The Effect of Electrode Gap on the Nucleation of CaCl₂·6H₂O by using Sharp End Copper Electrode

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Abstract
The performance of the calcium chloride hexahydrate (CaCl₂·6H₂O) to store the sensible and latent heats is mainly determined by its nucleation or liquid to solid phase transition. This is due to the barrier that has to be overcome when the material undergoes the nucleation process with a reduction in the entropy value. This material, with melting temperature around 29.8 °C, can be used as the thermal energy storage for building applications in tropical areas such as Indonesia, in order to reduce the electrical energy for airconditioning (AC) machines. In this paper, we report the results of experimental study for the effect of the electrical field to the supercooling degree and time period for liquid to solid phase transition. The variation in the magnitude of electrical field was achieved by variation in the gap of electrode for sharp end electrodes (cathode and anode), for the commonly sold copper electrode.

Keywords: electrofreezing, copper electrode, supercooling degree, induction time, nucleation time

I. Introduction

Phase change Material (PCM) is a material that can store and release in the form of sensible and latent heats [1]. The capability of PCM to store the relatively large latent heat around its melting temperature is possible by phase transition (solid to liquid) mechanism [2]–[4]. With this characteristic, PCM can be used to control or regulate the room temperature in the building as one of many criteria of thermal comfort of occupant [2], [5]. For this application in the tropical country such as Indonesia, calcium chloride hexahydrate (CaCl₂·6H₂O) is a suitable material. The melting temperature of this material is about 29.8 °C and melting enthalpy around 180 kJ/kg [6]. The use of this material, however, is hindered by a relatively large supercooling degree, in which case material’s temperature drop far below the melting temperature before the phase change occur at freezing temperature. This behavior surely inhibits the performance of material as Thermal Energy Storage (TES) system.

One method to reduce the supercooling degree of various PCM [7]–[10] is by application of DC electric field (DC voltage), or the so-called electrofreezing. This is a common active method that is effectively proved for nucleation of various materials, such as water [7], [11], salt hydrate [12], or salt solution [13].

The effectiveness of electric field to reduce the supercooling degree is depend on the magnitude of the electric field itself [14], the shape of edge electrode [15], and the type of the electrode [8], [14]. Copper is a kind of electrode materials that is the most effective for nucleation process of various materials mentioned above, with its effectiveness is measured by freezing probability [8], [14].

II. Theory

Spontaneously, nucleation happens when the change of Gibbs free energy is negative (ΔG < 0) [7]. Nucleation is influenced by volume contribution of Gibbs free energy, ΔGv (free energy between a very large particle and solute in solution) and the...
surface contribution of Gibbs free energy, $\Delta G_s$ (energy between surface of particle and the bulk of particle) [7], [16]. Gibbs free energy of spherical cristallite in a solution without supplied static electric field, $\Delta G_{0}$, is defined as,

$$\Delta G_0 = \Delta G_S + \Delta G_V = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G_v$$  \hspace{1cm} (1)

where $r$ is radius of the sphere, $\gamma$ is the surface free energy of the crystal fluid interface and $\Delta G_v$ is the free energy change of the transformation per unit volume,

$$\Delta G_v = \frac{\Delta H_{m,f} (T_f - T)}{T_f V_m}$$  \hspace{1cm} (2)

where $\Delta H_{m,f}$ is molar enthalphy of fusion, $V_m$ is the molar volume and $(T_f - T)$ is the supercooling degree.

For applied static electric field, $E$, the free energy of spherical nucleus, $\Delta G_{E}$, is expressed by

$$\Delta G_E = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 (\Delta G_v + PE)$$  \hspace{1cm} (3)

where $P$ is the permanent polarization [7], [16]. Based on the eq. 3, Gibbs free energy can be influenced by supplying static electric field. Static electric field can inresing negative $\Delta G_E$, in consequence to the nucleation processes [7], [16].

The ice formation is correspond to the critical nucleus, $r^*$ expressed by

$$r^* = \frac{2\gamma}{\Delta G_v + PE}$$  \hspace{1cm} (4)

that is obtained by maximizing Eq. (3) [17], [18]. Thus, with increasing PE term, $r^*$ decreases [19].

Electric field is influenced by the voltage, $V$, and the distance between the electrodes, $d$,

$$E = \frac{V}{d}$$  \hspace{1cm} (4)

where $V$ is in volt and $d$ is in meters. Based on the equation, the strengh of electric field can be modified by $V$ or by $d$ [10]. In this study, modifying electrode gap is used to increasing the electric field.

### III. Methodology

Experiment set up is shown in Fig.1(a) The experiment set up is consist of 10 kV power supply, 20 mL of CaCl$_2$·6H$_2$O placed in a 50 mL beaker glass, cold water bath, multichannel data logger with thermocouple for temperature sensor, and PC.

**Figure 1.** (a) The experimental set up, and (b) the package of the electrodes-thermocouple inside the sample.

In Fig.1(b), a thermocouple (channel 2) was placed inside of the cold water bath, while the second thermocouple (channel 4) was placed inside the sample in contact with the glass and the third thermocouple (channel 3) was placed inside the sample in the upper of the electrode gap. A package of the electrode and thermocouple channel 3 is placed in the middle of the sample. A pair of sharp end electrodes were used in this experiment. The electrode gap was varied (2.5 mm, 1.5 mm and 0.5 mm) to examine the effect of electrode gap on the nucleation activity of CaCl$_2$·6H$_2$O. The material of the electrode gap was copper (Cu) that has a 0.7 mm in diameter.

A 20 mL of CaCl$_2$·6H$_2$O was heated until the temperature of the sample reached approximately 52 °C using a hot water bath. After that, the sample was taken out from the hot water bath then it was placed...
and cooled inside the cold water bath. The temperature of cold water bath was kept in constantly at 7 °C. A continuous 1.5 kV voltage was given when the sample temperature reached up to 25 °C in the cold water bath.

New sample of CaCl2·6H2O was used for different variation of the electrode gap, with the electrodes that are cleaned by using a sandpaper. For each variation of the electrode gap, the experiment was repeated for about 3 to 5 times, to ensure the data repetition, using the same sample.

IV. Results and Discussion

Fig. 2 shows the temperature profile obtained during the cooling of CaCl2·6H2O at the first experiment for each variation of the electrode gap and the zero voltage applied. By cooling, the sample’s temperature decreases rapidly due to release of liquid sensible heat to reach a minimum that defined as the supercooling temperature (Ts), before suddenly increase to reach freezing temperature (Tf). After that the temperature is nearly constant or slightly decrease due to latent heat release, followed by the released of solid sensible heat with more pronounced temperature change. It is to be noted that the latent heat release is identic with liquid to solid phase transition, or crystallization process of the sample from its solution. For the following discussion, each graph is analyzed to reveal several important temperature and time characteristic, as illustrated Fig. 3, while the results are shown in table 1 (for temperature parameter) and table 2 (for time parameter).

![Figure 2](image-url)

**Figure 2.** Temperature profiles obtained during the cooling of 20 mL of CaCl2·6H2O at the first experiment for each variation electrode gap and the zero voltage applied.

Fig. 3(a) presents the temperature-time curve (T vs t), while Fig. 3(b) show the first derivative of temperature-time curve (dT/dt vs t) of experimental data. The temperature and time characteristic consist of: induction time (tin), supercooling temperature (Ts) that occur at time of supercooling (ts), freezing temperature (Tf), and inflection temperature (Ti) that occur at time of inflection (ti).

![Figure 3](image-url)

**Figure 3.** Determination of profile of typical temperature and time during cooling of 20 mL of CaCl2·6H2O.

Induction time, tin, is the interval time when the crystal nuclei was occurred, and it is determined during the sample’s temperature stay at a constant value, or deviation from a finite value to dT/dt = 0 in Fig. 3(b). Supercooling time and temperature, (ts, Ts), is the time and temperature when the crystal seed reach a significant size to attract another part of sample’s solution to become crystalline. The freezing temperature, Tf, is the maximum temperature of nucleation of latent heat release. The inflection time and temperature, (ti, Ti), is the end time and end temperature for the crystal growth or latent heat release. Besides that, we defined the supercooling degree (ΔTs) as the difference between Tf and Ts, and crystallization period (ti) as the difference between ti and tf.

**Table 1.** The experimentally result (temperature) of the first eksperimen for each various electrode gap (d) under different electrostatic field (E)

| V  | d  | E   | Ts  | Tf  | ΔTs | Ti  |
|----|----|-----|-----|-----|-----|-----|
| (kV) | (mm) | (V/m) | (°C) | (°C) | (°C) | (°C) |
| 0  | -  | 0   | 8.66 | 27.45 | 18.79 | 19.27 |
| 1.5 | 2.5 | 600 | 8.75 | 27.31 | 18.56 | 16.85 |
| 1.5 | 1.5 | 1000 | 12.95 | 27.17 | 14.22 | 20.99 |
| 1.5 | 0.5 | 3000 | 17.26 | 27.43 | 10.17 | 20.75 |

Table 1 present the results of temperature characteristics of the first experiment for each
variation of the electrode gap \((d)\) or under different electrostatic field \((E)\) according to formula (4). The smaller \(d\) is equivalent to higher magnitude of \(E\). From this table, \(T_s\) is strongly affected by the electric field, and have the tendency of increases for higher electric field. Meanwhile, \(T_t\) is relatively constant for various \(d\) or \(E\). It is clear that the increment of \(T_s\) and the relatively constant \(T_t\) resulted to smaller \(\Delta T_s\). The variation of \(T_s\) and \(\Delta T_s\) with \(E\) is also shown in Fig. 4.

![Figure 4. Relationship between temperature of supercooling and electric field, and supercooling degree and electric field](image)

As shown in Fig. 4, \(T_s\) (black square) and \(\Delta T_s\) (red circle) is almost unchanged for the relatively small \(E\) of 600 V/m. With further increase of \(E\), \(T_s\) increases, while the \(\Delta T_s\) decreases at almost the same magnitude.

Table 2. The experimentally result (time) of the first experiment for each various electrode gap \((d)\) under different electrostatic field \((E)\)

| \(E\) (kV) | \(d\) (mm) | \(E\) (V/m) | \(t_{ind}\) (s) | \(t_s\) (s) | \(t_c\) (s) | \(t_t\) (s) |
|---|---|---|---|---|---|---|
| 0 | - | 0 | 2100 | 2650 | 3440 | 790 |
| 1.5 | 2.5 | 600 | 445 | 1015 | 2065 | 1050 |
| 1.5 | 1.5 | 1000 | 95 | 480 | 1625 | 1145 |
| 1.5 | 0.5 | 3000 | 0 | 230 | 1360 | 1130 |

![Figure 5. Relationship between nucleation time and electric field](image)

![Figure 6. Relationship between the time of supercooling and the electric field](image)

Table 2 show the results of time characteristic of the first experiment for each variation of the electrode gap under a different electrostatic field. From this table, \(t_{ind}\) and \(t_s\) is significantly reduced with the increase of \(E\), signifying the effectiveness of electric field to the nucleation of the material. Nevertheless, compared to zero field, \(t_c\) is increased, but once the field is applied the \(t_c\) value is almost unaffected by the the magnitude of \(E\).

Fig. 5 and 6 shows the relationship between the \(t_{ind}\) vs \(E\) and \(t_s\) vs \(E\). From these figures, the decrease of \(t_{ind}\) and \(t_s\) with the increase of \(E\) is nearly exponential, \(y = y_0 + Ae^{-E/EC}\). \(E_c\) is the critical electric field of the \(t_{ind}\) and \(t_s\). The value \(E_c\) for \(t_{ind}\) is 382.1 V/m. The same parameters for \(t_s\) 513.5 V/m.

We note that although the experiment was repeated for 3 to 5 times for each variation of electrode gap, we could only take the results from the first experiment. This is due to the fact that at the second to the last experiment, the electrodes was changed due to crust that attached to the tip of the electrode, as shown in Fig 7.
These two mechanisms are intricately related to the nucleation kinetics of electrofreezing of this particular material [20], [22].

V. Conclusion

In this study, the effect of direct-current electric field on the nucleation of CaCl$_2\cdot$6H$_2$O was carried out experimentally to study the role of the electrode gap to the supercooling temperature, supercooling degree, induction time, supercooling time, and crystallization time. The experiment was carried out by using copper electrode with various electrodes gap of 0.5, 1.5, and 2.5 mm of sharp end electrodes. It was found that the smallest electrode gap of 0.5 mm is most effective to reduce the supercooling degree by increasing the supercooling temperature of material, which might be due to the relatively large magnitude of the resulted electric field. The induction time and supercooling time decreases exponentially with the increase of field. The crystallization time, however, is almost constant or it was unaffected by variation in the electrodes gap or magnitude of electric field, once the field is applied. We discuss two distinct interfacial mechanisms that influence the nucleation kinetics, namely, the electrolytic bubble formation from hydrolysis reactions and electrochemistry through the formation of copper ion complex-based coordination compounds. The experimental results could be improved by repetition experiment to get the average and standard deviation values. For each repetitive experiment, the electrode should be cleaned up from attached crust that occur due to chemical processes.

Acknowledgment

This paper is a result of Kerja Mandiri (FI-6097) study in Magister of Physics Teaching of Physics Department, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung.

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Putri, et al. The Effect of Electrode Gap on the Nucleation Activity of CaCl2.6H2O by using Sharp End Copper Electrode

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