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# Non-eutectic Phase Change Materials for Cold Thermal Energy Storage

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## Abstract

Phase change materials provide high-density thermal energy storage and a wide range of temperatures are required to meet different storage applications for cascaded thermal storage systems. Thus, non-eutectic phase change materials, namely aqueous ethylene glycol and ethanol solutions, are investigated in this paper for potential applications in high-grade cold thermal energy storage applications. The aqueous solutions of varying concentrations are characterized by differential scanning calorimetry and thermal response measurements for bulk PCMs. The phase change materials are able to meet a wide range of storage temperatures with no issue of phase separation. Graphene oxide powder of 1 wt.% is added as a stable nano-filler to enhance thermal conductivity and reduce supercooling degrees. Through thermal response measurements, improvements of charging times in the phase change of aqueous ethylene glycol and ethanol solutions are observed.

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*Keywords:* phase change materials; cold thermal energy storage; differential scanning calorimetry

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## 1. Introduction

Cold Thermal Energy Storage (CTES) systems have been applied to district cooling systems to meet

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increasing cooling demands arising from affluent modern lifestyles that emphasize the use of air-conditioning and refrigeration [1]. For higher grades of cold, CTES systems may be used for the recovery of high-grade waste cold energy in LNG regasification plants [2], expansion of CO<sub>2</sub> gas in a carbon dioxide-based Rankine cycle, deep freeze manufacturing processes [3], and as cascaded cold storage in liquid air energy storage which is a promising green energy vector [4]. There are three types of CTES systems: Sensible heat, latent heat and thermochemical storage [3, 5-7]. Among these three types, latent heat storage systems are found to meet the widest range of cold applications (< 20 °C) [3]. Most latent heat storage systems utilize high latent heat of fusion during the reversible phase transitions of materials from liquid to solid states to enable high storage densities. The main advantage of this nature of phase change is a smaller storage mass at almost constant pressure. The storage materials used are known as Phase Change Materials (PCMs).

This paper investigates the thermo-physical properties of a group of non-eutectic phase change materials based on aqueous ethylene glycol and ethanol. Aqueous alcohols may address a wide range of temperatures for CTES systems, but there are few studies that reported on the properties of aqueous alcohols. While there are more than a hundred materials listed as potential PCMs, all materials display either one of the several problems. These includes long-term stability, corrosion, low thermal conductivity, supercooling, and phase segregation [3]. PCMs for the mid-grade to high-grade cold are limited to eutectic salt water solutions and commercial PCMs because of a general lack of materials that can phase change at these extreme temperatures [8]. Organic alcohols form a category of PCMs that can meet a wide range of sub-zero temperatures [8]. They are, similar to salts, used as freezing point depressants of water and frequently found as anti-freeze heat transfer fluids in automotive and industrial applications. Kumano et al. [9, 10] has compared a number of solutions (ethanol, ethylene glycol, propylene glycol, NaCl and NaNO<sub>3</sub>) for ice slurries and among them, aqueous ethylene glycol (EG) was highlighted to have good potential [8]. However, Kumano did not evaluate these materials for CTES systems beyond -30 °C. There has been limited research to demonstrate aqueous alcohols as a PCM candidate for high-grade cold temperatures even though ethylene glycol and ethanol has eutectic points of -50 °C or lower [11]. Only one paper has studied the latent heat and freezing temperatures of aqueous EG solutions, compared it with glycerol aqueous solutions for up to 45 wt.% and showed a significant supercooling degree for both solutions beyond 25 wt.% [12]. The use of 70 wt.% aqueous EG solution as PCM in a small scale CTES through CO<sub>2</sub> based rankine cycle was reported, although no thermal properties nor the thermal performance of the PCM was mentioned [13].

## Nomenclature

$L_f$	latent heat of fusion (kJ/kg)
$T$	temperature (°C or K)
$t$	time (s)
$r$	ramp rate (K/min)
wt. %	weight percentage (wt.%)

## Abbreviations

EG	ethylene glycol
PCM	phase change material
CTES	cold thermal energy storage
DSC	differential scanning calorimetry
GO	graphene oxide

The challenges in a PCM CTES system often stem from some of the above-mentioned properties of PCMs. The PCMs investigated in this paper are considered for their advantages. These phase change materials do not suffer from phase separation at non-eutectic concentrations and thus, different temperatures may be formulated from different temperatures. This will be important in multi-stage thermal energy storage systems where some studies have reported on a faster thermal charge/discharge rate [14]. As they are less corrosive than the aqueous salt materials, they

can be macro-encapsulated in metallic containers which are preferred materials at cryogenic temperatures. Metallic fins may be included to improve their heat transfer rates. These advantages indicate that these PCMs may be excellent candidates for cascaded energy storage systems that enable high heat transfer rates for cold energy recovery applications. However, the thermal conductivity of aqueous alcohols PCMs are usually low and this may be a bottleneck in TES systems, reducing charging power of the systems. Thus, the effects of graphene oxide powder added to aqueous alcohols are investigated in this paper. This carbon nano-filler has been mentioned in literature as a stable enhancement to phase change materials [15].

## 2. Methodology

Ethylene glycol (ethane 1-2 Diol, 99% purity) and ethanol (absolute, reagent grade) were purchased from Merck Millipore in Singapore for the formulation of varying concentrations of aqueous alcohols PCMs. Graphene oxide powder (graphene oxide powder, purity > 99 wt.% and particle size: 0.5 to 3  $\mu\text{m}$ ) was purchased from Timesnano in China to be added into the PCMs. Homogeneous graphene oxide suspension (1 wt.%) was prepared by adding 101 mg of the graphene oxide nano-filler into a glass bottle containing 10 g of PCM. This was followed by vigorously mixing for several minutes by a vortex mixer. The suspension was further dispersed in the PCM using an ultrasonic bath at room temperature for about three hours. The ultrasonic bath's temperature was kept cool using ice water.

Differential scanning calorimetry (DSC) has been frequently used as a quick assessment of the thermo-physical properties of PCMs. Aqueous ethylene glycol and ethanol PCMs of varying concentrations were first evaluated by DSC (TA Instruments Q200) with a refrigerated cooling system of a lower temperature limit of  $-90\text{ }^{\circ}\text{C}$ . DSC measurements were used to determine the melting and freezing onsets, peak temperatures, and the latent heat of fusions of the proposed PCMs. The system was calibrated with an Indium standard. A second calibration point using pure de-ionized water was measured at five cooling rates ranging from 0.1 K/min to 5 K/min (0.1, 0.5, 1, 3, 5). It was determined that 1 K/min was the fastest cooling rate that could still provide a  $L_f$  approximately close to literature value of 333.6 J/g [10]. DSC samples were placed in Tzero<sup>©</sup> aluminium hermetic pans (from TA Instruments). The samples' weights were between 2.0 mg to 4.0 mg, measured by a Mettler Toledo microbalance with an accuracy of 0.01 mg. The PCMs have undergone some cyclic measurements at 5 K/min before the cooling rate was fixed at 1 K/min for the DSC curves shown in the figures. This ensured that the PCMs reached a stable and repeatable phase change behaviour.

On the other hand, thermal response measurements were self-calibrated, in-house designed systems that enabled bulk PCMs to be characterized but are dependent on the design and PCM container. The schematic of the setup of the thermal response measurements and the dimensions of the PCM container are shown in Figure 1. Selected low-temperature aqueous alcohols were placed in stainless steel (grade 316L) containers, placed in a thermal bath cooled by a Julabo ultra-low refrigeration system (FP89-HL) with a lower temperature limit of  $-90\text{ }^{\circ}\text{C}$ . A standard volume of 6.7 ml for all samples was measured to provide a height of 0.08 m in the PCM container. Four types of aqueous alcohols were selected to be tested individually. The container was placed first in a thermal bath of  $-20\text{ }^{\circ}\text{C}$  to achieve a stable condition before being placed in the colder bath. Different lower temperature limits were selected for the 50 wt.% ethylene glycol and 60 wt.% ethanol solutions due to different melting temperatures. The upper-temperature limit was set to  $-20\text{ }^{\circ}\text{C}$ . A thermocouple (RS Pro K Type with 310 stainless steel sheath of 1.5 mm diameter) was inserted in the centre of the PCM and another same type of thermocouple was placed next to the PCM container at the same height to measure the bath's temperature. Their temperature profiles were logged by a National Instrument data logger (NI cDAQ 9133 with a temperature module NI 9213) at intervals of 0.5 s. Their cooling curves provided realistic phase change freezing behaviours of the aqueous PCMs.

## 3. Results & Discussion

The melting ranges of selected aqueous alcohols solutions as a function of concentrations are shown in Figure 2. When compared to water, the melting curves of the solutions have significantly broadened. Concentrations of ethylene glycol are measured to 50 wt.%. There is no phase change observed near its reported eutectic concentration of 60 wt.% and for pure ethylene glycol with DSC measurements. The melt peaks, melt onset temperature, and freeze

onset temperatures are shown in Figure 3 with the phase change diagram of ethylene glycol from 0 to 50 wt.% from Cordray et al. [11]. It should be noted that the phase diagram has been obtained using seeding method to induce the freezing behavior and this has greatly reduced supercooling behavior of aqueous ethylene glycol. However, during DSC measurement, the supercooled behaviour has been largely due to homogeneous phase change behavior due to its small sample size. The freezing onset temperatures change significantly with heating and cooling rates. In these figures, the heating and cooling rates are fixed at 1 K/min. The supercooling degrees, as determined by the differences between the temperature onsets of the endothermic and exothermic peaks, remains fairly stable with increase in glycol concentrations. The addition of glycol has reduced the high supercooling degree of water. The experimentally obtained melt peaks of the DSC curves corresponded well with the phase diagram as observed in Figure 3.

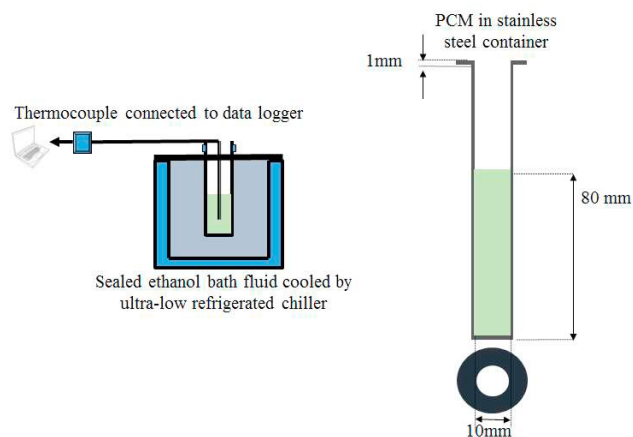


Figure 1 Schematic of thermal response measurements

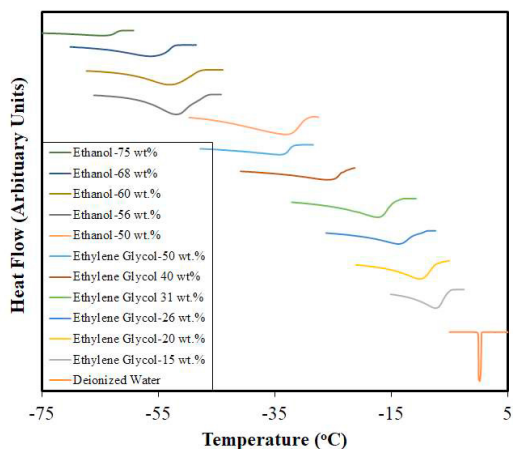


Figure 2 Melting ranges of selected aqueous alcohols with different concentrations

The latent heat of fusion for aqueous ethylene glycols and ethanol measured using DSC are shown in Figure 4. It is observed that the  $L_f$  of aqueous PCMs were mainly attributed to the concentration of water in the PCMs. Therefore, the latent heat of fusions decreased significantly with higher concentrations of water. Aqueous ethylene glycols are observed to reduce temperature more efficiently than ethanol when weight concentrations are smaller (< 50 wt. %). At about 50 wt.%, aqueous ethylene glycol melt peak temperature was  $-34\text{ }^\circ\text{C}$  with  $L_f$  of about 43 kJ/kg. From 50 wt.%, aqueous ethanol appeared to reduce temperature more efficiently and has higher  $L_f$  value. Aqueous ethanol solutions of 50 wt.% have a melt peak temperature of  $-33\text{ }^\circ\text{C}$  with  $L_f$  of about 51 kJ/kg.

Graphene oxide (GO) nano-filler have an unexpected effect when added into aqueous PCMs. From DSC measurement, the supercooling degrees for aqueous ethylene glycol of 49.5 wt.% decreased by 61% from around  $9\text{ }^\circ\text{C}$  to  $3\text{ }^\circ\text{C}$  after adding 1 wt.% graphene oxide. Melt onset and peak temperatures have been reduced by around two degrees to  $-53\text{ }^\circ\text{C}$  and  $-36\text{ }^\circ\text{C}$ , respectively. The same quantity of nano-filler was also added to aqueous ethanol of 60 wt.% and there was a reduction of the supercooling degree from 3.6 to  $0.7\text{ }^\circ\text{C}$ . Melt onset and peak temperatures were reduced by one degree to  $-62.7\text{ }^\circ\text{C}$  and  $-54\text{ }^\circ\text{C}$ , respectively. The latent heat of fusions decreased only by about 12% for 50 wt.% ethylene glycol and by about 6% for 60 wt.% ethanol.

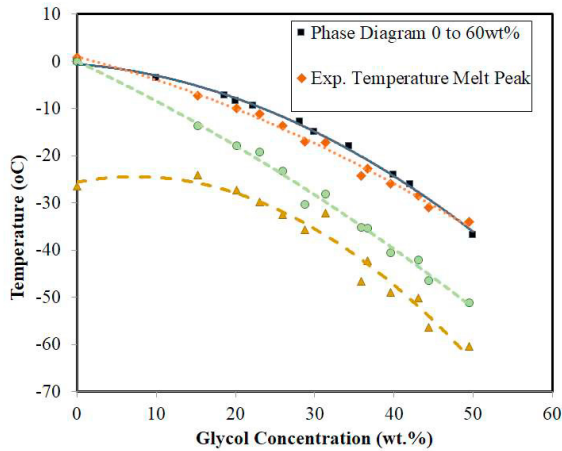


Figure 3 DSC melting and freezing points of aqueous ethylene glycol with the phase diagram of aqueous ethylene glycol

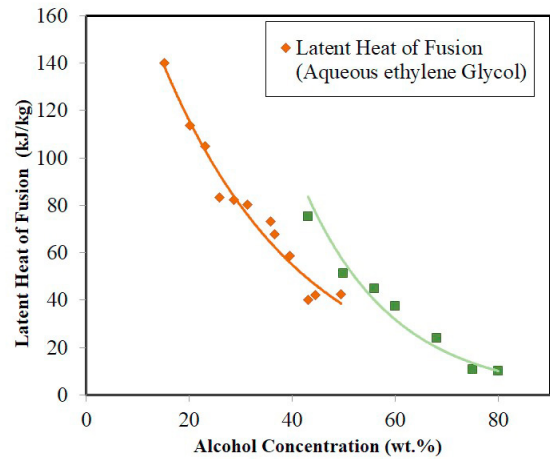


Figure 4 Latent heat of fusions of aqueous ethylene glycol and ethanol with different concentrations

The thermal response curves of four types of aqueous alcohols are shown in Figures 5 and 6. Small supercooling degrees of  $< 2\text{ }^{\circ}\text{C}$  were observed. This is expected in the phase change behavior of bulk systems as the effect of heterogeneous nucleation is significant in bulk systems and reduces supercooling degrees. GO enhances nucleation time and aqueous alcohols with nano-fillers having slightly higher phase change temperatures of around 1 to  $2\text{ }^{\circ}\text{C}$ . For aqueous ethylene glycol 50 wt.% with GO, the average charge time over four cycles is 571 seconds, about 59% faster than the solution without GO (1,404 seconds). In Figure 6, the addition of GO modifies the phase change temperature of the aqueous ethanol solution of 60 wt.%, but the impact on improving charge times is more difficult to establish as the aqueous ethanol solution at 60 wt.% does not have an obvious phase change duration. The discharge phases (melting) for both sets of PCMs have no improvements after adding nano-fillers. The use of nano-fillers is clearly more advantageous towards improving the solidification process in PCMs. The nano-fillers appear stable even after one month and this may be due to the functionalized COOH groups on the 2D graphene oxide, which may easily form bonds with other  $-\text{OH}$  groups found in water and alcohols.

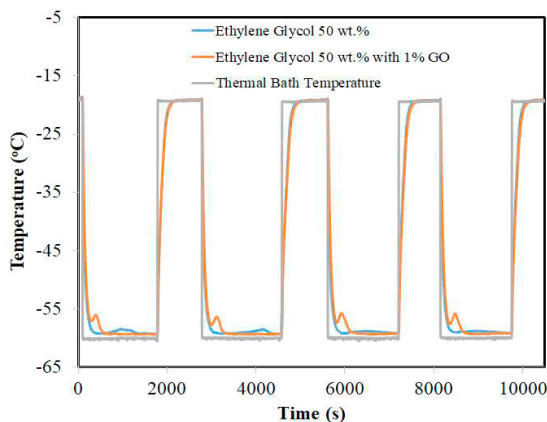


Figure 5 Thermal response measurements of aqueous ethylene glycol at 50 wt.% with and without 1% GO

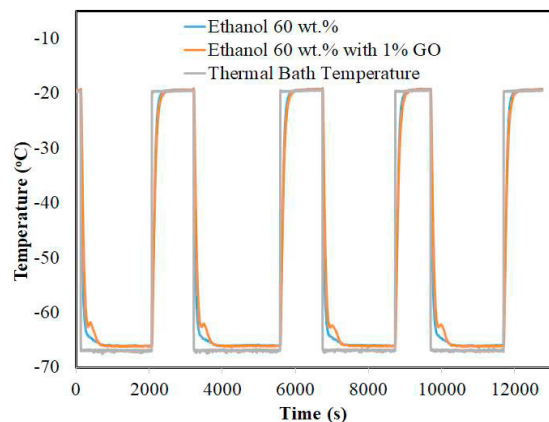


Figure 6 Thermal response measurements of aqueous ethanol at 60 wt.% with and without 1% GO

#### 4. Conclusion

Aqueous alcohol solutions have been shown to meet a wide range of low-temperatures with no issue of phase separation. These PCMs are recommended for high-grade cold CTES systems where there are few alternatives, and for fast charge and discharge applications. The supercooling degrees of PCMs was minimized by using GO which remained as a stable nano-filler with no observation of sedimentation. GO reduced the freezing temperatures of PCMs and reduced the total charging time. An interesting future research direction would be an investigation of the phase change behavior of aqueous solutions with other types of carbon nano-fillers.

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