

The Effect of Electrode Gap on the Nucleation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ by using Sharp End Copper Electrode

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Abstract

The performance of the calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) 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 aircond (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 ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) 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 ($\Delta G < 0$) [7]. Nucleation is influenced by volume contribution of Gibbs free energy, ΔG_v (free energy between a very large particle and solute in solution) and the

surface contribution of Gibbs free energy, ΔG_s (energy between surface of particle and the bulk of particle) [7], [16]. Gibbs free energy of spherical crystallite in a solution without supplied static electric field, ΔG_0 , is defined as,

$$\Delta G_0 = \Delta G_s + \Delta G_v = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G_v \quad (1)$$

where r is radius of the sphere, γ is the surface free energy of the crystal fluid interface and ΔG_v is the free energy change of the transformation per unit volume,

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

where $\Delta H_{m,f}$ is molar enthalpy 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, ΔG_E , is expressed by

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

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 increasing negative ΔG_E , in consequence to the nucleation processes [7], [16].

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

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

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 ,

$$E = \frac{V}{d} \quad (4)$$

where V is in volt and d is in meters. Based on the equation, the strength 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ placed in a 50 mL beaker glass, cold water bath, multichannel data logger with thermocouple for temperature sensor, and PC.

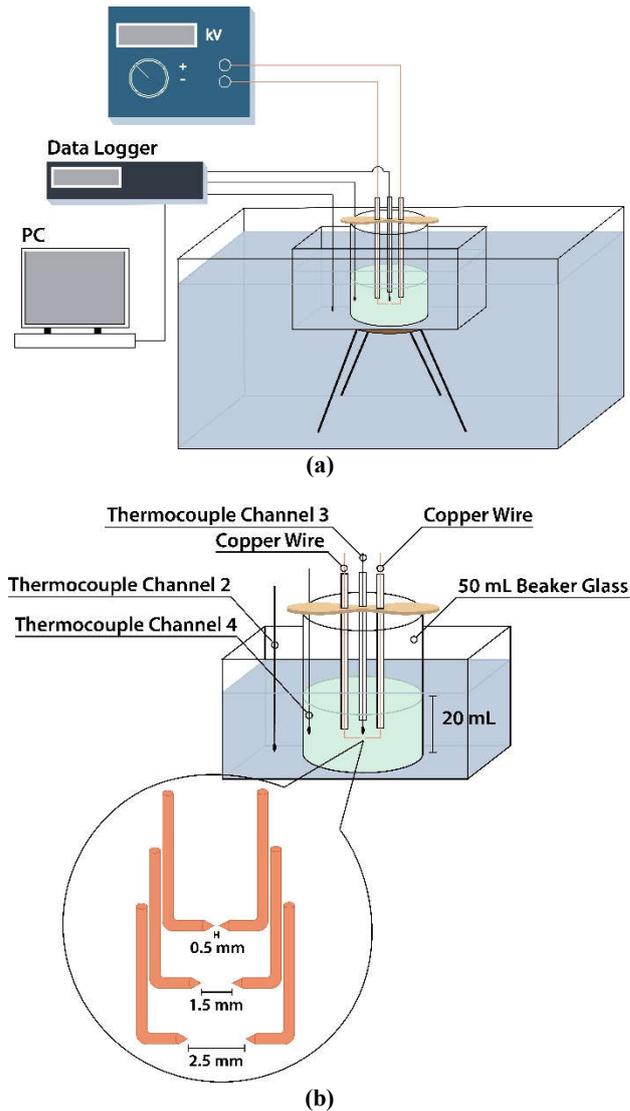


Figure 1. (a) The experimental set up, and (b) the package of the electrodes-thermocouple inside the sample.

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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The material of the electrode gap was copper (Cu) that has a 0.7 mm in diameter.

A 20 mL of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 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 (T_s), before suddenly increase to reach freezing temperature (T_f). 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).

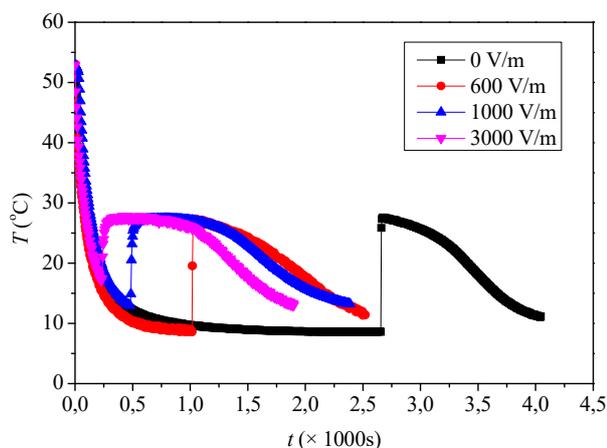


Figure 2. Temperature profiles obtained during the cooling of 20 mL of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at the first experiment for each variation electrode gap and the zero voltage applied

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 (t_{ind}), supercooling temperature (T_s) that occur at time of supercooling (t_s), freezing temperature (T_f), and inflection temperature (T_i) that occur at time of inflection (t_i).

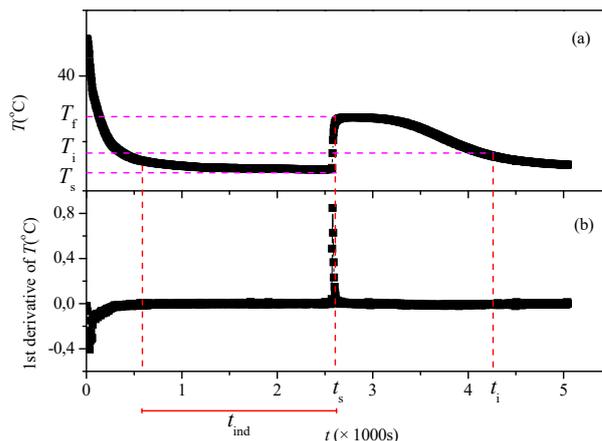


Figure 3. Determination of profile of typical temperature and time during cooling of 20 mL of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Induction time, t_{ind} , 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, (t_s, T_s), 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, T_f , is the maximum temperature of nucleation of latent heat release. The inflection time and temperature, (t_i, T_i) is the end time and end temperature for the crystal growth or latent heat release. Besides that, we defined the supercooling degree (ΔT_s) as the difference between T_f and T_s , and crystallization period (t_c) as the difference between t_i and t_s .

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

V (kV)	d (mm)	E (V/m)	T_s ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	ΔT_s ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)
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_f is relatively constant for various d or E . It is clear that the increment of T_s and the relatively constant T_f resulted to smaller ΔT_s . The variation of T_s and ΔT_s with E is also shown in Fig. 4.

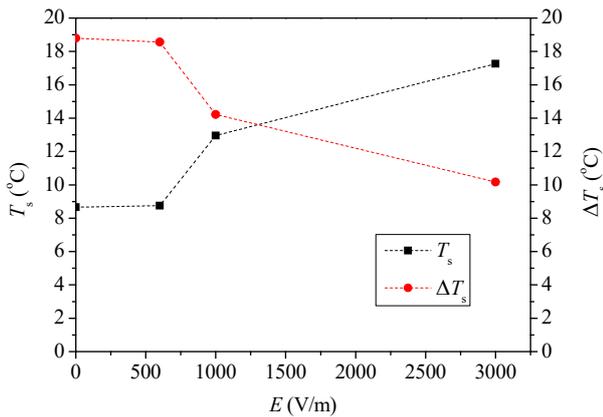


Figure 4. Relationship between temperature of supercooling and electric field, and supercooling degree and electric field

As shown in Fig. 4, T_s (black square) and ΔT_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 ΔT_s decreases at almost the same magnitude.

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

V (kV)	d (mm)	E (V/m)	t_{ind} (s)	t_s (s)	t_i (s)	t_c (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

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 .

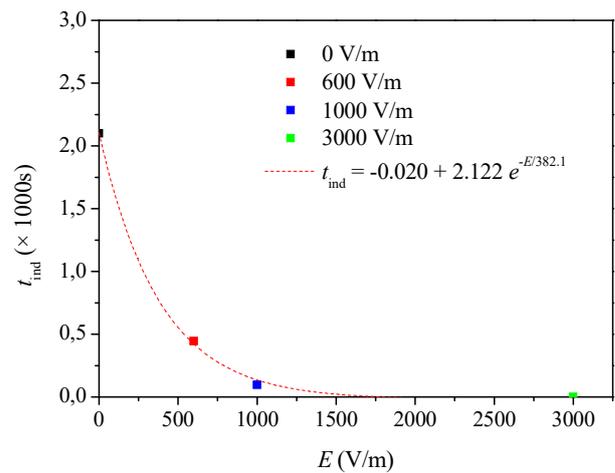


Figure 5. Relationship between nucleation time and electric field.

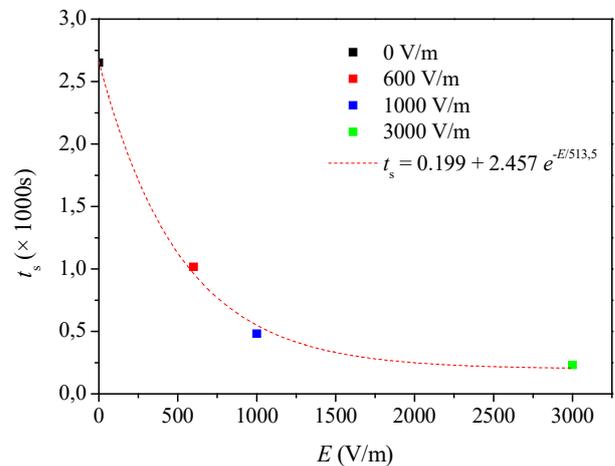


Figure 6. Relationship between the time of supercooling and the electric field.

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, $y = y_0 + Ae^{-E/E_c}$. 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.

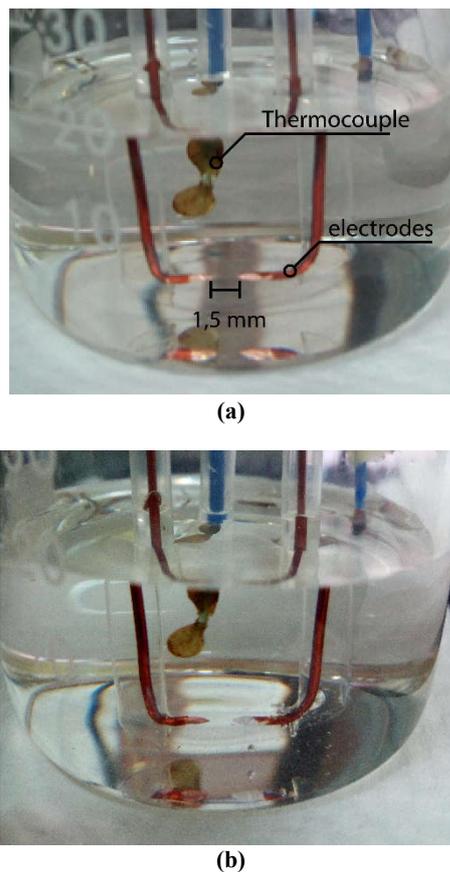


Figure 7. The electrode condition of the 1.5mm variation of the electrode gap (a) before applying a DC voltage (b) after applying a DC voltage.

Fig. 7(a) Shows the electrode condition before applying a DC voltage and Fig. 7(b) shows after applying a DC voltage. Before applying DC voltage, the electrode was clean and colorless. After applying DC voltage, the electrode gap undergoes white thickening. During the experiment, the bubbles occurred at the negative pole of electrode (cathode), which might be due to hydrolysis reactions [20]. In addition, the changed of electrode (erosion) is more pronounced for the positive pole electrode (anode), due to chemical process that occur during the experiment that transforms copper into Cu^{2+} ions [21]. These ions then coalesce with Cl^- ions from the melted $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to form ion-complex compounds that will immediately change in the water environment, to form greenish or bluish solution. These two mechanisms is 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 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 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.

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Reference

- [1] L. G. Socaciu, "Thermal Energy Storage with Phase Change Material," *Leonardo Electron. J. Pract. Technol.*, vol. 11, no. 20, pp. 75–98, 2012.
- [2] A. Kasaecian, L. Bahrami, F. Pourfayaz, E. Khodabandeh, and W.-M. Yan, "Experimental studies on the applications of PCMs and nano-PCMs in buildings: A critical review," *Energy Build.*, vol. 154, pp. 96–112, Nov. 2017.
- [3] B. Zalba, J. M. Marín, L. F. Cabeza, and H. Mehling, "Free-cooling of buildings with phase change materials," *Int. J. Refrig.*, vol. 27, no. 8, pp. 839–849, Dec. 2004.
- [4] M. A. Hamdan and F. A. Elwerr, "Thermal energy storage using a phase change material," *Sol. Energy*, vol. 56, no. 2, pp. 183–189, Feb. 1996.
- [5] X. Huang, C. Zhu, Y. Lin, and G. Fang, "Thermal properties and applications of microencapsulated PCM for thermal energy storage: A review," *Appl. Therm. Eng.*, vol. 147, no. August 2018, pp. 841–855, Jan. 2019.
- [6] N. Kumar, J. Hirsche, T. J. LaClair, K. R. Gluesenkamp, and S. Graham, "Review of stability and thermal conductivity enhancements for salt hydrates," *J. Energy Storage*, vol. 24, p. 100794, Aug. 2019.
- [7] M. Orłowska, M. Havet, and A. Le-Bail, "Controlled ice nucleation under high voltage DC electrostatic field conditions," *Food Res. Int.*, vol. 42, no. 7, pp. 879–884,

- Aug. 2009.
- [8] H. Kumano, H. Goto, Y. Toyama, and M. Kawakita, "Study on TBAB hydrate nucleating activity of electrode products due to DC voltage application," *Int. J. Refrig.*, vol. 93, pp. 10–17, Sep. 2018.
 - [9] N. R. Jankowski and F. P. McCluskey, "Electrical Supercooling Mitigation in Erythritol," in *2010 14th International Heat Transfer Conference, Volume 7*, 2010, vol. 7, pp. 409–416.
 - [10] P. Muthukumar and D. V. N. Lakshmi, "Nucleation Enhancement Studies on Aqueous Salt Solutions," *Energy Procedia*, vol. 109, no. November 2016, pp. 174–180, Mar. 2017.
 - [11] S. Wei, X. Xiaobin, Z. Hong, and X. Chuanxiang, "Effects of dipole polarization of water molecules on ice formation under an electrostatic field," *Cryobiology*, vol. 56, no. 1, pp. 93–99, Feb. 2008.
 - [12] B. Chen, Y. Gao, M. Yang, D. Wang, Y. Song, and N. Li, "The influence of electric field and peroxide of THF on the THF hydrate formation," *Energy Procedia*, vol. 142, pp. 3956–3961, Dec. 2017.
 - [13] A. Sugita, S. Masauji, R. Yamaguchi, A. Kubono, and S. Tasaka, "Melt-crystallizations of poly (l-lactic acid) under external DC electric fields," *Polymer (Guildf)*, vol. 84, pp. 185–188, Feb. 2016.
 - [14] H. Kumano, T. Hirata, K. Mitsuishi, and K. Ueno, "Experimental study on effect of electric field on hydrate nucleation in supercooled tetra-n-butyl ammonium bromide aqueous solution," *Int. J. Refrig.*, vol. 35, no. 5, pp. 1266–1274, Aug. 2012.
 - [15] T. Hozumi, A. Saito, S. Okawa, and Y. Eshita, "Effects of shapes of electrodes on freezing of supercooled water in electric freeze control," *Int. J. Refrig.*, vol. 28, no. 3, pp. 389–395, May 2005.
 - [16] M. Dalvi-Isfahan, N. Hamdami, E. Xanthakis, and A. Le-Bail, "Review on the control of ice nucleation by ultrasound waves, electric and magnetic fields," *J. Food Eng.*, vol. 195, pp. 222–234, Feb. 2017.
 - [17] J. H. Mok, W. Choi, S. H. Park, S. H. Lee, and S. Jun, "Emerging pulsed electric field (PEF) and static magnetic field (SMF) combination technology for food freezing," *Int. J. Refrig.*, vol. 50, pp. 137–145, Feb. 2015.
 - [18] P. K. Jha *et al.*, "A review on effect of DC voltage on crystallization process in food systems," *Innov. Food Sci. Emerg. Technol.*, vol. 42, pp. 204–219, Aug. 2017.
 - [19] E. Xanthakis, M. Havet, S. Chevallier, J. Abadie, and A. Le-Bail, "Effect of static electric field on ice crystal size reduction during freezing of pork meat," *Innov. Food Sci. Emerg. Technol.*, vol. 20, pp. 115–120, Oct. 2013.
 - [20] A. Shahriari, P. V. Acharya, K. Carpenter, and V. Bahadur, "Metal-Foam-Based Ultrafast Electronucleation of Hydrates at Low Voltages," *Langmuir*, vol. 33, no. 23, pp. 5652–5656, Jun. 2017.
 - [21] M. TANIMIZU, Y. TAKAHASHI, and M. NOMURA, "Spectroscopic study on the anion exchange behavior of Cu chloro-complexes in HCl Solutions and its implication to Cu isotopic fractionation," *Geochem. J.*, vol. 41, no. 4, pp. 291–295, 2007.
 - [22] I. Sutjahja *et al.*, "Electrofreezing of the phase-change material CaCl₂·6H₂O and its impact on supercooling and the nucleation time," *Hem. Ind.*, vol. 4, no. 00, pp. 34–34, 2019.