### From AI to Drug Delivery:

### How Phase Change Materials are Disrupting Your Industry

PRESCOUTER

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### Editor's Note

### MARIJA JOVIC

The term Phase Change Material (PCM) refers to a substance that has the ability to absorb and release large amounts of latent heat in the moments of its phase change. Put simply, a material that can store and release energy. Water is the simplest example of such a material. People have been familiar with PCMs for a long time, using them mainly for the heat management applications. Today they are widely being used in commercial applications such as building and construction. However, the era of PCMs has yet to come, with emerging high-tech applications varying from drug delivery to data storage, sophisticated biomarkers to artificial intelligence.

It is hard to think of an industry that is not affected in some way by these fascinating, yet simple materials. From the chemical industry providing the materials, to the construction industry using them as building blocks for smart houses, the energy industry using them for storing heat in off-peak hours, the electronics industry for developing new ways to store data, the food industry for more efficient storage and transportation of products, the automotive industry for safer and more efficient battery usage and motor protection, the aerospace industry for easy ice removal, the telecommunications for protecting telecom shelters, the textile industry for high-tech garments, to numerous applications in healthcare — containers for sensitive materials, medical devices, drug delivery and biomarkers.

This report serves as a guide through the emerging applications for PCMs. It gives a background on the materials themselves, discusses the current state and trends in the market, and describes ways of manufacturing these materials via the encapsulation process. It then goes into applications that have only recently become commercially available, but are not yet considered mainstream (like applications in textile industry and in control of body temperature), to applications that are further out, like barcoding and drug delivery. Finally, it concludes with an article separating facts from myth.

The aim of this report is to not only provide insight in the field of PCMs, but also to inspire ideas of how industries can leverage and use these materials in their own way and for their own applications. If you are unsure how these materials could impact your industry in the future, this is the right read for you.

### Introduction to Phase Change Materials (PCMs)

SIWEI ZHANG

The concept of PCMs and their applications go back to mid-1950s and therefore are not new. However, only recently have PCMs entered the "high technology" sector and are being given emerging potential from rewritable data storage to ultra-high capacity barcoding. In this section, we will introduce the general concepts, as well as the physical and chemical principles that contribute to the properties of PCMs and their applications.

As anyone who has taken physics and chemistry courses in high school might recall, substances, such as water, usually exist in one of the four fundamental states: solid (ice), liquid (water), gas (water vapor), and plasma (rarely seen, but fire provides an example). In addition, transitions between different phases are



**FIGURE 1:** Several bottles of cooled beer in a bucket with ice, an example of PCMs used for cooling purposes. As the ice in the bucket melts, its enthalpy of fusion (latent heat) absorbs energy in the form of heat as the phase changes from solid to liquid, therefore presents a cooling effect to its surrounding environment (i.e., the beers)

accompanied by changes of enthalpy or, in simple words, the store or release of heat.

As noted, the advantage of PCMs is in their ability to retain or release a significant amount of heat at their phase-changing temperature. Two common examples of PCMs are ice buckets and portable heating pads (Figure 1, Figure 2). Ice buckets, as the ice (solid phase) melts into water (liquid phase), absorb a great amount of heat at 333.35 kJ/kg and cool everything inside them (such as beverages). The portable heating pads work the opposite way by filling a reinforced plastic bag with ultrapure, saturated sodium acetate solution. At room temperature, due to a lack of sufficient seeding crystal or nucleus, the saturated sodium acetate solution remains in a supercooled liquid form. Once sufficient



**FIGURE 2:** The person uses a heating pad, an example of PCMs used in heating purpose. The heating pad, which is filled with super-saturated sodium acetate solution, releases significant amount of energy in the form of heat as the phase changes from liquid to solid. This process is reversible, usually done by microwaving the spent heating pad to restore its phase to liquid.

seeds are provided, the liquid content of the heating pad quickly crystallizes and becomes solid, simultaneously, releases large amounts of heat that is sufficient to keep bare hands warm at 40 °C for several hours.

Theoretically every type of phase transition possesses the ability of retaining or releasing energy in the form of heat however, only a few types of phase transitions can be applied to PCM technology due to practical limitations. For example, liquid-gas PCMs are generally not considered useful for routine applications since there is a large volume change associated with their phase transition. So solid-liquid PCMs have become the most popular application in both research and industrial use for their high latent heat capacities as well as their negligible volume change during phase transition. Generally, solid-liquid PCMs can be classified into two types: organic and inorganic. Organic PCMs, as the name implies, are a collection of both hydrocarbons and hydrocarbon-derivatives. With melting points ranging from 0-200 degrees Celsius and the majority of which reside between 0-100 degrees Celsius, organic PCMs have been extensively applied in situations involved in near-ambient temperatures. Organic PCMs can be further divided into two sub-classes: paraffins and non-paraffins. Paraffin PCMs refer to those PCMs with a chemical composition of linear alkane, or saturated linear hydrocarbons. When the carbon atom counts in the alkane chain stays in a range of 20-40, the resulted alkane usually appears as white, wax-like blocks at room temperature (paraffin wax). Upon crystallization, the long, disordered hydrocarbon chains of paraffins are



**FIGURE 3:** Energain<sup>TM</sup>, a wall panel from DuPont. Its core consists of copolymers with a paraffin PCM. The melting temperature is 22 °C and the solidification temperature 18 °C. The specific heat of melting is 515 kJ/m2. The panel is relatively thin (5.26 mm) combined with a low weight (4.5 kg/m2).

Image source: DuPont



**FIGURE 4:** Fatty acids and fatty alcohols are biodegradable and show no toxicity if ingested, therefore are great candidates for products such as temperature-sensitive nanoparticles for precision drug delivery.

straightened and release the latent heat stored within in a reversible pattern. Non-paraffin PCMs include a wide range of hydrocarbon derivatives such as esters, fatty acids, fatty alcohols and glycols. Among these, the fatty acids and fatty alcohols are the most commonly used chemicals because of their high surface tension in the liquid phase, which allows successful impregnation into host materials. In addition, fatty acids and fatty alcohols are easily biodegradable and show no toxicity if ingested, which enables production of "food grade" products such as temperature-sensitive nanoparticles for precision drug delivery. However, both sub-classes of organic PCMs generally share the same types of disadvantages; low thermal conductivity, flammable if ignited and instability at high temperatures (Figure 3 and 4).





**FIGURE 5:** Needle-like crystals growing in super-saturated sodium acetate solution, providing an example of a salt hydrate PCM. The shown process, triggered by seeding the super-saturated solution with a single tiny sodium acetate crystal, releases energy and heats up its container significantly.

Image: Courtesy of Nielson School



**FIGURE 6:** Gallium melts from the heat of the hand, an example of a metal PCM. Gallium has a characterizing low melting point of 29.7 degrees Celsius, which contributes significantly for its application in near-ambient temperature conditions.

Image: Courtesy of Oddity Central

additional nucleation seeds. Metals, not previously considered as part of PCMs because their relatively high melting points, recently received a boost from nanotechnology that has made them substantially more viable. Very different from the other PCMs, metals are characterized by their extremely high thermal conductivity and sharp, well-defined phase-transition behaviors that meet the crucial requirements of ultra-high capacity barcoding and optical data storage systems. However, the inherited high density of metals may still present restrictions on metal PCMs in weight-sensitive applications.

Since the size of the PCM structure plays a crucial role in determining its melting behavior (and therefore its responsiveness and efficiencies), PCM structures should be as small as possible to facilitate speed during phase transition. So, PCMs have to be prepared as colloidal particles and further encapsulated into individual enclosures to avoid previously mentioned problems. This is usually done by first processing PCM materials into micro-sized particles, followed by a separate micro-encapsulation process to insulate each PCM particle with surfactant, stabilizing matrix, or other type of casings. Such processes are critical in ensuring both the efficiency and the endurance of manufactured PCM materials in real-life applications.

Traditionally, PCMs have been widely applied for two functions: to serve as a means of latent heat storage and to serve as a heat sink device. The former function has been extensively used in home construction industry as a measure to increase heating efficiency as well as increase heat output of the heating surface. For example, 1 cm thick paraffin colloid paint may retain up to 37 percent of heat absorbed during the day and release it at night. The latter function is more closely related to the rapid collection and transfer or removal of thermal energy from a hot source to a cold source. Traditional heat transfer media, such as liquid sodium or water, are either too low in thermal conductivity (in the case of water) or too low in specific heat capacity (liquid sodium). Adding encapsulated, inert PCM particles into such heat transfer media greatly increased the heat transfer coefficient by 5-6 times with demonstrated results.

Recently, there has been a resurgence of research interest in PCMs, mainly related to the inherited properties of stage change involved during the PCM phase transition process. Such modern applications of PCMs include, but are not limited to, temporally and spatially controlled drug release, optical information storage and ultra-high capacity barcoding techniques. This report will selectively discuss emerging applications of PCM technology.

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## Market Analysis

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**GREG PILGRIM** 

Since 2010 roughly 1.1 million research articles on phase change materials have been published. Correspondingly approximately 27,000 patents have been filed in the same time frame. Those technical advances are beginning to bear fruit, bringing more and more PCM consumer products to the market.

The global market for advanced PCMs is projected to reach **\$1.5 billion** by **2020** (rising from \$563 million in 2014)

The growth will be driven by the increasing demand for advanced PCM for building and construction, HVAC (Heating, Ventilation, and Air Conditioning), cold chain, thermal energy storage (TES), shipping, packaging and transportation, textiles, and electronics, among others. The demand comes from the strong emphasis on energy conservation, stringent standards on gas emission, the rising preference for biodegradable materials, the recovering construction industy and the urbanization of development countries. Europe is the largest market for advanced PCMs (more than 30 percent) followed by the Americas and Asia-Pacific. Growth in Europe is directed by the stronger regulations of energy efficiency for buildings (the European Union passed a binding legislative resolution in 2007 to decrease greenhouse emissions by 20 percent and simultaneously to improve energy efficiency by another 20 percent by 2020) and the need to reduce operating costs. Europe is also estimated to have the highest growth in the market (21.4 percent CAGR) due to the increasing awareness about the benefits of advanced PCM and the level of commercialization of advanced PCM in the region.

The Americas is the second-largest market for advanced PCM and is expected to have steady growth until 2020. North America is also projected to see growth as energy costs are expected to rise long term making PCMs an attractive investment in new construction. Similarly, other energy conscious construction markets, such as those in warm climates like Brazil, South Africa and India are expected to grow as well.

The Asia-Pacific market is projected to have a high growth (with CAGR of 20.4 percent) on account of the demand for higher energy efficiency, and increased construction works due to urbanization. China, with increasing government efforts to control pollution in city centers is also expected to expand utilization of PCMs in the next decade to decrease fossil fuel usage.

Organic PCM market segment (especially paraffin based) holds the largest market size by value, while inorganic PCM dominates the market in terms of volume. Currently paraffin, sold predominantly by BASF and DuPont, is the single most common PCM used in thermal management, currently accounting for 45 percent of the total market. Its stability and simplicity make it popular for building, construction and HVAC systems. However, other PCMs like metal-salt hydrates, are on the rise. Their low cost, tunable nature and high melting points make them attractive. However, complications in application, including issues of chemical stability have hampered the metal-salt hydride market. Some regions, such as the European Union, have strict regulations for their stability, which must be accounted for before this metal-salt hydrate segment of the market can grow. With increasing concern over and stiff regulation environment against biodegradability, bio-based PCMs are expected to gain the fastest growth in coming years with CAGR of 21.6 percent between 2014 and 2019.

Major application for the advanced PCM market is in construction and building components, accounting for 20 percent of the market share in terms of volume in 2013. The HVAC and the thermal energy storage application, the other siginificant parts of the market are predicted to have a CAGR of 20.7 percent and 22.0 percent by 2019 respectively. These applications are more mature in the commercialization cycle compared to emerging applications like shipping, packaging and transportation, textiles and electronics, which are projected to experience high growth between 2014 and 2019. Leading players with the most significant product developments include BASF (Germany), Honeywell (China), Rubitherm Technologies (Germany), Entropy Solutions Inc. (U.S.), DuPont (U.S.), Pluss Polymers (India), Phase Change Energy Solutions (U.S.), China National Bluestar Group (China), Outlast Technologies (U.S.) and Sonoco (U.S.).

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### Microencapsulated PCMs

XINZHI ZHANG

### INTRODUCTION

When PCMs change state, there is an associated change in volume making PCMs hard to handle for their practical applications. To overcome this disadvantage, microencapsulated phase change materials (MicroPCMs) were invented. As the name suggests, in MicroPCMs, tiny particles or droplets of PCM are encapsulated in an outer shell made of polymer or inorganics, which remains solid, therefore maintaining a constant volume regardless of the state of the PCM (gas, liquid or solid). This article will discuss MicroPCMs in more detail, including their fabrication methods and applications.

#### FABRICATION METHODS

The key to MicroPCM fabrication is the encapsulation process, during which the PCM particles are confined in the outer shell. Although encapsulation can be achieved through physical methods, such as centrifugation and spray drying, particles created with these methods are often greater than 100 µm in diameter. Therefore, chemical methods are often used to fabricate MicroPCMs. Along with methods such as phase separation, pre-polymer mixing, mini-emulsion, and emulsion polymerization, there are situ polymerization, interfacial polymerization, suspension-like polymerization and complex coacervation, which are often used to fabricate the MicroPCMs, and will be discussed further.

In situ polymerization and interfacial polymerization are similar. In these processes, two immiscible liquids (usually water and the organic PCM) are mixed and stirred, together with an emulsifier, which forms micelles with a PCM core and water as the continuous phase. Into the mixture, complimentary, direct-acting, organic intermediates are also added, which encapsulate the micelle to form the MicroPCM. In the in situ polymerization, the core does not contain reactants; the polymerization only occurs within the continuous phase, while polymerization occurs in both phases in the interfacial polymerization process.



**FIGURE 1:** A schematic (adapted from Zhang et al., 2009) demonstrating the in situ polymerization of MicroPCM, with n-octadecane as the core PCM and melamine-formaldehyde as the co-polymer shell.



### FIGURE 2:

A schematic (adapted from Rodríguez et al., 2010) of encapsulating PCM with suspension-like polymerization process.

The suspension-like polymerization is based on suspension free radical polymerization. In this process, the continuous phase, which contains water and emulsifier, is stirred and the PCM, mixed with monomer and initiator is added to the continuous phase to form microparticles, as they are immiscible to the continuous phase. The polarity of the initiator is carefully chosen, so that the radical polymerization takes place only at the interface between water and organic droplet, without altering the properties of the PCM. Complex coacervation happens in colloid systems. In this method, the PCM is prepared as colloids and dispensed in macromolecular colloids rich coacervate droplets. Due to the interactions between different types of colloids through charges, the macromolecular colloids accumulate onto PCM colloids to form a viscous encapsulation wall, which can be further solidified through polymerization.



**FIGURE 3:** A schematic (adapted from Basal et al., 2009) demonstrating the formation of MicroPCM with complex coacervation, a) the PCM, b) the PCM with a primary coacervate layer, c) the encapsulated PCM with a second layer of colloids. The first and second layers could be the same or different.

For a particular application with MicroPCMs, the fabrication method is selected based on the application and desired properties of the particles. For example, the in-situ method can be used to make microcapsules in the range between 5 and 100  $\mu$ m with a great diffusion-controlling wall.

#### APPLICATIONS

Because microcapsules remain solid regardless the phase change of the core PCM, MicroPCMs have a wide range of applications, including food storage, health care, building and construction, textile and thermal energy storage (TES).

When the concept of micro encapsulated PMC was first mentioned in the 1970s, it was primarily considered for building applications and tested in Brookhaven National Laboratory. Since the MicroPCM stores energy, it could regulate room temperature without using fuel or external energy. Based on an analysis prepared by Frost & Sullivan, titled *Microencapsulated Phase Change Materials Market in Building and Construction—Outlook and Trends*, the market "earned revenues of \$56.0 million in 2013 and estimates this to reach \$111.4 million in 2018". Currently, MicroPCMs have been integrated into conventional building materials such as plasters for their use in buildings. For example, BASF provides Micronal® PCM, which are MicroPCMs designed specifically for applications in buildings. The MicroPCMs can either be mixed with plaster or placed in capillary tube mat cooling ceiling for their usage. DuPont provides Energain® panels that can be used in addition to insulation panels, that contain PCM material embedded in a polymer matrix.

Another area MicroPCMs are useful is in textiles and mattresses, as they could act as passive thermal systems. For example, when used in clothing, the MicroPCMs could store thermal energy created by the body at high temperature and release energy when body temperature decreases. According to the report *Global Microencapsulated Phase Change Materials* 



FIGURE 4: An example of using the BASF Micronal® in building. The MicroPCMs are embedded in gypsum core and used together as ThermalCORE<sup>™</sup> panel by National Gypsum.

#### Image Source: BASF

(MicroPCM) Market in Textile and Mattress-Outlook and Trends from Frost & Sullivan, "MicroPCM incorporated in textile and mattress components such as fibers, yarns, fabrics, foams, and gels", such market "earned revenues of \$45.1 million in 2013 and estimates this to reach \$99.0 million in 2018". There are currently companies working in this space that have products readily available. One example is Outlast Technologies Inc. Its MicroPCM-based Outlast® technology was first developed by NASA, and it is the only PCM to date that carries the certified space technology seal of approval. The Thermocules<sup>™</sup> MicroPCMs are specifically designed to be incorporated into fabrics and fibers, including bedding, apparel, footwear and seating. MicroTek Laboratories Inc. is another example; it has been working with MicroPCMs since 1985. The company has a series of MicroPCMs that are in the form of macrospheres and dry power. Two of them, MPCM28 specifically for and MPCM28D are designed incorporation into bedding materials, such as foam of mattresses, pillows, mattress covers and in linens.

MicroPCMs can also be used for thermal energy storage application. One company that is a leader in this area is Terrafore Technologies, LLC. It is a Minnesota-based

company that is active in the fields of renewable energy and energy efficiency, with a specific focus on TES for concentrating solar thermal power. One of their current efforts is to create EPCMs from TES that could meet the Department of Energy's SunShot cost goal of \$15 per kWh for thermal storage. Their solution is to use a combination of different types of salt-capsules with phase changing salts, which packs better and reduces the container size by 50 percent. One challenge of current EPCM is when the encapsulated salt melts at high temperature, the increase in liquid volume can rupture the outside shell, making them non-reusable. The company created TerraCaps, that contain voids in the capsules to accommodate the volume increase, so the capsules can be used at high temperature when salt melts.

The selection of PCM depends on the temperature range it needs to operate under. Quite often, either paraffin or salt hydrates are used, because their melting points are often within the temperature range of operation, and they are relatively cheap to obtain. In addition to the applications mentioned previously, which are well established, MicroPCMs are currently being considered and tested for their applications in the



FIGURE 5: MicroPCMs in textile (Left: scanning electron micrograph showing the MicroCPMs with fiber, right: textile with MicroPCMs embedded).

#### Image Source: Schoeller

areas such as smart drug delivery, information storage, barcoding and detection.



**FIGURE 6:** Formation of voids in the capsule to accommodate expansion in volume of PCM material during phase change (adapted from Mathur DAPA report).

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### Macroencapsulated PCMs for High-Temperature Heat Storage

**VIKAS PATIL** 

### INTRODUCTION

This report has discussed how PCMs offer an efficient method of storing large quantities of heat owing to their high latent heat of phase change, the most practical being solid-liquid transition. However, most PCMs also have a drawback in that they have a low thermal conductivity, sometimes too low to allow their usage in a pure form for fast charging-discharging rates. A number of methods have been employed in research and industrial applications to enhance the thermal conductivity of PCMs, including: finned tubes, insertion of metal structures into the PCMs, dispersion of thermally conductive nano- or micro-particles within the PCM matrix and encapsulation.

Microencapsulation, in particular, has been studied extensively and offers a fast charging-discharging rate, but so far has been mainly applied to PCMs with melting

points between 50 to 120 degrees Celsius (e.g., inorganic salt hydrates and organic compounds like paraffin waxes). However, various thermal energy resources such as concentrated solar thermal, geothermal and industrial waste heat are normally available at higher temperatures, up to 500 degrees Celsius. Higher temperature means higher thermodynamic efficiency. It would be desirable to have storage of such heat resources at high temperature, preferably using PCMs owing to their large heat storage capacity. This calls for the need to enhance the thermal conductivity of PCMs in the high temperature range. In this article we discuss macroencapsulation that allows the use of PCMs in the high temperature range.

### FABRICATION METHOD

The size of Microencapsulated PCMs typically varies from 1  $\mu$ m to 1 mm, while the capsules larger than 1



mm are classified as Macroencapsulated PCMs. At the moment, macrocapsules are manufactured through containment methods which comprises the inclusion of PCM in a package of some kind, such as tubes, pouches, spheres, panels, tin-plated metal cans and mild steel cans or other receptacles.

An emerging solution for heat storage in the high temperature range (120–350 degrees Celsius) is the macro-encapsulation of PCMs with high melting points. In this method, PCMs such as inorganic salt nitrates are encapsulated in metal alloy capsules, which are usually greater than 1000 microns in size.

### APPLICATIONS

Macroencapsulation of PCMs has its major application in heat storage. One example of such application is in the field of renewable energy – compressed air energy storage. Renewable energy sources are intermittent in nature, and their time of energy generation may not match the time of demand over a given day. In this context, energy storage technologies, including compressed air energy storage (CAES) technology, with a large energy and power density, play an important role in managing grid level energy supply and demand.

In the CAES concept, a compressor is driven by electricity during times of low demand. Compression heats up the air to high temperatures. This heat can be stored in a PCM and the cooled air can be stored in a large reservoir, such as unused tunnels and mineral caverns. This is commonly referred to as 'charging'. During times of high demand, the compressed air is released from the reservoir, then gets re-heated by exchanging heat with the PCM and is finally expanded in a turbine to generate electricity. This step is called discharging.

The CAES technology is a proven concept, but a major challenge lies in management of high temperatures associated with compressed air. This is where macro-encapsulated PCMs show a promising application, when used in combination with a sensible heat storage medium such as rock or sand. CAES has already attracted attention in Switzerland. A research group at the Swiss Federal Institute of Technology in Zurich is currently working on the selection of PCMs and materials for their encapsulation as well as investigating the long-term performance of this approach over multiple charge-discharge cycles.

As compared to microencapsulation technology, macroencapsulation is a cheaper technique that enables the use of PCMs at high temperatures and will continue to be a popular technology. Macroencapsulation of PCMs is a promising field and companies such as Microteklabs and PCM Products Ltd. are specializing in encapsulating PCMs.

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# PCMs in the **Textile Industry**

ALEXANDROS ATHANASIOU-IOANNOU

### FROM NASA TO EVERYDAY LIFE

Innovative textile products are increasingly becoming more complex, using more and more sophisticated technologies. One such technology takes advantage of the phase change of PCMs (i.e., from a solid to a liquid and vice versa). By using this, fibers and textiles will have automatic acclimatizing properties, prolonging the thermal comfort of the wearer. The idea for PCM microcapsules to be incorporated into a textile structure to improve their thermal performance comes from a NASA research program during the 1980s. The original goal was to use these fabrics in the astronauts' space suits for improved thermal protection against the extreme temperature fluctuations in outer space. Since then, textiles incorporating PCMs have started finding their place in the market of consumer apparel products, creating a fledgling area for PCMs.

Textiles with PCMs are able to react immediately to changes in environmental temperatures and the temperature across the body. When a rise in temperature occurs, the solid PCM reacts by absorbing this heat and storing it, as it has now melted. When the temperature falls again, the liquid PCM releases this stored heat energy and then solidifies again. The thermal insulation capabilities of clothing materials significantly improved may be through the implementation of PCMs. The ways of implementing these materials in our clothes vary, ranging from microcapsules to lamination and foaming technologies.

#### THE EMERGING SOLUTION - HOW IT WORKS

The main technological solution right now is the microcapsules technology, as illustrated in Figure 1. Other types of implementation lay in methods such as



FIGURE 1: Schematic representation of the microencapsulation technology incorporated in textiles. *Image Source: Masood Textile Mills Ltd* 

coating, foaming and lamination; all targeted at reducing the added weight of the fabric. In more detail, coating technology incorporates microspheres of PCM, well dispersed throughout a polymer binder, a surfactant, a dispersant, an antifoam agent and a thickener. This coating is applied on the cloth, usually via dip coating or spin coating. Foaming on the other hand, uses microspheres of PCM blended into a water-blown polyurethane foam mix; the foamy matrix is then implemented in the fabric. The existing air inside the foam decreases the weight of the garment and, at the same time, decreases its thermal diffusivity, acting as an extra insulation. Finally, the lamination technique uses a thin polymer film, with PCM microspheres inside, and then, as the name of the technique suggests, lamination is used to incorporate the polymer film to the fabric.

### CHALLENGES AND FUTURE DEVELOPMENT

It should be noted that the implementation technology is not only a significant factor for the weight problem but for other technical issues, as well. For instance, one of the current limitations of the microencapsulation technology is the burning behavior of the PCM layer, since microcapsules are mostly made of paraffin. One possible solution to stop flame propagation is through adding a flame retardant treatment to the coating. Other ways to overcome this predicament can be found in improving the flame retardant treatment or using PCM in a sandwich construction between two garments. which would insulate the PCM. Therefore, there are still a handful of open challenges for this technology. Research is still going on in the area to come up with an optimal result, combining thermal comfort and lightweight properties for the wearer.

Areas for possible use range from highly complex life support systems to the convenient or fun, and from lifesaving military uniforms to stain resistance or entertainment. Currently, the main areas of focus for smart and interactive textiles are the military, healthcare, and performance sportswear. Some specific examples include, gloves that can withstand more time at higher temperatures used by firefighters, fleece vests that allow the wearer to stay exposed in low temperatures for long amounts of time, or space blankets for emergency situations. These are just a fistful of sectors where PCM materials in textiles could make a difference.

The main PCM materials used in textile application are paraffin, polyethylene glycol (PEG) and hydrated inorganic salt, primarily due to their low cost and non-toxicity, high stability and low phase change temperatures.

There are several companies using PCMS (Schoeller Textiles AG, Everest Textiles Ltd., Masood Textile Mills Ltd., Textile Testing LLC, etc.) but commercialization of this type of cloth is still restricted to specialized and not widespread clothing.

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### PCMs Used in **Body Temperature Control**

MING ZHANG

The normal temperature of human body is about 37 degrees Celsius. It may vary a little depending on the person, the age, the time of day and whether someone is active or not, but ranges from 36.1 to 37.2 degrees Celsius are generally accepted as normal. An abnormal body temperature can be serious, even life-threatening. Generally, the body can keep its temperature within a narrow and safe range although the temperature outside the body could be largely varied. However, the body may fail to regulate its temperature if exposed at an extreme environment for long time or if the body lost its ability to regulate its temperature due to the health problem.

Currently, there are methods to control the temperature outside the body such as air conditioning and incubators. However, they are not suitable for outdoors and their costs also limit their application, especially in developing countries. Phase Change Materials, which could adsorb or release large heat when they change phase, could be a good solution to regulate body temperature if the phase change temperature is around the normal body temperature. Two examples of application of PCM in controlling body temperature are an infant warmer and cooling vest.

**INFANT WARMER** 

One million babies die on within 24 hours of their birth each year. 98 percent of these deaths happen in the developing countries. The leading causes of these deaths are preventable and treatable complications related to prematurity and low birth weight, including hypothermia. Premature infants lack the enough body fat to regulate their temperature. The room temperature can feel ice cold and it is very dangerous. In the developed countries premature babies can be placed in an incubator until they're able to make it on their own, however, babies in developing countries rarely have the chance to be cared for in the incubators. Other solutions, such as radiant warmers, thermal boxes, hot coals, hot water bottles and light bulbs are inaccessible, ineffective or even dangerous.

In 2007, a team of graduate students, Jane Chen, Linus Liang, Naganand Murty and Rahul Panicker, in a class at Stanford University was challenged to design an infant warmer to help families in the poorest regions of the world. Their initial prototype was a terry cloth bag with a PCM that melts at body temperature. After



**FIGURE 1:** Embrace infant warmer. a) an image of an Embrace infant; b) taking the melted phase change material from a heater; c) putting the phase change materials in the Embrace infant warmer; d) the Embrace infant is ready to keep warmer for infants.

Image Source: The Embrace Warmer

graduating, the team continued working on the product and conducting field research in India. They refined the design and the final working model, named the Embrace Infant Warmer, consists of a hypoallergenic bag, a removable pouch containing a PCM (PureTemp 37 from Entropy Solutions), and an electric warmer to heat the pouch.

After the phase change material melts in the warmer, the pouch remains at 37° degrees Celsius for at least four hours. And if the baby gets too hot, the PCM can absorb heat as well. An indicator on the pouch can indicate if the pouch needs to be reheated, and the pouch can be reheated up to 50 times. The cost of the infant warmer is less than \$25, which is less than 1 percent of the cost of a standard incubator.

The first Embrace infant warmer was delivered to Little Flower Hospital in Bangalore, India. Embrace currently has over 100 active programs across 11 countries: Afghanistan, China, Guatemala, Haiti, India, Mexico, Mozambique, Somalia, South Sudan, Uganda and Zambia. In 2014, the Embrace warmer was used to care for nearly 150,000 infants. environment. A PCM based solution could be an effective way.

Glacier Tek, an American Veteran-owned business, has been developing cooling vests for various applications since 1997. The technology is based on renewable PCM made from high-technology bio-based materials using material that is safe for use. Those materials could absorb heat generated by the wearer or from the environment and keep the wearer comfortable for long time. Even in the most extreme heat (e.g., more than 40 degrees Celsius), the cool vest could keep a comfortable temperature for several hours and recharges in just minutes. Various cool vests have been developed for outdoorsmen, sportsmen, soldiers and working dogs.

Several other companies such as, First Line Technology, TechNiche International, and Polar Products, also provide PCM based cooling vests. These vests are

### COOLING VEST

Extended exposure to heat can cause illnesses such as heat edema, heat rashes, heat cramps, heat exhaustion, heat syncope, heat stroke and so on. Many people, such as firefighters, outdoorsmen, soldiers, industrial workers and athletes, have to be exposed to hot environments for long time and they often find themselves at the mercy of extreme heat. Convenient methods were desired to help them keep the body cool while in a hot



#### FIGURE 2:

An image of a cooling vest from Glacier Tek. *Image Source: Glacier Tek*  comfortable and don't feel as cold as ice vests and typically weigh only 3-5 pounds. They can be recharged in the refrigerator, freezer or even at room temperature. The typical cost of those cooling vests is \$100-200, and the customers could easily purchase the cooling vests from their company website or their distributors. Overall, PCMs release or absorb heat during the phase change and keep the temperature consistent. This special property makes them a good solution to help regulate body temperature. Additionally, many bio-based phase change materials are nontoxic and environmentally friendly, their application in healthcare will continue to attract interest.

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### **High Temperature PCMs** for Thermal Energy Storage

XINZHI ZHANG
### INTRODUCTION

As conventional energy sources such as coal and petroleum-based fuels are becoming scarcer, there is an urgent need for renewable energy. However, the high cost associated with renewable energy makes it a less desirable option. One method to reduce the cost of renewable energy is the use of thermal energy storage (TES) technologies. TES stores thermal energy in a medium so the stored energy can be used at a later time for heating, cooling or power generation applications. TES has been utilized in buildings and power plants. An important application of TES is in the concentrating solar power (CSP) plant, as it enables dispatching electrical output to match the peak demand period of the CSP and reduces the cost of energy of the plants.

To achieve a high TES efficiency, materials with high energy density are desired as they reduce the amount of material needed for storing the same amount of energy. To this end, PCMs are suitable, because of their ability to store latent heat, which means charging and discharging a large amount of heat at a constant temperature during its phase change. Utilization of latent heat is more practical than sensible heat, which is released with a change in temperature, and at a smaller scale. For CSP, a high temperature PCM is needed because of the high operating temperature of the power plant. Specifically, the ideal PCM for this application should have a specific melting point (instead of a range), high working temperatures (more than 500 degrees Celsius), low vapor pressure, good thermal and physical properties, low corrosivity and toxicity, as well as low cost. In addition, solid-liquid transformation is preferred as it produces large enthalpy changes without significant change in density compared to vapor-liquid

transformation. Taking this into consideration, metallic alloys are good PCM candidates for high temperature TES application.

#### POTENTIAL APPLICATIONS

The selection of PCM for a TES application depends on the condition of the power plant. For example, Kotez et al. performed a proof-of-concept case study to select and evaluate PCM as a high temperature TES material in a solar power plant. In this study, the authors were looking for a high energy density PCM that operates at temperature higher than 560 degrees Celsius. Because the TES unit and steam generator need to be integrated into one unit, a commonly used liquid metallic for heat transfer purpose, NaK (sodium-potassium alloy) is not suitable due to high reactivity with water. The two most important criteria for PCM selection identified in this case study are the melting temperature and heat of fusion. The melting temperature should be within the operating range of the power plant, and higher latent heat of fusion indicates less material is needed. By plotting the latent heat of fusion versus melting temperature, the authors selected AlSi12 (an aluminum-silicon alloy with 12 percent weight of silicon) for this application since it has a melting point close to the required range and a high energy of fusion (Figure 1). Although a prototype was not fabricated in this study, authors evaluated the cost of the PCM in this study, considering the cost of equipment and storage materials, based on the size of the plant, which was designed to deliver 100 MW of energy with 15 h of storage; use of AlSi<sub>12</sub> is a viable option as the associated cost is \$14.7/kWh of stored thermal energy.



from Erens et al., 2013)

Recently, microencapsulated PCMs (MPCMs) were developed for TES application. Compared to conventional PCM, MicroPCMs provide the following additional benefits: with increased surface area to volume ratio, they provide sufficient surface area for faster heat transfer. They are structurally stable and can be handled as solid particles. Furthermore, the capsule wall acts as barrier against harmful environmental reactions during the heat transfer process. Although several methods, such as complex coacervation and polymerization have been developed for encapsulating PCMs, they are currently only suitable for low temperature PCMs. Nomura et al. reported a method to develop MicroPCMs for high temperature TES application. There are three critical concepts for the development of such MicroPCMs:

1) alloys generally expand less in volume during solid-liquid transition, have high thermal conductivity, and provide high thermal response during heat storage and release than molten salt,

2) oxide resists corrosion caused by liquid metal, and can be formed by oxidation of metallic particles, and

3) encapsulating PCMs in the liquid state (where volume is largest) creates voids for solid to liquid phase expansion. To this end, the authors selected an aluminum-silicon alloy with 40 percent weight silicon and created core-shell type capsules with  $AI_2O_3$  (aluminum oxide) as the shell through heat treatment of the core in  $O_2$  (oxygen) environment. Results demonstrated the encapsulation of the PCM in the shell (Figure 2). Although not tested in the actual energy storage study, characterization studies demonstrated that the resulting MicroEPCMs has a melting point of 573 degrees Celsius, a large latent heat of 247 J/g. Furthermore, cyclic tests were performed on the MicroEPCMs to evaluate their durability by repeating the melting and freezing processes up to 10 cycles, and



**FIGURE 2:** Encapsulated aluminum-silicon alloy PCM. Aluminum and silicon are distributed in the core, and oxygen is seen in the shell (adapted from Nomura et al., 2010).

the MicroEPCMs showed no leakage, making it suitable for high temperature TES.

# FURTHER DEVELOPMENTS

Currently, the application of high temperature phase change materials for TES is still under research, with a focus on material selection and evaluation. Some challenges associated with this research are 1) material selection depends on the operating temperature of the plant and it is a balance between performance and cost, 2) encapsulation of the PCM for better handling, which is challenging due to the high operating temperature. Although this technology is very promising for its commercial application, realization of it will still take some time and efforts for the researchers to solve these challenges.

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# PCMs for Thermal Management of Batteries

VIKAS PATIL

Overheating has historically been a major issue for electronics, especially with increasing miniaturization resulting in higher heat fluxes. In the case of batteries, elevated temperatures decrease their output power and can even lead to uncontrolled heating or fire, something which scientists refer to as thermal runaway. The use of fully electric and hybrid electric vehicles is expected to rise significantly in the next decade. A battery is a critical component of any electric vehicle, and determines driving range and maximum power. So, effective cooling of batteries plays a crucial role in ensuring performance and safety. Use of PCMs to achieve this thermal management first appeared commercially in 2011, and can be identified as an emerging trend over the next 5-10 years.

# THE PROBLEM

Accelerating an electric vehicle extracts high current from the battery cells, leading to local heat generation. Driving over long distances can accumulate heat in the system if not removed efficiently. High temperature is detrimental to battery performance, and can potentially result in thermal runaway. Effective and efficient battery cooling is of critical importance. PCMs can absorb large amounts of heat with minimal temperature rise, owing to their latent heat of phase change. This property has been conventionally applied for storage of solar, geothermal and industrial waste heat. In recent times, this unique property of PCMs has also seen applications in the batteries and electronics sector, in which the prevention of overheating is the objective, rather than bulk storage of energy.

#### THE EMERGING SOLUTION - HOW IT WORKS

Conventional thermal management for batteries involves the use of air or liquid flow around the cell surfaces to cool them. Liquid cooling is effective, but requires active flow control and increases overall system weight. Air-cooling may not be enough for heavy-duty use or in hot weather conditions. This is where use of a PCM around the cells offers a passive yet high performing cooling solution. The PCM can occupy the space between cells, where normally air or liquid channels are present. As the cell heats up, its temperature rises until it reaches the melting point of the PCM. As the PCM starts melting, this phase change



**FIGURE 1:** The effect of using PCM thermal management on cell temperature over time

Image Source: CHARGED Electric Vehilces Magazine

absorbs large amounts of heat without letting the temperature increase further. In this way, overheating of the battery is either prevented (if the system eventually achieves thermal equilibrium with the environment) or is delayed altogether, allowing longer operating time without the risk of high temperature (Figure 1 shows a schematic of this process).

When the cell stops generating heat during a period of rest, thermal energy stored in the PCM is dissipated back partly into the cell and to the environment.

# APPLICATION EXAMPLE

One company that is exploiting the benefits of this technology is the Chicago-based firm AllCell Technologies, which produces battery packs enhanced with PCM thermal management. AllCell owns the applications patent for PCM use in thermal management of electrochemical energy storage devices, including lithium-ion batteries, supercapacitors and fuel cells. This intellectual property right was a result of a long-term research work at the Illinois Institute of Technology, carried out in the 1990s as part of Dr. Said Al-Hallaj's doctoral study, who is now the Founder and CEO of AllCell. The research program was initially developed in conjunction with the U.S. Department of Defense's Future Force Warrior Program, for developing small, lightweight batteries that could withstand high discharge rates in extremely hot weather. AllCell appears to be the major player in the field of passive thermal management of batteries. Outlast Technologies LLC is another company that produces PCM-based battery sleeves.

Figure 2 shows a cut-section of AllCell's Phase Change Composite (PCC<sup>™</sup>) block, provided with holes for easy insertion of cylindrical lithium-ion cells.



FIGURE 2: Lithium-ion cells (red) inserted into AllCell's PCM-absorbed graphite matrix (gray) *Image Source: AllCell Technologies* 

# POTENTIAL FOR COST-REDUCTION

Lithium-ion batteries are the preferred choice for electric vehicles owing to their high energy density and power density. In the light electric vehicles sector (electric scooters, for example), thermal management is typically not employed because it would increase weight, consume more battery power and end up reducing the driving range rather than increasing it. AllCell claims that use of their PCM is capable of extending the cycle life of the cells by at least 50 percent potentially even up to 100 percent. In fact, AllCell's PCM equipped battery packs helped push up the driving range of French company Matra's electric scooter from 30 to 55 km. AllCell is clearly carving out a niche market for PCMs in the near future. Full-size electric vehicles are an even larger market. However, it is usually difficult for new technologies to make an entry into existing vehicle designs. Larger battery packs are in the \$10,000-\$15,000 range. Cooling systems roughly constitute 20 percent of this cost, and AllCell aims to bring down this cost component to below 10 percent using their PCM enhanced battery packs. This would translate into savings of at least a few thousand dollars per battery pack.

Apart from electric vehicles, decentralized storage of solar power is a promising avenue for lithium-ion batteries, as also evident from the recently launched Tesla Powerwall home battery. Thermal management is expected to play an important role in this sector as well.

#### CHALLENGES AND FUTURE

A typical challenge associated with use of PCMs is prevention of the molten material from leaking and getting in contact with other surfaces. To deal with this, AllCell uses paraffin wax microencapsulated within a graphite matrix, branded Phase Change Composite (PCC<sup>™</sup>). When the wax melts, there's enough surface tension between the wax and the graphite matrix so that it doesn't leak out.

Another important factor is selection of a PCM whose melting point lies below the safe operating limit of batteries, which is around 30 degrees Celsius for lithium-ion batteries. Paraffin waxes lie in this range and offer large heat absorption potential, but their low thermal conductivity hinders the rate of heat removal. Studies have shown that using a graphite matrix is the best option for enhancing thermal conductivity of paraffins. On this note, AllCell has started on the right path. The company expects its products to go mainstream by the year 2020.

Addition of PCM may not remove the need for active cooling altogether, but it can very well absorb the spikes of heat associated with sudden acceleration. Given this, engineers would be able to downsize the active cooling system to the average thermal load rather than the peak. This would reduce the overall weight of the cooling system.

AllCell is also involved with an Advanced Research Projects Agency-Energy (ARPA-E) project spanning from 2014 to 2017 with Stanford University, with the major goal to develop a multifunctional battery chassis system that, in addition to being the electrical energy storage for the electric vehicles, also serves as a structural member of the vehicle, thus reducing overall weight and improving the range. Using a PCM matrix for thermal management of such a battery system would also play a role in supporting structural loads and absorbing shock in the event of a collision. If successful, Stanford's battery system would potentially reduce overall vehicle weight more than 40 percent by serving as a structural component, resulting in increased driving range. Leading the research of this project at Stanford is Dr. Fu-Kuo Chang, Professor in the Department of Aeronautics and Astronautics at Stanford.

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# PCMs as a New Barcoding System

XIN YAN

# INTRODUCTION

Over the past decade, the commercial requirement for an ultrahigh capacity coding system with small dimensions to identify an object has been unsatisfactory. The reported data from the United States Department of Justice showed that in a firearm related crime, there was over 37 percent chance to end up with never finding suspects. In 2008, only 64 percent hit-and-run accidents received follow up investigation. If the bullet and paints themselves can be identified, the efficiency of law enforcement would be significantly enhanced due to an accessible avenue to solve the problems.

Commercial identification techniques are widely applied in the market. The current identification systems can be categorized as: number based system, pattern (optical barcode), materials (microfiber) and radio frequency devices. However, they all have limitations. Series numbers are engraved on bullets, but it can be damaged during collisions to lose its identifying function. The optical barcode system cannot be used in cases where invisibility is required, such as paints. Radio frequency devices are expensive and cannot be miniaturized to identify small items. Microfiber seems to be a good option, however, it is limited by the coding capacity.

# HOW DOES IT WORK?

Advanced research in nanotechnology provides one possibility: barcoding with nanoparticles of PCMs that can be encoded and decoded through thermal treatment. This was an idea brought by Dr. Ming Su from University of Central Florida in 2009. One of the advantages of this technique is the ultrahigh capacity. It is well known that the temperature of a single component solid does not go above melting point until the entire solid is molten. A homogeneous mixture of nanoparticles with different melting points can provide a few melting peaks if the components have sharp and distinguished melting points. It can be encoded through mixing the nanoparticles in different phases. The capacity depends on the total number of peaks (assuming n components contribute n non-overlap peak) through 2<sup>n</sup>. It can be easily calculated as long as n is reasonably large, say 50, the capacity can reach 2<sup>50</sup> which is sufficiently large for most of the identification requirement. The mixture can be dispersed uniformly inside an object without a change of the initial properties.



**FIGURE 1:** Thermal barcode. From left to right, the blue, green, purple, dark blue peak are corresponding to indium, lead-tin alloy, tin and bismuth (adapted from Su et al., 2009)

Researchers carried out a small sample of the coding system with 4 metallic materials: indium, tin, bismuth and lead-tin alloy. High melting point silica shells are used to cover the metallic materials and form the nanoparticles. The encapsulated nanoparticles have stable morphologies, structure and compositions. Incorporating a homogeneous mixture of nanoparticles in objects can carry out the encoding (Figure 1 shows the possible "codes").

As shown in the Figure 1, 16 different codes are generated through mixing nanoparticles at different phases. In decoding, 5 mg of the mixture is added into an aluminum pan and counting the melting peaks in temperature increasing process. One thing must be noted; the nanoparticles have to be stable long-term at room temperature, which needs to be confirmed by the identical melting behaviors after one year or longer.

# WHAT ARE THE CHALLENGES?

The challenge of this technique is that it is difficult to find so many materials that have sharp and distinguished melting points.

After Dr. Ming Su's move to Northeastern University (his group is funded by National Institute of Justice and some other departments) they continued research in this approach and found out a way to increase capacity with limited elements. This is done by using both the pure metal substances and their eutectic mixtures. For example, 10 different metals can form 45 types of binary alloys, 120 types of ternary eutectic alloys, 210 types of quaternary eutectic alloys and so on. Of course, they still need to have distinguished melting peaks, however, the capacity can be dramatically increased. Table 1 shows some of the possible metal candidates for barcoding system and Table 2 lists the possible organic candidates. Besides metals, for some applications (drugs and ink, for example), in order to keep the chemical properties unaltered, organic phase change materials made into nanoparticles can be used for barcoding.

Metal	Composition (% mass)	Melting point (°C)
Field's metal	32.5 bismuth: 16.5 tin; 51 indium	58
Indian bismuth eutectic alloy	66.3 indium; 33.7 bismuth	74
Fusible alloy 203	52.5 bismuth; 32 lead; 15.5 tin	95
Fusible alloy 255	55.5 bismuth; 44.5 lead	124
Fusible alloy 281	58 bismuth; 42 tin	138
Indium	100 indium	157
Tin63lead37 alloy wire	63 tin; 37 lead	183
Bismuth	100 bismuth	271.5
Zinc	100 zinc	419.5

#### TABLE 1: List of possible metal candidates

Molecule	Melting point (°C)
Stearic acid	68°
Palmitic acid	59°
Paraffin wax (C <sub>18</sub> H <sub>38</sub> )	28°

The accuracy of decoding depends on both the mass of nanoparticles and the minimal heat flow detected by differential scanning calorimetry (DSC). Apparently, the more nanoparticles in a testing item, the more accurate it can be. Also, if the heating rate increases, the decoding time can be reduced and the signal intensity can be amplified. However, the limitation is the increased heating rate will make peaks wider, which may bring confusion if two peaks are close.

### POSSIBLE APPLICATIONS

An example using 4 metal substances and their eutectic alloys forming a barcoding system for DNT which is a trinitrotoluene (TNT) simulator was shown. The nanoparticles were encapsulated inside silica shells to prevent explosion while mixing metals or alloys with explosive materials. Nanoparticles are mixed with DNT powders at a mass ratio of 1 to 100 and the yellow color of DNT doesn't change at all. The average particle size of the particles was 200 nm to ensure the melting points of each element are the same as bulk material (melting points are stable). Using this system, it can form 15 types of different barcodes. They were added to different batches of DNT powders. Several testes were carried out with the mixtures. For example, the DNT-nanoparticle mixture was dissolved in ethanol and nanoparticles were collected by centrifugation. The melting temperature of 120 degrees Celsius confirmed the existence of nanoparticles. For another case, DNT-nanoparticle mixture was ignited inside a container, and the debris is collected and tested. The result showed the existence of all peaks, proving that this method can be used to trace explosives after detonation.

Another example is for testing the application of labeling drugs and inks. For these cases, organic solids are used to manufacturing nanoparticles, such as stearic acid, palmitic acid, paraffin wax and polyethylene. In order to prevent agglomeration, nanoparticles are encapsulated inside polystyrene shells. Similarly, eutectic organic solids with distinguished melting points can also be used. The nanoparticles are mixed with drug powder (acetaminophen, for example) homogenously. After making the drug in the required format, capsules or tablets, the appearance of drugs doesn't change. DSC testing can be used to find out the melting peak and finish the decoding process.

Additionally, phase change nanoparticles can also be added in polymers and inks, which provides the potential of tracking textile and printing products for anti-counterfeiting purposes.

# FUTURE DEVELOPMENT

Compared with current barcoding techniques, this method has advantages based on its high capacity and invisibility. The current limitation of this method is that decoding time usually lasts around 20 minutes. Researchers have already submitted several patents with this technology and it can be expected that in the near future this technology may benefit our everyday life.

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# PCMs as New Biomarkers

XIN YAN

### INTRODUCTION

It has been proven that the use of multiple biomarkers could greatly enhance the detection reliability for a variety of diseases, including cancer, cardiovascular disease, Alzheimer's disease and autism. The multiplexed detection approach can be used to monitor disease progression. The current existing detection methods are not sufficiently powerful, lacking either sensitivity or specificity.

It is well known that during the melting process, solid materials absorb heat without a rise in temperature according to Gibbs' phase rule. Put another way, if a solid phase exits, all absorbed heat is used to melt the solid and the temperature of the solid-liquid mixture is constant. Based on this principle, PCMs (metals) can be used as biomarkers as long as their thermal properties are stable.

#### HOW DOES IT WORK?

In the newly developed thermal biosensing method, nanoparticles of solid-liquid phase change materials are used as thermal probes to detect multiple biomarkers, including proteins and oligonucleotides. The nanoparticles will first be modified with ligands that can bind to biomarkers, and then incubated in a buffer or body fluid that contains biomarkers. After incubation, a high thermal conductivity solid substrate, modified with multiple ligands (different from the ones on the nanoparticles) will be immersed into the solution to capture nanoparticles by forming sandwiched complexes. After washing away unbound

nanoparticles, those attached onto the substrate will be read out using differential scanning calorimetry (DSC), where the heat fluxes of the sample and a reference are measured simultaneously during a linear thermal scan. А series of alloy nanoparticles with composition-encoded melting points can be used to detect multiple protein and DNA biomarkers after creating a one-to-one accordance between one type of nanoparticle and one type of biomarker. According to the combination rule, even though the gualified metals in the periodic table are limited, they can form eutectic alloys in binary form, ternary form, and so on. In this way, the total number of candidates for biomarkers is great, which could provide the possibility of tracking different proteins and DNA. The size of the nanoparticles is larger than 20 nm, which ensures the thermal stability of nanoparticles. When nanoparticles are smaller than 20 nm, the melting point is affected significantly by the size of the nanoparticle.

The advantages of this type of biomarkers are distinguished from other approaches: high multiplicity (track multiple proteins or DNA at the same time) owing to a sharp melting peak, large scan range and wide choice of materials; high sensitivity and an adjustable detection range using nanoparticles of various sizes, composition and ligand grafting density; minimal sample preparation by detecting biomarkers contained in body fluid; and simultaneous detection of different biomarkers at the same time, under the same conditions.

### APPLICATION EXAMPLES

#### Multiplexed protein detection

Thermal biomarker has been used to detect protein with nanoparticles. The multiplicity of thermal detection is reflected in simultaneous detection of four proteins (rabbit IgG, human IgG, biotin and PSA) using nanoparticles of indium, lead-tin, tin and bismuth that are modified with the associated antibodies. The aluminum substrate is incubated with a mixture of 2 ng/ml of each protein in PBS. After washing, the aluminum substrate is tested by DSC as shown in Figure 1. There are 4 distinguished peaks at 156, 183, 230 and 270 degrees Celsius that correspond to four types of nanoparticles as well as 4 proteins.



#### **Multiplexed DNA detection**

This method has been used to detect two types of ssDNA as well. The probe ssDNA-modified indium and lead-tin nanoparticles were used as markers.

# FUTURE DEVELOPMENT

The PCM based nanoparticles could be used as biomarkers for disease detection and similar applications. However, further research such as surface modification, grafting density of ligand, specificity or selectivity of detection determined by biological interactions is needed for further development of this technique.

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# PCMs and **Drug Delivery**

ADITI JOSHI

# INTRODUCTION TO THE CHALLENGES IN THE DRUG DELIVERY

As the science of drug delivery advances, it explores new techniques to meet challenges such as the controlled delivery of drugs or a continuous and sustained release of drugs. Additionally, many disorders or diseases are triggered by the changes in external environments such as time of the day or physiological status. A smart drug delivery system that is sensitive to these changes is much needed.

Factors such as pH of blood, temperature of body or mechanical signals can serve a stimulus necessary to trigger drug delivery. PCM drug delivery systems



**FIGURE 1:** Cyclophosphomide drip: A 'Traditional' Drug Delivery system.

Image Source: Wikipedia

respond to the changes in temperature to effectively deliver drugs when needed.

# PCMs AS A POSSIBLE SOLUTION

Microencapsulation using PCMs can provide a solution to meet the previously mentioned therapeutic challenge. Microencapsulation is a technique where a core material is covered by shell material to avoid its interaction with the environment. PCMs, generally used as a shell material for drug delivery purposes, are bio-based materials such as fatty acids or oils. These molecules are compatible with human tissues and are biodegradable. Researchers and the biotech industry envision great potential for smart drug delivery systems using PCMs.

# POSSIBLE APPLICATIONS

Biotech research has primarily focused on temperature release drug delivery.

One successful solution to achieve a temperature released drug delivery is the use of PCM as a "cork". A polymer particle with a hole on the surface is used to load the drug molecules. To keep the drug encapsulated, the small hole on the surface is sealed with a PCM that remains in solid state until its melting point is achieved. As the temperature rises, the seal changes into liquid form and releases the drug. A research study has successfully employed a thin film of Poly-4-vinyl-pyridine (P4VP) as a "cork" and used polystyrene (PS) beads to contain the drug (Figure 2).



**FIGURE 2:** The procedure of generating hollow polymer particles with a small hole on the surface: diffusion of toluene into PS beads partially embedded in thin film of P4VP, quick freezing with  $N_{2'}$  evaporation of toluene under freeze drying and removal of P4VP film (adapted from Xia et al., 2013)

By using various PCM particles, the rate and initiation temperature for drug release can be controlled. In a research study, two PCMs - 1-tetradecanol (melting point at 38–39 degrees Celsius) and dodecanoic acid (melting point at 43–46 degrees Celsius) were used to contain FITC-dextran. As the temperature reached the melting points, the PCMs melted and the drug was gradually released. Because of different initiation temperatures, the pattern of drug release was successfully controlled.

Along with temperature, the release rate of drugs can be controlled by using PCMs that are sensitive to light (e.g., photothermal Au nanoparticles (AuNPs)). Recently, for delivering the anticancer drug doxorubicin, which is toxic to the cells in the body, the drug was blended with PCM and other compounds to form a "nano chocolate waffle" (Figure 3). The release of the drug can be controlled by monitoring the exposure to light and temperature (photothermal). Similar technique can be employed for bioimaging in cancer patients. The field is evolving and newer applications are being developed.



**FIGURE 3:** Synthesis and principle of work of near IR-responsive drug releasing system;

**a)** Mesoporous silica-coated graphene oxide (GO@MS) was synthetized by sol-gel condensation of a silica precursor on GO under basic conditions with cetyltrimethylammonium bromide (CTAB) as the template

**b)** DOX (doxorubicin)/PCM-loaded GO@MS (DOX/PCM-GO@MS) was prepared by a simple mixing and extraction method devoid of any toxic solvents

**c)** Near IR-induced melting of PCM triggers the rapid release of the loaded anticancer drug. (adapted from Kim et al., 2015)

# FUTURE DEVELOPMENT

More research and, in particular, clinical trials are needed before the use of PCMs becomes routine. As of Oct 31, 2015, the USPTO has awarded 11 patents related to PCMs and drug delivery. Various organizations such as ResMed Ltd., and the Invention Science Fund have owned patents related to PCMs. This number will continue to grow as further research is carried out regarding PCMs. PCMs bring a promising future to the science of drug delivery and may provide better patient care.

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Solid-Solid Phase Change Material (SSPCM) – Phase Change without a Phase Change

SUBRAT JAIN

The right material used at the right time can solve many problems, save money and help build a sustainable environment. That's why research in the development of PCMs has increased rapidly in that past few years. Solid-Liquid Phase Change Materials (SLPCMs), though very useful, have limitations like leakage, large volume and encapsulation. Because of these limitations some attention has been directed toward Solid-Solid Phase Change Materials (SSPCMs), as they do not have those limitations. Solid-Solid PCMs have been researched since the 1980s but it is in the last couple of decades that some real progress has been made.

A SSPCM is a material where a solid transforms from its (one) crystalline structure to another, remaining in solid state. The SSPCM does not change its state but only soften or harden slightly in different phases. While changing its crystallographic structure, the SSPCM either releases or absorbs sufficient amount of latent heat to be useful for thermal energy storage. The fact that it remains in solid state and absorbs or releases latent heat, makes it favorable for most applications, especially where SLPCMs are hard to apply. SSPCMs are rare in natural substances and so they are artificially created. The most common type of SSPCM on which majority of the research is based on are polymers, like polyalcohols and polyethylene.

# FABRICATION METHODS

It is difficult and rare to find a natural solid-solid PCM. This is one of the reasons SSPCMs are not gaining ground like SLPCM. A lot of research on SSPCM has been focused around creating SSPCM in laboratory using various fabrication methods.

Typically, there are two ways to fabricate a SSPCM. The first is physical blending. In this method a PCM (generally an SLPCM) is dispersed into polymeric matrix. The polymer acts as a supporting material and holds the PCM during phase change to keep it solid. The melting point temperature of the supporting material should be less than the temperature of the application as otherwise the whole SSPCM will lose its solidity. The more technical term for these types of materials is form-stable PCM and they generally are not considered as SSPCM. The second method is chemical binding. In this method PCM moieties are chemically bonded to a supporting polymeric material. This way, the PCM loses its fluidity at temperature greater than melting point. This chemical synthesis is done using 3 methods: chemical grafting, blocking and cross-linking copolymerization. Generally, a hard material is used for the structural support and a softer material would be PCM. Figure 1 explains the copolymerization method. In simple terms, a phase change unit is given a skeleton of a polymer that prevents it from becoming liquid.



Most SSPCMs have low thermal conductivity, which can make many of them practically useless. One of the researchers have suggested that by adding Extended Graphite (EG) in a PCM, the thermal conductivity would increase as EG is a good thermal conductor.

PEG (Polyethylene glycol) is the most common phase change ingredient to create SSPCM. Although, only PEG with a molecular weight of more than 4000 is able to generate sufficient latent heat. The reason PEG is so favorable to create SSPCMs is because it is a very safe, chemically flexible and environmental friendly material. More specifically it is non-toxic, biodegradable, hydrophilic, biocompatible, resistant to corrosion, easy to chemically modify and provides wide molecular weight selectivity. It has a melting temperature from around 3.2–68.7 degrees Celsius across its different forms and a very high phase change enthalpy depending on its molecular weight. These properties also make PEG a very favorable material for SL PCMs. **TABLE 1:** Some examples of solid-solid phase change materials.

S.No.	Name of compound	Enthalpy, J/g		Transition temperature, °C	
		Heating cycle	Cooling cycle	Heating cycle	Cooling cycle
1	PEG 1000-HMDI	109	113	19	26.3
2	PEG 10,000-HMDI	171	173	57.7	48.9
3	PEG 1000 - TDI	69.5	65.6	26.9	3.8
4	PEG 10,000-TDI	162	162	57.1	46
5	polystyrene-graft-PA copolymer	19.23	39.40	18.43	40.81
6	di-nhexylammonium bromide (dC6Br)	85	-	78	-
7	Glycidyl methacrylate	70	-	25	60
8	PU ionomer-6	142.5	137.7	57.1	33.2
	PU ionomer-10	152.3	149.7	60.8	34.8

Abbreviations used in the table:

- PEG Polyethylene glycols
- **PU** Polyurethanes

There are very few companies that sell SSPCM commercially. Two such companies are PCM Products Ltd. in the UK and Kaplan Energy in France.

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SSPCMs have many advantages over other PCMs, which is why they are being researched for applications like building material, textile materials, electronic cooling and more.

An SLPCM requires a protective covering to isolate it from its surroundings, to prevent leakage, or prevent unwanted reactions. This protection is given by encapsulating the SLPCM. Encapsulated PCM deteriorates incredibly after 1000 cycles. Encapsulation also creates additional thermal resistance and increases the cost of the material, which makes encapsulation undesirable. As SSPCMs are always in solid state, they would require minimal to no containers, which also means no encapsulation is needed. In addition to that, leakage is not a concern.

As these solids can be molded in any shape or size, it can cover a much broader area of practical usage. Smaller volume changes during phase change means space constraints are well handled. SSPCMs also have better structural integrity compared to SLPCMs, which gives another reason for it to be considered for building and textile applications.

#### DISADVANTAGES OF SSPCMS

As good as they look, SSPCMs come with number of drawbacks as well, which is the reason they are not researched as much or used yet for practical applications as SLPCMs.

- SSPCMs are very difficult to find naturally
- The transition between the phases is very slow
- Even though some SSPCMs can have comparable enthalpy generation, the thermal conductivity of an SSPCM is very low in most cases which restricts its usage in many applications
- Low temperature applications of SSPCMs are restricted due to their higher phase change temperatures
- In general, most SSPCMs have very low latent heat to be practically of any use
- The SSPCMs are also known to have unstable thermal properties.

# POTENTIAL APPLICATIONS

PCM could potentially be very useful in thermal management system of a building. According to research, PCM has the potential of partially replacing insulation, meaning that using a PCM can reduce the amount of thermal insulation in a building. It would eventually save money after the initial costly investment. An SSPCM would help save wall space and prevent possible leaking along with other advantages. Some examples have been practically tested. Two of them are listed below.

#### Ice removing material

A very interesting application of SSPCM was discussed in research conducted in Massachusetts. Extensive research and practical experiments were conducted to prove the usefulness of SSPCM in removing ice from structures. Conventional methods for controlling icing are toxic deicing fluids, coatings that do not last long or removal by costly thermal and mechanical systems. Here the researchers used organophosphorous PCMs as ice-phobic coatings in the form of a SSPCM. Then large-scale experiments were conducted to validate that SSPCMs can address the larger problem of aerospace, marine, power transmission and telecommunication, which is formation of ice on the surfaces.

The way it works is that when this specific SSPCM whose heating cycle temperature is 0 degrees Celsius, expands and contracts at that temperature due to phase change, it puts stress on the ice interface. Due to this stress, the ice becomes weak and can be easily removed. During the testing, they coated SSPCM on a radome and its communication equipment (Figure 2)

and then blasted it with ice and snow. Most of the ice of thickness 12-20 mm that was accumulated on the structure came out automatically and rest was easily removable.

# Photovoltaic modules

In 2014, Honeywell International Inc. patented SSPCMs with a polyolefin backbone polymer and a crystallizable side chain for use with Photovoltaic (PV) modules. The backsheets of PV modules are commonly made of composites of fluoropolymers and polyethylene terephthalate (PET). These composites lose their effectiveness in very hot or humid conditions. To solve this problem, the use of SSPCM film in a PV module was proposed. The SSPCM heat absorbing cycle temperature will be set at a value such that it will store excess heat and keep the backsheets relatively cool, making the solar panel effective even in very hot and humid conditions.

# FUTURE DEVELOPMENT

With vast possibilities, SSPCMs may help create a sustainable environment and solve many energy issues, but it is still too early to adopt them in the real world. Further development is needed to make them widely and commercially available.



 FIGURE 2: SSPCM coating is applied on the communication equipment (left). Test radome with communication equipment (right).

 Image Source: Novel Phase Change Material Icephobic Coating for Ice Mitigation in Marine Environments, 12th Annual General



FIGURE 2: Ice coming off of the structure because of the SSPCM coating.

Assembly of International Association of Maritime Universities, 2012

Image Source: Novel Phase Change Material Icephobic Coating for Ice Mitigation in Marine Environments, 12th Annual General Assembly of International Association of Maritime Universities, 2012

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# PCMs in **Rewritable Data Storage Devices**

SUBRAT JAIN

# INTRODUCTION

The term PCM is generally used for a material that changes its phase by releasing or absorbing latent heat and that is their property/characteristic of interest for various heat storage applications. These materials typically do not possess any significant electrical properties. However, in this article we will discuss Thermoelectrical Phase Change Material where phase change takes place when electricity is supplied. Though they share the same name, their properties and characteristics are very different. This PCM is specifically intended for rewritable data storage applications. When a voltage is applied on certain types of phase changing alloys in their amorphous state, which is highly resistive, it converts into a conductive crystalline phase from heating induced by electrical resistance. When the voltage is removed, it remains in the crystalline state. To switch it back to its original phase, the alloy is melted and quenched very rapidly. This method makes the phase change process reversible. This concept, when used in data storage application, is named memory switching. And the term for this type of memory when used as Random Access Memory (RAM) is Phase Change Memory (PCM).

All phase change alloys until now are based on chalcogenide compounds. The two phases of chalcogenide alloys have different optical and electrical properties, the crystalline phase has a higher optical reflectance and electrical conductance than the amorphous phase and the heat to convert phases can be also generated via lasers (as in a CD/DVD reader). These different properties are used in optical and electrical data reading and writing, giving rise to Phase Change Memory where the "on" state is amorphous state and "off" is crystalline. During the 1970s when the first rewritable optical storage was created, the problem with them was that the phase change process from amorphous to crystalline was very long. The credit for the discovery of fast switching alloy goes to Yamada et al. in 1987.

PCMs have very useful combination of features such as fast access time, large electrical and optical contrast, non-volatility and high scalability. Before discovering PCMs for this application, these properties were not available in a single device or were not up to par with the fast paced development of other instruments around it.



**FIGURE 1:** Flexible Chalcogenide for electronic applications Magazine

Image Source: Opli, The Photonic Magazine

# CURRENT AND EMERGING APPLICATIONS

The most common application of Phase Change Memory has been around since 1990. Rewritable CDs, DVDs, Blu-rays and other such storage disks have a film of Phase Change Material, the transition of which is triggered by laser. Using the laser of the writer, the heat will be focused on the part of the disk that needs to store data and will make it crystalline. In this way a Phase Change Disk will store data. In the past decade, to increase the capacity and speed of these type of optical storage devices, the wavelength of laser has been reduced from red to blue, numerical aperture of the lens has been increased from 0.5 to 0.85 and number of layers per disk has also been increasing continuously. These "spec bumps" are the main reason the recording density has increased by 100 times and data transfer rate by thousand times. The most recent development in optical storage is super-RENS (super-resolution near field structure) that uses near-field recording. Near-field recording is a growing area of research in optical data storage.

Another application of Phase Change Memory is in electronic memory, which uses electrical voltage for phase change of alloys instead of lasers. As optical storage devices are close to reaching saturation point, the electrical properties of PCMs have attracted considerable interest. Though still in the research phase, they have huge potential in storage application due to their advantages, such as non-volatility, scalability, etc. The data storage application makes use of the stark difference in electrical resistivity in the two phases of PCM that can be used to read and write data. Currently, for computers and mobile phones, we are using flash memory for non-volatile permanent data storage and DRAM (Dynamic Random Access Memory) for fast but temporary storage. Flash memory is extremely slow comparative to DRAM but a Phase Change Memory can change all that. It is the most promising successor to flash memory as it has the speed of DRAM and non-volatility of flash memory. Although, in most cases the read and write cycle number for Phase Change Memory is still smaller compared to DRAM (~10<sup>16</sup>), some researchers have tried achieving a similar cycle number by scaling down the Phase Change Memory. Scaling feasibility is one of the strongest aspects of phase change memory.


Phase change memories can be a game changer in mobile and computer storage fields. It can technically replace RAM and flash memory with its powerful properties. Some of its advantages especially over DRAM and flash memory are:

- It requires smaller current for reading and writing
- PCM is non-volatile, whereas DRAM is volatile, which means a PCM does not require a constant power supply to retain information, while a RAM does.
- The random access time (read and write) for PCM is comparable to DRAM and much faster than flash memory. This way codes can be accessed directly from PCM without the need for RAM.

The current NOR and NAND flash memories are difficult to shrink in size and after years of upgrades, they have almost reached the limit of their shrinkability. But as PCM does not store charge, it does not need a charge storage structure like flash memory, which means Phase Change Memory has high scalability (up to nano-scale). Because of this, it provides high density, less space and superior performance.

- A Phase Change Memory does not require a separate erase step. Similar to RAM and unlike flash memory, the stored information can go from zero to one and vice versa without any additional steps.
- PCM has faster write and erase speed and much lower input-output delay than NAND flash.



**FIGURE 2:** On the left is the current standard of Solid State Drives using NAND memory, invented by Toshiba in 1989. In the future, this will be replaced by Phase Change Memories because of its various advantages. The chip on the right is developed by UC Sand Diego team and it is 2 to 7 times faster in reading and writing than current NAND flash memory. *Image Source: Toshiba and NVSL* 

#### CHALLENGES

The functionality of the phase change memory cell is decided by the material being used. PCM can make a Phase Change Memory cell superior or inferior by affecting factors like phase transition and switching speed, data retention, voltage requirements, etc. Even though it has numerous advantages, the technology would have to overcome some hurdles in order to set their base in the market. Some of these technical and non-technical hurdles are:

- A void can be formed in a cell over the bottom electrode contact, which can prevent the material from going into crystalline (lower resistance) state.
- The opposite is also possible. Elemental segregation of some elements in the PCM can prevent it from going to higher resistant amorphous phase. This will create the problem of data retention.
- A major thing to consider in order to be successful in the market is low cost and compatibility with CMOS processes.
- To run ahead in the race of rewritable data storage field, the factors that will determine the winner are high switching speed, large reading and recording cycle numbers, stability of the data stored and energy efficiency.
- PCMs will need high current density to erase the memory however if cell size is reduced, then the current required will reduce as well.

#### CURRENT STATUS

Due to the concerns of saturation of NAND's (flash memory like SSD) scalability, many companies are prototyping storage devices using PCM as it seems to be the main contender in replacing NAND soon. IBM's Project Theseus is about developing a hybrid storage system of NAND, PCM and DRAM. This system was demonstrated in 2014. In the same year, Western Digital also demonstrated an SSD that uses Phase Change Memories. The problem with both of these demonstrations and many other such developments is that their hardware is based on Micron's PCM and Micron has pulled out of PCM business at least for now. The top companies that have patents on PCM technologies are shown in the Figure 3.

Besides PCM, there are other data storage devices that can possibly be the next memory device in the future. Meena et al. did some comparison of the features of the following non-volatile memories (Table 1).



FIGURE 3: Number of patents applied by major companies developing PCMs *Image Source: UBM Techinsights* 

### TABLE 1: Feature Comparison of FeRAM, MRAM, STT-MRAM and PCM

Features	FeRAM	MRAM	STT-MRAM	РСМ
Storage Mechanism	Permanent polarization of ferroelectric material like PZT	Permanent magnetization of a ferromagnetic material	Spin-polarized current applies torque on the magnetic moment	Amorphous/ Polycrystal phases of chalcogenide alloy
Read time (ms)	20 to 80	3 to 20	2 to 20	20 to 50
Write/Erase Time	50/50	3 to 20	3 to 20	20/30
Cycle Number	10 <sup>12</sup>	>1015	>1016	10 <sup>12</sup>
Write Power	Medium	Med to High	Low	Low
Maturity	Limited Production	Test Chips	Test Chips	Test Chips
Applications	Low Density	Low Density	High Density	High Density

Meena et al. Nanoscale Research Letter, 2014



#### FIGURE 4: Future trend of various type of non-volatile storage (adapted from Meena et al., 2014)

In the same paper they have predicted the usage of different memory technologies. As we can see in the Figure 4, the requirement of data storage in the market is only going to increase. Although, various different technologies for memory storage are progressing at the same time, the competition in the future will be stiff between STT-MRAM, PCM and RRAM, whereas MRAM, although still present, will reach a stagnation stage.

#### FUTURE DEVELOPMENT

Phase Change Memory cells are not going to be limited to just data storage for computers, because of their property of electrical contrast, they have the possibility of being an artificial brain. Researchers are making attempts to design a neuromorphic computer that will have electronic hardware mimicking brain elements using PCM. The characteristic that makes this possible is that Phase Change Memory cells don't just consist of 0 or 1 binary resistance but can attain intermediate resistance levels as well. This characteristic can be used to program it to mimic the behavior of brain elements (e.g., synapse). This can make way for devices that can learn, adapt and associate like a brain.

PCM can be a revolutionary product in the memory market especially considering the requirements of smartphones are ever increasing and space constraints are applied very strictly. Although, for now the price of PCM is still more than NAND and the technology has not been thoroughly tested, which is preventing it from taking off.

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# Shape Memory Alloys

ALEXANDROS ATHANASIOU-IOANNOU

#### INTRODUCTION

Shape memory alloys are materials that can store energy in one of the oldest forms used by mankind, the mechanical one. As the material gets heated up, its stores the energy by changing shape. When the temperature changes again, the material re-elongates and gives back the energy – in a way analogous to a spring. How much energy can they store? That depends on the alloy, its geometry and how fast we want the material to change its shape. Shape memory alloys (SMAs) are metallic alloys that undergo solid-to-solid phase transformations induced by appropriate temperature or stress changes; during these transformations, they can recover permanent strains, "remembering" their initial shape. The most important families of these alloys are the NiTi, CuAlNi, although there are many other alloys exhibit these properties (i.e., iTiCu), as seen in Table 1.

#### TABLE 1: Main families of Shape Memory alloys.

Alloy	Composition	Transformation Temperature Range [°C]	Transformation Hysterisis [°C]
Ag-Cd	44/49 at% Cd	-190 to -50	15
Au-Cd	46.5/50 at% Cd	30 to 100	15
Cu-Al-Ni	14/14.5 wt%Al 3/4.5 wt% Ni	-140 to 100	-220 to 212
Cu-Sn	~15% at Sn	-120 to 30	
Cu-Zn	38.5/41.5% wt% Zn	-180 to -10	10
Cu-Zn-X (X=Si, Sn, Al)	Few wt% of X	-180 to 220	10
In-Ti	18/23 at% Ti	60 to 100	4
Ni-Al	36/38 at% Al	-180 to 100	10
Ni-Ti	49/51 at%Ni	-50 to 110	30
Fe-Pt	~25% at Pt	~ -130	4
Mn-Cu	5/35 at% Cu	-250 to 180	25
Fe-Mn-Si	32 wt% Mn, 6%wt Si	-200 to 150	100

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SMAs were first discovered by Arne Ölander in 1932, and the term "shape-memory" was first described by Vernon in 1941 for his polymeric dental material. Nevertheless, the importance of Shape Memory Materials (SMMs) was ignored until 1962, when William Buehler and Frederick Wang discovered the Shape Memory Effect (SME) in a nickel-titanium (NiTi) alloy. Since then, and for over half a century, new applications continue to be developed for SMAs and up to 2014, more than 10,000 U.S. SMA related patents have been proposed.

#### HOW DOES IT WORK?

The main working principle of SMAs is rather simple and illustrated in Figure 1. When the material is at lower temperatures, is under the form of martensite, which is the relatively soft and easily deformed phase of SMAs. When deformation occurs, this phase takes on the second form shown in Figure 1, on the left. When heated at higher temperatures (these temperatures depend on the composition of the alloy), the material transforms at austenite, the stronger phase of shape memory alloys. Austenite and martensite are also the names of steel phases, but here they are used in order to describe the crystal lattice change through a diffusionless transformation (a so called military) under different temperatures. Once the material is heated beyond a set temperature (or activated by other methods such as via magnetic field), it starts transforming into the austenite structure and reshaping (i.e., regaining its original form). This transformation is possible even under high-applied loads, and consequently, results in high actuation energy densities. During the cooling process, the transformation starts to revert to the martensite and at this state (and temperature) the SMA is permanently deformed like any ordinary metallic material.



**FIGURE 1:** Transformation of one austenitic grain to one grain containing many allotropes of martensite during cooling. The deformation introduces dislocations of crystal twinning, which favorises specific alltropes of martensite in favor of others. During heating, the thermal energy given to the crystal grain, is used for recrystallization of the material and the crystal grain regains its original shape, since now there are no dislocations to keep the previously introduced plastic deformation. *Image Source: EPFL* 

All these Shape Change Effects, which are known as the SME (Shape Memory Effects) and pseudoelasticity (or superelasticity), can be categorized as follows:

#### **ONE-WAY SHAPE MEMORY EFFECT:**

During this transformation, the SMA (OWSMA) retains the deformation, even after the mechanical stress, and then regains its original shape upon heating. The exact mechanism has been described before.

### TWO-WAY SHAPE MEMORY EFFECT OR REVERSIBLE SME:

During this transformation, the SMA can remember its shape at both high and low temperatures, upon special thermomechanical training (like spontaneous and external load-assisted induction). Nevertheless, this family does not concentrate commercial interest due to the 'training' requirements and to the fact that it usually produces about half of the recovery strain.

#### **PSEUDOELASTICITY OR SUPERELASTICITY:**

Here, the material is able to regain its original shape after applying mechanical loading at, without the need for any thermal activation. When SMAs are loaded in the austenite phase, the material will transform to the martensite phase above a critical stress (and this stress depends to the transformation temperatures). If the loading continues, the twinned martensite will start detwinning, permitting the SMA to undergo large deformations. Once the stress is gone, the martensite transforms back to austenite, and the material recovers its original shape. These materials can reversibly deform to very high strains – up to 8 percent.

### POTENTIAL APPLICATIONS

Possible sectors where the SMAs can find applications include aerospace (tailoring the inlet geometry and orientation of various propulsion systems, hingeless ailerons), automotive (in actuators and as vibration dampers), bioengineering (dodontics, stents, medical tweezers, sutures, implants, etc.), white goods (actuators and as acoustic and vibration dampers), civil engineering structures (in active vibration control and as fasteners), in micro-electromechanical systems (MEMS) (as actuators), robotics (actuators or artificial muscles), and even art and fashion. Although iron-based and copper-based SMAs (such as Fe-Mn-Si, Cu-Zn-Al and Cu-Al-Ni) are low-cost and commercially available, due to their instability, brittleness impracticability (e.g., and poor thermo-mechanic performance; NiTi- and CuAlNi based SMAs are preferable for commercial applications.



FIGURE 2: Golf clubs made out of shape memory alloys by Nicklaus Golf Equipment Company Image Source: Nasa SpinOff

#### LIMITATIONS AND CHALLENGES

Nonetheless, several limitations exist that prevent for the time being the extensive use of SMAs in commercial applications. One well-documented issue is the response of a SMA when it has undergone multiple transformation cycles. The issue of material stability is open for many SMAs families and until now, only SMAs that have developed a sufficiently stable thermomechanical response via repeated training cycles appear as a solution.

Another open problem is the limited frequency of response the difficulty in rapidly transferring heat into and even more, out of an SMA element. By being alloys, SMAs have relatively high heat capacity and densities, resulting in also high thermal diffusivities. This results in limitation of repeated actuation of SMA elements, and therefore to limited frequency of system response. The material mechanisms may be diffusionless (and take place almost instantaneously), the time-dependent process of changing temperature that drives the diffusionless transformation sets limits on actuation speed.

Finally, there are challenges because the information available to design engineers is not transparent and easy to digest. The majority of models demand a high level of metallurgy, and consequently, a close collaboration between material scientists and engineers is demanded, which is not always easy or practical.

#### FUTURE DEVELOPMENTS

Despite the existing limitations mentioned before, the advantages offered by SMAs are appealing and new applications will continue to appear as this field continues to grow and the cost of materials continues to fall. Development of new material families, design approaches and information platforms will give this sector a boost. The medical industry seems to be a key driver of this trend. The "smart materials" market worldwide is growing at a strong pace, and will continue to grow into the foreseeable future. BCC research reported that the global market for smart materials was about \$19.6 billion in 2010, and predicted overpassing \$40 billion in 2016. Since SMAs represent a percentage close to 15 percent of the smart materials market, the future is forecasted bright for this class of phase change materials.

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# PCMs as Magnetocaloric Materials

ALEXANDROS ATHANASIOU-IOANNOU

#### INTRODUCTION

Magnetocaloric materials, which have a curie temperature near ambient temperature, are of significant interest due to their possible application for high-efficiency, environmentally friendly heat pumps and refrigerators. Advantages of this solid-state technology are the lack of the volatile refrigeration gases used in conventional refrigeration cycles, and the prospect of recycling materials and magnets at end-of-life. This makes the technology attractive from an environmental point of view. Furthermore, the lack of compressive devices makes magnetic refrigeration able to be built more compact and to produce less noise during operation. Another key difference between vapor-cycle refrigerators and magnetic refrigerators is the amount of energy loss incurred during the refrigeration cycle. The cooling efficiency in magnetic refrigerators working with gadolinium has been shown to reach 60 percent of the theoretical limit, compared with only about 40 percent in the best gas-compression refrigerators. The concept of near-room-temperature magnetic refrigeration using the magnetocaloric effect, originates from 1976, when GV Brown, not only suggested that gadolinium would be suited for such an application but also demonstrated a laboratory device as a working proof-of-concept.

Research in magnetocaloric materials and their application in refrigeration devices and heat pumps has been a rapidly growing field for the past 20 years, if not longer. The most important material groups that show promise for actual application and with an emphasis on materials that can be used for graded regenerators are:

- (1) Gd and its alloys
- (2)  $Gd_5Ge_2Si_2$  and similar compounds
- (3) La(Fe,Si)<sub>13</sub> and similar compounds
- MnAs and similar compounds
- (5) Manganites



FIGURE 1: Mechanical Drawing of the US Patent, no 4069028A by GV Brown, referring to the first magnetocaloric refrigeration device *Image Source: USPTO* 

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#### HOW DOES IT WORK?

In its simplest form, the magnetocaloric effect consists in a reversible temperature change experienced by a magnetic substance upon adiabatic magnetization or demagnetization. This can be qualitatively explained as the interplay between the electrons' spin and the lattice of the material, through their degrees of freedom upon magnetization the spins order, causing the magnetic entropy to decrease. Under adiabatic conditions, must be compensated by an equal but opposite change of the entropy associated with the lattice, resulting in a change in temperature of the material. Alternatively, under isothermal conditions the substance will experience a change in entropy corresponding to a flux of heat to its surroundings. In theory, all magnetic substances exhibit the magnetocaloric effect. Nevertheless, it is mostly exhibited for materials near magnetic phase transitions where even a small external field can change the spin state significantly. Consequently, except at very low (sub-kelvin) temperatures where paramagnets can be utilized, the relevant magnetocaloric materials for cooling purposes are magnetic materials with a transition temperature near the temperature region of interest.

The amount of heat exchanged during this process depends on the structure of material, its geometry and the applied magnetic field.



FIGURE 2: Schematic representation of the working thermodynamic cycle during magnetocaloric refrigeration *Image Source: ScienceNordic* 

#### FURTHER DEVELOPMENT

Up till now, there has not yet been a commercial application. There are however, several new material classes with promising characteristics, and a recent device review counted more than 40 working lab devices reported in the literature. At least two additional companies, Cooltech Applications in France and Camfridge Ltd in the UK, have presented working prototypes. The first, founded in 2002, based in Holtzheim (near Strasbourg) has filed more than 270 patents and has spent more €30,000,000 (\$43 million in U.S. dollars) in research and development. The second, started in 2005 as a spin-off from Cambridge University, is based in Cambridge and has Cambridge CapitalGroup and the University of Cambridge as its principle shareholders.

An open challenge remaining is fully delving into the interrelation between microstructure, shaping and performance of magnetocaloric materials, if they are to be used commercially. This is also relevant to the problem of how to achieve an optimal grading of the regenerator properties, which is a difficult task. Finally, the device concepts also need more work. As of now, the most promising direction for continued device development remains the active magnetic regenerator is porous, allowing a heat transfer medium (typically helium gas) to flow through it. However, this concept is mainly limited by the temperature span of magnetic refrigeration ( $\Delta$ T~9 degrees Celsius).

Nonetheless, even at this poor present state of the science and technology of room-temperature magnetocalorics, we are at the cusp of renaissance for magnetocaloric applications and breakthroughs are coming.

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# PCMs: A Bright Future

LINDSEY PARKER

The arguably ambiguous term "phase change materials" (PCMs) belies the reality of a class of substances of unrivalled versatility, with PCM solutions ranging from construction to medicine. This myth-busting article attempts to address key misconceptions surrounding PCMs.

#### Myth 1: All PCM materials are "high tech"

In the first instance, the concept of phase change materials gives the impression of highly complex, unfamiliar technology. However, in reality a variety of materials may find uses as PCMs – some of which we already use at home.

To be considered a phase change material, a substance must be capable of releasing or absorbing large amounts of latent heat upon phase transition. The amount of energy involved is determined by the type and quantity of bonding formed between individual molecules. This bonding — termed intermolecular bonding — is distinct from and significantly weaker than the intramolecular bonding that maintains connectivity between atoms within a molecule. Stronger types of



intermolecular bonding, such as the hydrogen bonding found in water, store larger amounts of energy and hence release more latent heat on phase transition. Thus the simplest of temperature regulation technologies – the humble ice cube – can be described as a PCM as it liquefies and cools your drink.

#### Myth 2: PCMs are expensive

Like all new technologies, concerns surrounding the cost of implementation of PCM technology abound. In fact, PCM materials may serve to significantly reduce energy consumption.

Perhaps the most obvious use of PCMs is in temperature control – PCMs have a thermal storage capacity of 5-14 times that of conventional building materials and can be incorporated into buildings via flooring, walls, roofs, insulation materials, and even furniture. The European Union estimates that buildings account for 40 percent of the total energy consumed in the region, with temperature control being responsible for the majority of this. Statistics for the US tell a strikingly similar story.

Phase change materials may reduce energy bills by storing electrical energy as latent heat during off-peak times for later release. In many countries, including the U.S., energy fees are up to 50 percent lower during times of low usage. Air conditioning or heating appliances could be used solely during cheaper periods, recharging the PCM for climate control during higher fee periods. Similarly, the heat storage capacity of PCMs allows the natural temperature variation between night and day to be harnessed, drastically minimizing energy consumption. In one study, the inclusion of PCMs in the fabric of buildings reduced a daily temperature variation of 4 to 12 degrees Celsius, saving vast amounts of energy. At Explore -At-Bristol, a technology museum in the U.K., 40,000 PCM balls work in concert with a heat pump for climate control. During summer nights, the roof-mounted electric heat pumps use cheap-rate electricity to remove heat from the ball tank, causing the encased PCM to freeze. As the temperature of the building increases during the day, the balls melt and store excess heat energy. In winter, the heat pumps work in the opposite manner: night-time electricity is used to melt the balls, which release latent heat after the pumps are switched off and the temperature drops.

Additionally, solar panels have long been touted as a green, energy saving solution, but concerns have persisted, with units taking considerable time to recoup installation costs. While electricity must be supplied when needed, solar panels are only operational during the day, reducing their utility. PCM materials offer improvements over conventional batteries in solar panels and can generate at least three times more power by generating electricity during cold, dark periods using a thermoelectric device.

#### Myth 3: PCMs are used only for energy applications

Finally, although phase change materials are characterized by their large latent heats and show potential in green energy applications, they show potential in many industries in which other key properties may be harnessed.

Energy storage solutions, the most obvious application for PCMs, make use of latent heat. However, there are a number of high-technology challenges that may be met with PCMs that capitalize on other properties. Most PCMs operate through solid-liquid phase changes, but solid-solid transition PCMs are widely used in household items such as DVDs. As described in more detail in an associated article, materials may undergo crystalline-amorphous phase changes that alter their reflectivity, allowing the encoding of optical information in the form of our favorite movies. Nontoxic PCMs, such as the fatty acids 1-tetradecanol and lauric acid, have been explored as targeted, temperature-sensitive drug carriers, since inflamed, infected and cancerous tissues are known to have elevated temperatures. Conventional chemotherapy drugs are known to also kill tissues targeted drug delivery using PCMs could leave cancer patients with fewer adverse effects.

The sharp melting point and unique thermal signatures of PCM nanoparticles can be combined with chemical/biological species for the detection of disease markers for improved detection. Differential scanning calorimetry, a method in which the melting of substances within a range of temperatures is recorded, can be used to detect the presence of disease after the addition of PCM particles. Using these same principles, miniaturized thermal barcodes can be produced that give rise to unique thermal profiles when attached to objects. In this application, a combination of different particles would be used to give a "signature." The use of just 50 different particles gives rise to a thousand trillion possible different combinations, with obvious benefits in security and law enforcement.

Like many new technologies, PCMs will suffer from misconceptions until the general public becomes accustomed to their use. In this article and the remainder of the report, we highlight that many of these concerns are unfounded, and that the benefits of embracing this technology far outweigh any caveats.

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# Interview Section

## INTERVIEW WITH **DR. ANOOP MATHUR,** TERRAFORE TECHNOLOGIES



**Microencapsulation and Thermal Energy Storage Application** 

Mr. Anoop Mathur is CTO and founder of Terrafore Technologies, LLC. Prior to founding Terrafore Technologies, he was the Director of Honeywell Automation and Control Systems global advanced technology laboratories, managing research groups in the U.S., China, India and Romania.

Mr. Mathur holds a master's in Chemical Engineering from University of Minnesota, an executive MBA from Carlson School of Management, MN, and an accelerated program on Global Enterprise Management from Thunderbird School of Management, AZ. Mr. Mathur has over thirty-five years of experience developing and managing diverse advanced technologies including predictive controls, energy systems, sensors, neural networks and advanced composite materials. Several of the innovative technologies he led at Honeywell have led to at least six new products including the recently developed secure reliable wireless mesh sensor network technology OneWireless™ product for monitoring and control of industrial process. He designed parabolic trough collectors, concentrating PV systems, and thermal energy storage using molten salts and holds over twenty patents including four on thermal energy storage.

#### Please give us an overview of the development of the EPCM capsules designed for TES application at Terrafore.

Terrafore was established in 2007 and we work on microencapsulated salt as phase change materials. Salt is used as phase change material because of its high energy density, however, it has one disadvantage that makes it less attractive as thermal energy storage material: it has low thermal diffusivity, meaning it is hard to transfer energy in and out of the material.

We tried to solve this problem, and encapsulation will be a good solution since the small capsules have very large surface area to volume ratio, which enhances heat transfer. Although encapsulation has been widely utilized in different industries, making capsules for the salt at high temperature has never been done since the salt expands in volume at elevated temperature. After more than 100 experiments to test different materials and methods, we have identified a polymer, together with some additives that can be used for salt encapsulation. Basically, this polymer forms a sacrificial layer between salt and the encapsulating clay material. The polymer melts away during encapsulation, which creates a void space that allows salt to expand. We have tested its stability and it remains stable after 5,000 thermal cycles (for an expected duration of 30 years of the PCM, at least 10,000 thermal cycles are needed).

#### Have you scaled-up the fabrication process of the capsules?

We are waiting for funding to support the scale-up process. There is no fundamental scientific issue for mass-producing these capsules. The only issue would be in the scaling-up itself, such as reactor design and process control.

#### Could you please make some comments on the cost of making these capsules?

These capsules are very cost effective. They cost 30-40 percent of the conventional heat storage material. An added benefit of these capsules is that they can be used for transferring and storing energy from steam, which is a great energy source. Currently no one is harvesting energy from steam due to the difficulty of dealing with the steam, but the microencapsulated PCM will able to do that.

#### Are you working with any industrial partners on the development of this technology?

We are in the process of talking to several potential partners who are interested in this technology.

#### What is the status of the project with the U.S. Department of Energy? What is the future plan?

This project has concluded. We have successfully demonstrated the fabrication of the microencapsulated salt with the sacrificial polymer layer and its durability. The next step is to build a full-scale plant, once we secure enough funding, we expect the plant to be built and in operation in 18 months.

## INTERVIEW WITH **MARIA ANGELES BONET**, UNIVERISTAT POLITÈCNICA DE VALENCIA.

#### **PCMs in textiles**



Maria Angeles Bonet Aracil obtained her Bachelor from Universitat Politècnica de València (UPV) and then moved in Universidad Politécnica de Catalunyafor her master's studies. She came back to València for her doctorate, during which she worked both for UPV and a private textile company. After completing her doctoral thesis, she joined the UPV in the Department of Textile and Paper Engineering (DITEXTPA). Her research interests focus on how microencapsulation, enzymes, nano particles or any other finishing can be incorporated in textiles. Her work in textiles has also lead to one European Patent and videos of her lectures in UPV can be found in YouTube (in Spanish).

#### What is the biggest obstacle, that prevents the implementation of PCMS into textiles, from thriving?

I wouldn't say there is only one obstacle. PCMs are microparticles comprised of a wax (active core) protected by a polymeric shell. One of the main properties of wax is the ability of changing the state depending on the temperature. In this process, energy is released or absorbed. Knowing that the wax can become a liquid, the polymeric shell must prevent the wax to be spread around the surface where it has been placed. The shell should be strong enough to resist the requirements it is exposed to. Textile products can be used in a wide variety of applications and the PCM must resist at least all the lifespan.

The benefits of PCM are consequence of the property of wax to change its state. However, the main setback could be that the range of temperatures depends on the wax characteristics and energy exchange occurs at a constant temperature. Thus, makes them suitable only for specific situations and cannot be effective in the vast range of temperatures textiles can be exposed to.

Another inconvenience is the cost; it increases the price of the textile considerably and should be used in garments that cannot be sold in a cheap market.

Finally, I would reflect that fibers are not heat conductive, what means they must be placed in the outer part of the fibers or in their surface.

#### In how many years do you believe we could see large-scale commercial applications?

Sincerely, I do not know exactly. In the past, ten years ago, I was convinced that microcapsules were going to become really important, and many sectors would profit from their benefits. However, it has been in the last two years when I could see companies considering their use seriously.

#### Could you name two sectors that can benefit significantly from this technology?

The main benefit of including PCM in textiles is the protection to the human body form quick changes in temperature. Obviously, I would say that jobs dealing with this situation would accept it gratefully. But not only jobs, outdoor leisure activities can be an interesting field to use them, mainly sports in extreme situations, bed linen, etc.

#### How do you imagine the consequences of this technology in 75 years from now?

Well, it can be really difficult to answer this question as science evolves considerably fast. Imagine that microcapsules have been known for more than 60 years, and there are many research groups working on the subject. Thousands of experiences are conducted in the laboratories in order to discover new applications or properties of the materials. What I can be sure about is the fact that they will be improved, for example would be made of different cores increasing the ranges of temperature, or the shells would be reactive with some surfaces. Consequently, new applications would be performed and perhaps they will allow textiles to be used in new fields. They are likely to be applied in challenging fields such as medicine or the storage of energy.

#### Do you believe it is possible to see, in some years, in haute couture shows, garments using this technology?

Well, why not? But always provided the improvement in their efficiency and their effect should be more sensitive. Otherwise it won't be accepted by users.

## INTERVIEW WITH **DR. SAID AL-HALLAJ,** ALLCELL TECHNOLOGIES

#### PCMs for thermal management of batteries



Dr. Said Al-Hallaj is the Chairman and CEO of AllCell Technologies LLC. Prior to AllCell, Dr. Al-Hallaj was a Research Professor of Chemical Engineering and Coordinator for Renewable Energy Programs at IIT.

Dr. Al-Hallaj earned his bachelor's and master's degrees in Chemical Engineering from Jordan University of Science and Technology and a doctorate in Chemical Engineering from IIT. He has published over 30 technical peer-reviewed journals and over 20 conference papers. Dr. Al-Hallaj is the co-author of four issued patents and several patent applications in the area of energy storage and conversion with emphasis on renewable energy, hydrogen, batteries and fuel cells for stationary and transportation applications. Said's efforts have led to the formation of two start-up companies at IIT: AllCell Technologies, to commercialize lithium-ion batteries for portable and transportation applications, and Sun Phocus Technologies, to commercialize a hologram plan concentrator (HPC) technology in the building integrated photovoltaic (BIPV) market.

# Could you please give us an overview of AllCell and its work? Specifically, for thermal energy storage for battery using PCMs?

AllCell is a lithium-ion battery manufacturer and assembler for advanced applications where energy storage requirements are extreme for power to energy ratio, heat rate and environment. We specialize in high-end application specialty products, our key technology is the phase change composite that allows us to pack high energy density cells safely and enhance performance and cycle-life.

#### Can you give us some background on how this technology was developed?

The technology itself was developed at the Illinois Institute of Technology (IIT). 20 years ago IIT received one of the first and largest lithium-ion battery research grant from the Army's research office to develop power pack for Solider of Future program. We looked at lithium-ion battery and direct methanol fuel cell, and we discovered at the time that lithium-ion batteries have safety issues that need to be addressed. We developed the phase change composite materials at IIT, when I finished my Ph.D. study; I joined IIT as a research professor and also started AllCell and licensed the technology back from IIT to commercialize it.

# Your technology seems most suitable for lightweight electric vehicles like scooters. Following your success with Matra, do you now expect a rise in demand for your PCM-enhanced batteries in the electric scooter market worldwide? Are there still some hurdles?

There are two aspects to this question, we actually work on several high profile programs with leading companies who are introducing new light-weight electric vehicles (LEV, scooter being one type), but in the fully electric market, we are working on 2-3 programs that will be launching at large scale with big companies this year and next year.

On the technical side, the requirement that we are getting more and more from the industry for premium application is that people want really high energy density. For example, for scooter application, people are looking for energy density greater than 200 Wh/kg, which is 50-70 percent higher than what everyone in automotive industry has. The second thing is that the industry is looking for very high C-rate ratio, which means that the battery power needs to be pushed very high, which is critical for lithium-ion because it generates a lot of heat.

The combination of high power to energy density ratio and high C-rate means that battery at high energy density is needed. At that point, packing them together becomes big problem for safety and thermal management. AllCell's technology is very well suited to solve this problem; we have been working with leading developers (both on the battery side and application OEMs) to demonstrate that this problem can be solved by using our technology, in combination with high energy density cells.

The other problem is the nature of the business; most of the LEV market in the world (outside Europe and US) is driven by cost. To save cost, people would cut corners. For example, the safety requirements might not be as stringent, and a lot of incidents happen because of low engineering and low quality of design, either on the cell or the package. There were several recalls in the past 2-3 years for both e-bikes and e-scooters because of safety issues.

For us, as a start-up and small company, we focus on application where people are developing premium products with the highest technical performance in terms of energy density and high safety performance. That is where AllCell has a very strong value proposition and very competitive.

### What challenges do you face while entering markets of full-sized electric vehicles and renewable energy storage? When do you expect to establish ground in these sectors?

The first thing AllCell assessed was what our strength is and where we can be competitive in the market. It was clear that for us (a start-up company) that even with good engineering and good technology, it is hard for us to compete in the automotive market since it has a very long development cycle and a very small margin. So we licensed our technology to a large company who has been working on it with some progress. We decided at the time that we would focus on two markets: LEV and renewable energy, where we have very strong competitive advantages.

## So is it fair to say that currently, the full-sized electric vehicles are not the targets of AllCell's and you are not expecting to establish ground in this sector in the near future, say in 2-3 years?

That's accurate. We have R&D programs and industry collaborators for automotive applications, but they are not our commercialization targets for now and they are not entering the market anytime soon.

#### Which other market players or technologies could potentially compete with your product?

There are two direct competitions for us. One of them is alternative cooling technology. Typically, these are active cooling such as liquid cooling and air-cooling. But for LEV market, these are not even options since it is hard to have active cooling system in the scooter, so we have advantage in this market. On the non-engineering side, the other challenge is that when companies are trying to develop inherently safe material for lithium-ion battery (for example, material that doesn't catch fire, cause safety issue or heat up), they are mainly working towards solid state electrolyte, which is very promising technology, but it is still at early stage and we feel for the next few years this will probably not be in direct competition yet, but it will be in the long term.

# What are the technical challenges that need to be overcome for establishing PCM-based thermal management in electrochemical storage devices?

There are two major challenges.

One of them is material development. Companies and customers that use batteries need more and more energy density, which means there is less and less room to play in the pack. At the same time, increase the energy density within the cell means the thermal management needs are increasing exponentially. That means we need to continue inventing new PCM with higher latent heat. AllCell works closely with key players in the PCM market for developing new material with higher latent heat. We have increased the latent heat of our PCM by 30 percent in the last two years and we are testing new material with 50 percent increase that we should be able to introduce in the next 2 or 3 years.

The second one is scalability, although AllCell has been in the large-scale commercial market in the last couple of years, we are at a scale of several thousand packages per year. With the potential of our technology, within the next 5-10 years we are expecting tens of thousands per month to meet the high demand of our customers. We need to find a way to scale our processes, continue to increase the quality, increase the efficiency and reduce cost.

#### Are you currently working with any partners on scalability?

Yes. The good news for us is that our suppliers are big companies and we are opening a new market with new applications for them, as we grow, they continue on investing for developing new manufacturing technologies to help us to scale our production, which is very helpful for us.

#### Can you make some comments on the cost of using PCM?

We have demonstrated that batteries with our technology have a 50-100 percent increase in battery life and we can guarantee the safety, even if a bad quality battery is used. For these two key value propositions, the additional cost is about 5-10 percent for adding our technology to the battery.

#### INTERVIEW WITH NEIL WILSON, CAMFRIDGE



#### **Magnetocaloric Materials**

Dr. Neil Wilson is the founder and CEO of Camfridge. Dr. Wilson holds a doctorate in Physics from the University of Cambridge, following a bachelor's in Physics from Edinburgh, and an MBA from Collège des Ingénieurs. He previously worked as a civil servant, spending 2 years with HM Customs & Excise, and then 2 years with HM revenue & Customs. He has also worked in the private sector as a consultant for Philip Morris and Microstrategy Inc.

#### In your opinion, what is the biggest obstacle that prevents this technology from thriving?

The biggest obstacle is cultural – getting the existing refrigeration and cooling industry to constructively engage which is key to reaching scalable production at the right quality and cost.

#### In how many years do you believe we could see retail store, selling refrigerators using magnetic refrigeration?

We estimate the product can be in the shops in 2020.

#### Can you name two sectors that can benefit significantly from this technology?

Domestic refrigeration appliances and commercial beverage cooling appliances.

#### How do you imagine the consequences of this technology in 75 years from now?

Refrigeration and cooling will still be critical in 75 years' time. Magnetic cooling, certainly for sub-10kW applications, should be ubiquitous. Advances in materials may make device designs even simpler.

# Do you believe that it is possible to see a Nobel Prize rewarded to scientists because of their work in magnetocaloric refrigeration?

If there was Nobel Prize for Engineering (which there isn't) then certainly this is high impact technology that would be in the running. The underlying physics is 100 years old, and the relevant physics Nobel prizes in the areas of magnetism and phase transitions have already been awarded. However, there is perhaps opportunity for Chemistry Nobel for a fundamental breakthrough in the materials area.

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# About the Authors



**DR. SIWEI ZHANG** is currently a postdoctoral research associate in the Feinberg School of Medicine, Northwestern University in Chicago, IL. Raised as a cell and developmental biologist by heart in the University of Manchester, England, he has accumulated approximately ten years of experiences with the field of neurobiology, signaling, cytoskeletal dynamics, and advanced microscopy. Dr. Zhang has published over 10 papers during his career in science and has been cited for numerous times. Recently, Dr. Zhang's research interest focuses on the fate determination and pluripotency of neural stem cells during early embryo development.



**DR. GREG PILGRIM** is a materials scientist focusing primarily on fabrication and application of nanostructured systems. He earned his doctorate at the University of Rochester for work on carbon nanotube based membranes for solar energy conversion and storage.



**VIKAS PATIL** graduated recently with a master's degree in Energy Science and Technology from the Swiss Federal Institute of Technology (ETH) at Zurich, where he worked on topics related to solar thermal and thermo-chemical energy technologies. He obtained his bachelor's degree in Mechanical Engineering from the Birla Institute of Technology and Science (BITS) Pilani, India. He has completed multiple academic projects and industrial internships broadly in the field of renewable energy technologies. His research interests include engineering thermodynamics and heat transfer, especially with applications in sustainable energy and thermal energy storage.



**DR. XINZHI ZHANG** obtained her bachelor's degree in chemical engineering from University of Toronto and her doctorate in biomedical engineering from Columbia University, where she worked on designing, characterizing, optimizing and evaluating a novel biomimetic scaffold for orthopedic soft-hard tissue regeneration.

Xinzhi joined PreScouter as a PreScouter scholar, and is now working as a Research Scientist at PreScouter.



**XIN YAN** is pursuing a doctorate in the field of computational material science at the University of Houston. In her research, she is using traditional MD simulation method combined with sampling method that has the potential to break the time scale limitation in traditional MD simulation to study lithium-ion diffusion and mechanical behavior in LiSi electrode.



**DR. ALEXANDROS ATHANASIOU-IOANNOU**'S research focuses on manufacturing an integrated heat sink to cool power electronics, using aluminum foams. The project aims to offer efficient solutions in terms of cost, space and power in the challenging field of electronic packaging and is industrially funded. Among other accomplishments, he designed a sea wave harvesting device, which won an Innovation Award from NTUA and a Best Poster prize from EPFL. Alexandros received a degree in Mechanical Engineering from NTUA in 2010 and a master's in Nanoscience in 2011 from École Polytechnique in Paris (during which he was a recipient of a scholarship from La Fondation de I'X). He is currently finishing his thesis in LMM laboratory of École Polytechnique Fédérale de Lausanne.

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**DR. MING ZHANG** obtained his doctorate in Chemical Engineering in Texas A&M University and currently he is a postdoctoral fellow in University of Akron, Department of Polymer Engineering. He has worked on many projects in the areas of nanotechnology, surface science, and material science for the application in Healthcare, Food safety, Environmental Science, and Oil & Gas. Dr. Zhang has published 10+ referred journal articles and Dr. Zhang has been invited to service as a reviewer to review manuscripts for publication for 40+ times for 10+ journals. Meanwhile, Dr. Zhang is a guest editor for International Journal of Polymer Science. Dr. Zhang joined PreScouter in Jan. 2014 and he has worked with 30+ companies on advanced technology in fields of Healthcare, Materials, Energy, etc.



**DR. ADITI JOSHI** received her doctorate from the University of Oregon in Human Physiology, and her research work has focused on the mind-body interactions. Further, she has conducted postdoctoral research work at the Department of Neurology, University of California at Los Angeles. She studied emotional reactions to stress in the patients with dementia. Her work was presented at prestigious conferences such as American Academy of Neurology.

She joined PreScouter as a global scholar and has worked on over 20 PreScouter projects. She has often contributed articles to the PS journal. Currently, as a Staff Scientist at PreScouter, she analyzes in detail technologies that are potential solutions to the business problem and provides unbiased reports.

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**SUBRAT JAIN** graduated with a Master's degree in Mechanical Engineering from SUNY at Stony Brook, NY which was in continuation to his undergraduate studies in the same field from University of Pune, India. Currently, his full time job is as a Mechanical Design Engineer and in some of his remaining time, he writes technical and engineering related articles. Subrat has strong interest in product designing and he has built a walking device as a part of his research project, which was featured in one of the TEDx Stony Brook talks. Kinematics of linkage systems was a major part of his research during the Masters program.



**LINDSEY PARKER** atained a first class bachelor's and master's degree in Chemistry from the University of Leeds, and is currently completing her doctorate in tissue engineering and regenerative medicine, at the same university. During her academic career at the University of Leeds she has completed research projects in protein surface behavior, the production of composite crystals and stem cell mechanobiology, in addition to a research secondment in stem cell culture on gels at the University of Pennsylvania.



**DR. MARIJA JOVIC** obtained her master's degree in Chemical Engineering from Belgrade University and completed her doctorate in Organometallic Chemistry and Catalysis at Swiss Federal Institute of Technology (ETH Zurich). Marija's research was focused on understanding reaction mechanisms in order to rationally design catalysts for polymerization and metathesis reactions. Prior to her doctorate, Marija worked in industry on synthesis of new textile dyes. She was part of the PreScouter's Global Scholar Network before moving into a full-time role. She now provides scientific advice and manages projects for PreScouter.



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