, Huang et al. [26] increased the thermal conductivity of myristyl alcohol and looked into the impact of the type and pore size of metal foam on PCM thermal conductivity. Myristyl alcohol was used as the PCM, while copper foam or nickel foam served as the backbones, to create the CPCMs. The copper and nickel foam had pore diameters of 40, 70, and 90 PPI, respectively. The high pore density of copper foam results in high thermal conductivity of the CPCMs, according to measurement results for this property. Lauric acid/iron foam PCMs were made by Zhu et al. [27] using the melting infiltration process. Iron foam was chosen to have pore densities of 40, 70, and 90 PPI. Accordingly, CPCMs have thermal conductivities of 0.351, 0.946, and 1.071 W/(mK), respectively. The thermal conductivity of lauric acid/iron foam PCMs was higher than that of lauric acid (0.115 W/(mK)). The lauric acid/iron foam PCMs' thermal conductivity rose as the pore density of the iron foam increased. Cong et al. [28] used experimental measurement to examine the impact of copper foam on PCM thermal conductivity. Palmitic acid was employed as the PCM, and copper foams with pore densities of 40, 80, and 110 PPI were used to increase the PCMs' thermal conductivity. The thermal conductivity of PCMs made of copper foam and lauric acid with various copper foam pore densities is 0.34, 3.02, and 3.16 W/(mK), respectively. As a result, CPCMs have higher thermal conductivity the higher the pore density of copper foam is.

### 3.2 Metal oxide

Nano oxides, such as nano-silica, nano-titanium dioxide, nano-copper, nano-alumina, and others, are defined as having a particle diameter that reaches the nanoscale. The phase change material is coupled with the nanoscale oxide to create a nano-enhanced phase change material, which can increase the characteristics of the original phase change material. The alumina has great adsorption capacity, which can improve thermal conductivity of CPCMs and prevent leakage of the PCMs. However, with the increase of mass fraction of alumina, the latent heat of CPCMs also decreases accordingly. By using nano alumina as an addition to improve the thermal conductivity of CPCMs, Tang et al. [29] created the shape-stable myristic acid/high density polyethylene PCMs. In CPCMs, the mixture of myristic acid and high density polyethylene was 7:3. The CPCMs had nano-alumina contents of 0, 4, 8, and 12 weight percent, respectively. Thermal conductivity measurements reveal that nanoalumina significantly improves the thermal conductivity of CPCMs, and that the thermal conductivity of CPCMs rises as the amount of nanoalumina in the material increases. Copper oxide nanoparticles were utilised by Ezhumalai et al. [30] to improve the thermal conductivity of palmitic acid. The production of CPCMs with copper oxide nanoparticle contents of 0.1, 0.2, and 0.3 wt%. According to the experimental findings, CPCMs' thermal conductivity increases by 0.2, 0.46, and 0.66 times at 25 °C. As demonstrated, copper oxide nanoparticles might increase the thermal conductivity of CPCMs. In order to overcome the issues of low heat conductivity and polyethylene glycol leakage, Tang et al. [31] produced CPCMs employing SiO2 as a supporting material and Ti4O7 as an addition. The thermal conductivity of the CPCMs is 0.43 W/ (mK), 2.53 times that of polyethylene glycol (0.17 W/(mK)), when the mass fraction of Ti4O7 is 3 wt%.

### 3.3 Carbon based

The PCMs with carbon-based materials include PCMs with expanded graphite, carbon fiber, carbon nanotube and graphene. Carbon nanotubes (CNT), graphite, and graphene had thermal conductivities that were about five times greater than those of metals and fifty times more than those of metal oxides. Due to the added benefit of having a relatively low density [32], materials made of carbon derivatives are also favoured. New methods are greatly reducing the cost of producing carbon nanoparticles. As a result, the researchers are concentrating more on carbon-based materials.

#### 3.3.1 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are cylindrical structures that have been twisted or rolled up and have varying amounts of carbon layers. They are referred to as single-wall nanotubes (SWNT) or multiwalled nanotubes (MWNT) depending on the number of layers**.** Shen et al. [33] changed the original multi-walled carbon nanotubes (OMWCNTs) using ball milling, mechanical processing, and acid oxidation, resulting in the B-MWCNTS, BB-MWCNTS, and A-MWCNTS, respectively. CPCMs were created by Shen et al. [33] utilising erythritol and modified carbon nanotubes, and their thermal conductivity was examined. The thermal conductivity of the CPCMs is 5 times greater than that of erythritol when the loading of carbon nanotubes is 1 wt%. A new phase change nanocomposite was created by Zhang and Liu [34] by encasing sebacic acid inside a CNT sponge. This composite system was proven to be stable after 200 heat cycles. SWNT was used by Qian et al. [35] to increase the thermal conductivity of polyethylene glycol PCM. SWNT was added to the PCM at various mass fractions ranging from 2 to 10 weight percent. Over 400 heat cycles, the stability of the composite was discovered. The volume fractions of MWNT used by Kumaresan et al. [36] compounded paraffin was 0.15, 0.3, 0.45, and 0.6. The composites showed a considerable improvement in thermal conductivity but no discernible change in latent heat.

#### 3.3.2 Expanded graphite

Natural graphite flakes that have been quickly enlarged at high temperatures make up expanded graphite (EG). It has a worm-like, porous structure. The distributed impregnation of expanded graphite in binary nitrate salt of NaNO3 and KNO3, as demonstrated by Xiao et al. [37], significantly improved thermal conductivity. D-Mannitol (C6H14O6) and EG were used to create a new composite by Xu et al. [38] for the storage of solar thermal energy. In order to guarantee equal dispersion, the basic PCM, D-mannitol, was loaded in the EG nanopores in the ratio of 92:8. It was discovered that heat transport has improved by 68%. Five nanocomposite samples of MgCl26H2O with various EG weight percentages were created by Song et al. [39]. It considerably (143%) improved PCM's thermal conductivity. When Jin et al. [40] investigated the thermal conductivity of a composite salt (sodium acetate trihydrate, potassium chloride, and urea), they experimentally discovered that adding expanded graphite to the mixture may improve the CPCMs' thermal conductivity.

#### 3.3.3 Carbon fibers

Carbon or graphite fibres arise when graphite grows axially parallel and forms a sp2 link to the base surface. They range in diameter from 2 nm to 100 nm, and more than 99% of them are made of carbon. Carbon nanofibers (CNF) were added by Wang et al. [41] to palmitic acid (PA) to increase its thermal conductivity. Dong et al. [42] squeezed the carbon fibre sheets to create a three-dimensional network structure, and then they prepared CPCMs by impregnating them with liquid erythritol to achieve a 32.4-fold increase in heat conductivity. In order to create shape-stabilizing PCMs, Zhu et al. [43] combined stearic acid, high density polyethylene, and carbon fibre. They also looked at how carbon fibre affected the thermal conductivity of CPCMs. Thermal conductivity of the CPCMs is 0.4043 W/(mK), which is 2.22 times that of pure PCMs (0.1255 W/(mK)) at 20 °C, as loading of carbon fibre is 5 wt%.

### 3.3.4 Graphene

Two-dimensional carbon atoms that have undergone sp2 hybridization make up graphene. It is only one carbon atom thick and the interconnected carbon atoms may move around. Due to its two-dimensional layer structure, graphene exhibits superior thermal and phonon vibration conductivity and has lower surface thermal resistance. Octadecanoic acid PCM was given a graphene aerogel boost by Zhong et al. [44] by combining it with graphite oxide to increase its thermal conductivity. The impact of introducing graphene nanoplatelets to lauric acid on its thermal behaviour was examined by Harish et al. [45]. Graphene nanoplatelet loadings of 0.1 vol. %, 0.25 vol. %, 0.5 vol. %, 0.75 vol. %, and 1.0 vol. % were used to generate six nanocomposite samples. Using the transient hot-wire method, the thermal conductivities of these samples were compared to those of pure PCM.

## 4. Properties of nanoaddtives

The PCM’s thermal conductivity may be influenced by the phase change material's particle size, mass fraction, shape, size, type, and interaction with other nanoparticles. This section discusses the effect of nanoparticles size, mass fraction on the performance of the PCMs.

### 4.1 Size

The contact between particles is increased, chain structures can develop, and the phase change material's thermal conductivity improves with decreasing nano-additive particle size. On the other hand, thermal conductivity decreases with increasing nanometer added particle size. In mannitol composite phase transition materials, Ma et al. [46] incorporated 5-10 nm copper oxide nanoparticles and 50 nm multiwalled carbon nanotubes. The results showed that the small-size multi-walled carbon nanotubes had superior thermal conductivity. The PCM’s thermal conductivity can be improved by adding nanoparticles with tiny particle sizes that can be evenly disseminated. Sodium dodecyl sulphate (SDS), an anionic surfactant, is used by Kathiravan et al. [47] to oscillation copper nanoparticles over 10 hours. In order to efficiently boost the thermal conductivity of carbon nanotubes, Wusiman et al. [48] modified multi-walled carbon nanotubes using sodium dodecylbenzene sulfonate (SDBS) and sodium dodecyl sulphate (SDS).

### 4.2 Shape and mass fraction

Zhang et al. [49] investigated the impact of erythritol's thermal conductivity on carbon nanofibers with various aspect ratios. Compared to carbon nanofiber phase change materials with small aspect ratios, phase change materials with high aspect ratio carbon nanofibers exhibit better thermal conductivity. According to Tang Y et al.'s research [50], thermal conductivity increases more rapidly the more nano additives are present at a given temperature. At the same concentration, thermal conductivity will be improved to a greater extent at lower temperatures. The thermal conductivity of the nanocomposite phase transition material tends to increase with increasing nano additive content.

### 4.3 Dispersion uniformity

Both solid and liquid phase transition materials' thermal conductivity can be improved by the aggregation of nanoparticles. The aggregation of nanoparticles, however, can dramatically improve thermal conductivity in solid phase change materials as opposed to liquid phase change materials [51]. The production of stable and suitable heterogeneous nuclei, promotion of heterogeneous nucleation, acceleration of crystallisation, and greatly decreased subcooling are all benefits of well-dispersed nanoparticles [52].

## 5. Effect of nanoaddtives on latent heat storage-based applications

To address the imbalance between energy supply and consumption, PCMs may be used in solar energy utilisation, building communication, waste heat recovery, and temperature regulation of textiles. This section describes some of the performance enhancements due to the nanoadditives in the base PCM. Wu et al. [53] developed a form stable PCM with stearic acid as base and expanded graphite as additive for thermal energy storage. With an increase in packing density, thermal conductivity rose and may reach a maximum of four times. Choi et al. [54] reported that the thermal energy storage performance of the graphite NEPCM is the best of the three NEPCMs (MWCNT, Graphene, Graphite). Melting and solidification times reduced significantly when MWCNT was used with stearic acid to forma PCM [55]. The effectiveness of NePCM as a coolant for electronic chipsets under various situations, including as free and forced convection, was investigated by Alimohammadi et al. [56]. In both free and forced convection, the cooling scenarios comprised basic heatsinks (HS), heatsinks including phase change materials (HS/PCM), and heatsinks containing NePCM (HS/NePCM). As a basic PCM, Mn(NO3)2 was combined with Fe3O4 nanoparticles. The findings demonstrated that the presence of nanopartilces reduced the cooling chipset's steady state temperature by up to 14 °C. In their study on the improvement of the thermophysical characteristics of eutectics (oleic acid and capric acid), Hussain et al. [57] produced extremely porous activated carbon nanosheets that were utilised as nucleators to improve the thermophysical properties. The outcomes showed that the rate of heat transmission was enhanced while saving a maximum of 54% of the time compared to pure eutectics. This makes the composite suitable for cold storage application.

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