



ChemTech

International Journal of ChemTech Research

CODEN (USA): IJCRGG ISSN: 0974-4290

Vol.9, No.04 pp 192-196, 2016

Review on Phase Change Material as thermal energy storage for cooling

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Abstract: As the demand of air conditioners and refrigeration has increased during past many years, the cooling systems can be modified for economic advantage over these outdated cooling plants. In the comfort zone to maintain temperature cooling and heating systems are installed. To replicate the effect of thermal mass of the building, we can use of phase change material depending on the application. Phase change material should have high energy density of melting, high latent heat material and low temperature range. Thermal energy storage through phase change material is capable of storing and releasing large amount of energy and this depends upon shift in phase of material. Heat is absorbed or released when material changes from solid to liquid or vice versa during processes such as melting, solidifying/evaporation. A variety of substances like water, ice, inorganic salts or organic salts are used. In change of state, a large amount of energy known as latent heat can be stored or released at constant temperature. Thus a small difference in temperature is used for storing or releasing energy. Therefore the choice of phase change material mainly depends on the area of application. In this paper we are discussing about the various properties, types and applications of lithium, graphene, aluminum foam, polymer and ceramic Based Phase Change Materials. Due to huge variety of Phase change material, the designer will have more option to choose the material depending on the area of application.

Keywords : Phase change Materials, lithium, graphene, aluminum foam, polymer, ceramics.

I. Introduction

In this modern world cooling systems are used for cooling purposes which ensure that surrounding environment is cooled to a sufficient temperature in all weather conditions. These cooling systems consume a lot of electrical energy resulting in increased expenditure of common people. The temperature difference between day and night, and between cold and hot countries has peak difference between the uses of electrical energy. This type of problem also arise in heat recovery systems where heat energy available and its utilization period is different which requires thermal energy storage systems. Global warming and heat waves have brought attention to the energy efficient cooling systems using renewable resources. With the technological development cooling demand for comfort have also increased abruptly in the market. The most commonly used method of thermal energy storage is sensible heat storage. Phase change material plays an important role in thermal storage systems. It limits excessive temperature by storing heat during the day and releasing it during night. Thermal storage systems play an important role in building energy conservations. This method of heat energy storage provides much higher storage density with little difference in temperature as compared to sensible heat storage method. Difficulties generally arise in applying latent heat method due to low thermal conductivity, density variation, phase segregation and improper cooling of phase change material. All materials

are phase change materials, though they are characterized according to thermal energy storage and the workplace they are being used in i.e. household, commercial, or industrial sector. Paraffin and salt hydrates are useful phase change materials for household applications and Salts and sugar alcohols for high temperature ranges. Phase change materials have already been installed in the buildings to maintain the temperature difference between day and night. The application of phase change materials in buildings is to utilize natural heat and cold sources (solar energy) for heating during evening/night or cooling during day; or can use manmade heat or cold sources. These phase change materials can be inserted in walls or ceilings or in heat/cold storages. This stored energy is automatically released when indoor or outdoor temperature rise or fall beyond phase change point of material or can be used on our demand if energy is stored in separated medium from the building. This paper studies the various material used for phase change process. Materials used for this process must possess high latent heat and high thermal conductivity. The melting temperature of the materials should be in practical range of operation with minimum sub-cooling. The materials should be chemically stable, cheap, non-corrosive and non-toxic. Depending on application, various phase change materials have been studied in this paper

II. Lithium Based Phase Change Materials

The thermal energy that can be stored in a composite phase change material includes the latent heat of the phase change material and the sensible heat of both the solid and liquid phases. In composite, majority of the stored energy is through latent heat. Thermal conductivity of composite depends on the concentration, size, shape, orientation and spatial distribution of thermal conductivity enhancer— higher the concentration of the enhancer implies higher thermal conductivity; however, higher concentration of thermal conductivity enhancer would mean a lower energy storage density. Hence, a right balance must be ensured between thermal conductivity and requirement of energy storage density, for specific applications¹. The additions of carbon material can greatly influence the thermal conductivity—the conductivity increases with the increase in carbon content in the composite. Phase change material used in this work is eutectic carbonate molten salt (LiNaCO₃) made from sodium carbonate (Na₂CO₃) and lithium carbonate (Li₂CO₃). It exhibits a round shape and smooth surface. When Carbon Nanotubes are added, nanoparticles are found at the surface of phase change material particles. CNTs and graphite are less likely to be wetted by the liquid molten salt even though they have surface tension to allow wetting by water and other organic solvents. By using eutectic salt of lithium and sodium carbonates as phase change material, magnesium oxide as ceramic and carbon allotropes as thermal conductivity enhancer as composites enhances physical stability, chemical stability and high thermal conductivity. Good wettability of the salt densifies the composite structure, whereas poor wettability of the salt swells the composite structure. Hence, a proper balance has to be maintained for such competing processes – for better properties and behavior of composites. The formation of Nano layer is a pure physical change, caused by the addition of nanomaterial. The nanomaterial have large specific surface area, beneficial to form Nano layer (the formation of Nano layer is the reason that the nanomaterial can enhance phase change material specific heat)². The large specific surface area leads to higher surface energy that accelerates the nanomaterial aggregation and formation of nanomaterial blocks. The aggregation phenomenon significantly reduces the specific surface area of nanomaterial and weakens the enhancement effects of LiNaCO₃. The phase change material specific heat depends upon 2 factors: (i) formation of Nano layer that can enhance the specific heat; (ii) aggregation of nanomaterial that weakens the specific heat. To enhance the properties of lithium carbonate, it is purified by diminishing its solubility in hot water. Potassium carbonate is prepared by the electrolysis of potassium chloride. The electrolysis process produces potassium hydroxide, which is further carbonated (with CO₂) to form potassium carbonate. KHCO₃ is used to maintain equilibrium in neurons, and is used as an ingredient in welding fluxes, flux coating. It is also used as an animal feed ingredient to fulfil the potassium requirements of farm animals. The hydrogen bonds in KHCO₃ are strengthened with increasing atmospheric pressure. Higher pressure can also lead to repulsion between hydrogen atoms, causing amorphousization. KHCO₃ causes a substantial decrease in alkane group of ketone OZH₂O. The angle between the two oxygen atoms increases with increasing pressure up to 2.8GPa and results in distortion of hydrogen bond.

III. Grapheme-based materials

Grapheme has a two dimensional sp² bonded carbon sheet. Graphene is made by single graphite layer which interact poorly through Van Der Waal forces. Graphene is generally obtained through the oxidation of graphite, which gives Graphene oxide material³. Graphene unstable thermodynamically when Graphene sheet is

thickness is less than 20 Nano meter; it then converts into fullerene which is the most stable compound. Graphene has a soft membrane and possesses very good electrical conductivities and good thermal conductivities with high Young's modulus. A single-layer graphene material has zero band gap and also optical transmittance is nearly 97.7%. Its theoretical surface area of graphene material is 2600 m²/g. due to significant physical and chemical properties of graphene made scientists to conduct extensive research in Nano-electronics, fuel-cells, super capacitors, gas sorption, separation, storage, batteries, catalysis and sensing. The structure of graphene oxide have 2 oxygen-rich functional groups. The first functional group is hydroxide and epoxide groups and the second functional group is carbonyl and carboxyl groups on edges of the graphene sheets⁴. Graphene oxide material is hydrophilic and has very good solubility in water and in most of the solvents. The reduction and oxidation of graphene creates many defects on graphene sheet, which leads to very good advantages on gas absorption, storage and separation in functional site. Carbon based materials is used for gas sorption, storage, and separation, largely due to its high abundance, robust pore structure, light-weight, high thermal and chemical stability. It also offers several other advantages such as low cost and easy scale up. Graphene and graphene based composites is as adsorbents for high temperature chemical adsorption and low temperature physical adsorption of H₂, CO₂, CH₄, etc. The suspended graphene produces a thermal conductivity

of 5300 W·m⁻¹·K⁻¹, which is manifolds more than the pyrolytic graphite producing a thermal conductivity of

~2000 W·m⁻¹·K⁻¹, at the room temperature. Expanded graphite enhances the thermal conductivity of graphene.

When a constant voltage is applied to pristine EG flakes, an abrupt temperature change happens and then reaches equilibrium; however, when the voltage is removed, the temperature of flakes drops to room temperature rapidly. Thus, thermal energy is stored (or released) through a phase change process, when voltage is applied or turned off. This happens because the application of voltage changes the temperature of composite. The composites could store thermal energy by applying voltage, which opens ways for wide applications in areas related to electro-to-thermal energy conversion and storage.

IV. Al foams based phase change materials

The porous Al foam based phase change materials is manufactured by infiltration method and the porosity created infiltration method are of 62–72%. The pores created by the above mentioned method is e lower than 1mm size and having the density 103 kg/m³. Paraffin is an odorless, colorless, tasteless, waxy solid derived from petroleum products and fossil fuels. Paraffin is made by a mixture of molecules of hydrocarbon. It is solid at room temperature and begins to melt above approximately 37 °C and have a density of 900 kg/m³. The commercial paraffin has the starting phase change temperature of 33.0 1°C, the peak temperature of 64.1 1C, the final temperature of 70.0 1°C and the corresponding latent heat at value of 140kJ/kg⁴. It is insoluble in water, but soluble in benzene, ether, and certain esters. The feedstock for paraffin is slack wax, which is a mixture of oil and wax, a byproduct from the refining of lubricating oil. It is useful to modify the crystal properties of paraffin wax. Stearic acid is obtained from fats and oils by the saponification process using hot water which has nearly 200 °C. The starting temperature of stearic acid 54.7 1°C and the finishing phase change temperature of the stearic acid 70.6 1°C. The latent heat value of the stearic acid is 141kJ/kg. The paraffin wax and the stearic acid is best suitable for energy efficient building application and solar energy storage application due to the phase change temperature change and latent heat values. These shape-stabilized phase change materials/Al-foam composites exhibit considerable latent thermal storage potential particularly due to its enhanced dynamic-compressing yield strength, good interface, desirable phase change temperature range and latent heat values.

V. Polymers based phase change materials

Polymer based phase change materials have high melting point than organic phase change materials. They are less corrosive and easy to handle when compare with salt based phase change material. Polymers can be designed to fit different requirements and also polymer provide stability. In particular substances with high

molecular weights, Polyethylene glycol can be clearly divided in two groups: the shorter polyethylene glycols with $M < 1000$ show comparatively little sub cooling and a broad melting range, whereas the longer polyethylene glycols have large sub cooling⁵. The polyethylene glycols with $M > 4000$ show very little variation in the melting temperature. Melting enthalpy is larger for longer polyethylene glycols. Fatty acid ester can retain the high latent heat of fatty acid and avoid some weakness such as corrosively and smell. Paraffin and fatty acid are easily ignited at high temperature. The average pore diameters and the pore size distributions of the Silicon dioxide matrix did not change much with variation of polyethylene glycol contents. When polyethylene glycol content was higher than 50 wt%, the polyethylene glycol aggregates were formed with larger size and the shrinkage of the Silicon dioxide matrix was inhibited during the drying processes. The pore surface area depends on the pore diameter of Silicon dioxide matrix, the larger the pore size, smaller the specific surface area. The pore size of Silicon dioxide matrix gradually increased when the polyethylene glycol content increased. Due to the pore diameter becomes increased, which makes decrease in the pore surface area which leads to weaken the complexity between Polyethylene glycol and Silicon dioxide⁶. As a result, the surface area increased which leads to decrease in the confinement effect. The shape stabilized phase change materials are generally prepared by embedding the solid liquid phase change material substance into materials having mesopores or micropores. Shape stabilized phase change materials are the best suited materials for the various application due to the property that material entirely solid throughout the entire process and the capillary force induced by the material will prevent the leakage of the melted substance⁷.

VI. Ceramics based phase change materials

Ceramic and carbon materials (natural graphite flakes and carbon nanotubes) were chosen as the skeleton material and thermal conductivity enhancer. The eutectic salt was made by mixing thoroughly by 43% Li_2CO_3 and 57% Na_2CO_3 (mass percentage) and heating the mixture to a temperature above the melting temperature. Ceramic materials have high interfacial energy and small contact angle⁸. The wetting liquid provides a capillary force to pull the ceramic particles together and rearrange them to form a dense composite. This will increase the local rigidity of the structure. The liquid phase change material phase is likely to be able to wet the skeleton material, and spread on its surface to displace the solid–gas interface and instead of forming liquid–solid and liquid–gas interfaces. After sintering, the final structure consists of grains of skeleton material, bound by solidified liquid salt. Such a microstructure could prevent phase change material leakage during solid–liquid phase change. The low energy density, a capacitor forms the major bulk of the any device. The compact size and lightweight capacitor are desirable with accompanying high energy storage densities⁹. High energy storage capacity can be achieved by using materials with high dielectric constant along with large electric breakdown strength. Usually high dielectric constant is associated with ferroelectric materials due to dipolar polarizations and hence these materials are extensively investigated for electrostatic capacitors these materials have lower electric breakdown strength. In ferroelectric ceramics, oxygen vacancy is an important key factor to control domain growth and shrinking. The oxygen vacancy is mobile and generally trapped at the ferroelectric domain wall which results in domain wall clamping. Therefore, at lower electric fields trapped oxygen vacancies are high and domain switching rarely occurs due to suppression of the polarization. It is a result of domain wall pinning. The dielectric materials with high energy storage density which can effectively minimize the volume of the capacitor are urgently required by high voltage capacitor. Glass ceramics are widely used as high energy storage materials due to free of porosity¹⁰. Although, energy density only improves linearly with the increase of dielectric constant, appropriate crystallization is more effective to improve the energy storage density. Lithium Niobate (LiNbO_3) is an important ferroelectric material due to its excellent pyro electrical, piezo electrical and photorefractive properties. A transparent glass with the composition of 60 Silicon dioxide–30 Li_2O –10 Nb_2O_5 (mole %) was prepared by the melt quenching method. Ferroelectric glass ceramics are used in high energy storage devices such as barrier layer capacitors. Barium titanate is the first ferroelectric glass ceramics, whose crystal structure varies with temperature from rhombohedral to orthorhombic to tetragonal to cubic to hexagonal¹¹. The glass former B_2O_3 –Silicon dioxide in BST promotes the sintering at low temperature by the formation of liquid phase with a low melting point and dielectric constant is increased largely. The glass ceramics consist of grains, grain boundaries, major phases, secondary phases, pores and electrode ceramics surfaces¹². The conductivity of glass ceramics above constituent in glassy matrix is different and due to this conductivity difference, a space charge polarization takes place. Hence, the value of high dielectric constant is attributed in the glass ceramics. These contributions of polarization in dielectrics were analyzed by impedance spectroscopy. The resistance due to glass contribution is very high and its capacitance

contribution is low in RC network. These glass ceramic samples show the ferroelectric behavior due to addition of La₂O₃.

VII. Conclusions

The above study shows the characterization of various elements depending on their melting point, latent heat, stability and sub cooling properties. The most of the materials have high latent heat low vapor pressure per unit weight¹³. The disadvantage is that the materials have low thermal conductivity, change in volume and flammability. One of the great deal is to understand the best suited phase change material for various application in day to day life. After analyzed the various properties, types and applications of lithium, graphene, aluminum foam, polymer and ceramic Based Phase Change Materials. Based on the Environmental conditions each Phase Change Materials has advantages and limitations. Phase change materials is going to be a one of the best area of research for the scientist and it will create a new mile stone in the engineering field.

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