Proceedings of the ASME 2017 Summer Heat Transfer Conference
SHTC2017
July 9-14, 2017, Bellevue, Washington

HT2017-4812

ALUMINUM FOAM-BASED ULTRAFAST ELECTRONUCLEATION OF HYDRATES

Palash V Acharya
Department of Mechanical Engineering
The University of Texas at Austin
Austin, Texas, USA

Arjang Shahriari
Department of Mechanical Engineering
The University of Texas at Austin
Austin, Texas, USA

Katherine Carpenter+
Department of Mechanical Engineering
The University of Texas at Austin
Austin, Texas, USA

Vaibhav Bahadur*
Department of Mechanical Engineering,
Texas Materials Institute
The University of Texas at Austin
Austin, Texas, USA

ABSTRACT

Nucleation of hydrates requires very long induction (wait) times, often ranging from hours to days. Electronucleation, i.e. nucleation stimulated by the presence of an electric field in the precursor solution can reduce the induction time significantly. This work reveals that porous aluminum foams enable near-instantaneous electronucleation at very low voltages. Experiments with tetrahydrofuran hydrate nucleation reveal that open-cell aluminum foam electrodes can trigger nucleation in only tens of seconds. Foam-based electrodes reduce the induction time by as much as 150X, when compared to non-foam electrodes. This work also discusses two mechanisms underlying electronucleation. These include bubble generation (due to electrolysis), and the formation of metal-ion coordination compounds. These mechanisms depend on electrode material and polarity, and affect the induction time to different extents. This work also shows that foams result in more deterministic nucleation (compared to stochastic) when compared with non-foam electrodes. Overall, electronucleation can lead to a new class of technologies for active control of formation of hydrates.

---

*Corresponding author: vb@austin.utexas.edu

INTRODUCTION

Clathrate hydrates are water-based crystalline solids consisting of a guest molecule (methane, carbon dioxide, etc.) trapped in a lattice of hydrogen-bonded water molecules [1]. Hydrates are the subject of significant research activity, due to the fact they have a variety of applications such as storage and transportation of natural gas, hydrate-based desalination, carbon sequestration etc. [2-5]. Forming hydrates in laboratories is challenging due to the high pressure (>75 atmospheres) and low temperature (-10°C to 0°C) conditions required. Another significant challenge is the significant induction (wait) time, before hydrates nucleate. As per phase change thermodynamics, induction time is the time required to form the first hydrate 'seed' that is large enough to spontaneously grow [6]. Induction times for hydrate synthesis can range from hours to days, especially in quiescent systems [1]. This poses challenges for applications [2-4], which require rapid formation of hydrates. Surfactants such as sodium dodecyl sulphate (SDS) have been used to promote hydrate formation in a number of studies [7-10]. The underlying mechanism behind the surfactant promotion effect is based on the fact that they tend to increase the gas-liquid interfacial area by inducing a morphological change in the structure of hydrates, thereby promoting hydrate formation [11]. The use of mechanical agitation of the hydrate precursor solution is another technique that promotes nucleation [7]. However, both these techniques have issues related to performance, cost, and environmental impact.

Recently, the present group demonstrated the concept of electronucleation for rapid and controlled nucleation of hydrates [12], which originated from our previous work on the use of electric fields to achieve freezing at an elevated temperatures for supercooled liquid water [20]. Experiments on tetrahydrofuran hydrate formation demonstrated a hundred fold reduction in induction times by applying electrical voltages across the precursor solution. The voltage-dependent induction time was

---

+ Presently associated with Raytheon

reduced to a few minutes, at very high voltages approaching 100 V.

This work demonstrates that aluminum foam-based electrodes can significantly reduce the induction time, as compared to non-foam electrodes. The underlying hypothesis is that the augmentation in surface area and the accompanying polarity-dependent reactions will enhance nucleation. This work accordingly uncovers two mechanisms (bubble generation, formation of metal-ion complexes) underlying electronucleation, which depend on the electrode material and polarity. Importantly, aluminum foam-based electrodes trigger near-instantaneous nucleation at low voltages. Induction times of tens of seconds were observed at 20 V, which is a significant advancement from previous findings [12]. Also, foams have high thermal conductivity, which will help speed up hydrate formation by rapid removal of the heat of hydrate formation [13,14]. Furthermore, the large number of nucleation sites on these foams will help in trapping hydrate molecules, thus ensuring higher gas to hydrate conversion ratios.

EXPERIMENTAL DETAILS

Electronucleation of tetrahydrofuran (THF) hydrates was studied presently. THF hydrates are used as a substitute for methane hydrates [15,16], since they are easier to form. THF (C_4H_8O) forms structure II hydrates [12], from a THF-water mixture (molar ratio of THF:water is 1:17) at atmospheric pressure, and below 4.4 °C. In this work, excess THF was used to prevent ice formation, and the ratio of THF to water was 1:15.

Figures 1(a-b) show a schematic of the experimental setup. Experiments were conducted in a cold bath which provided isothermal conditions. The cold bath contained a 50/50 mixture of ethylene glycol and water which had a freezing point lower than 238 K. THF electronucleation was studied in glass tubes (inner diameter: 14 mm) with a stopper. The stopper held the two electrodes and a T-type ungrounded thermocouple.

Open-cell aluminum foams with a surface area-to-volume of 1720 m^2/m^3 and 92 % porosity were used. A 6 mm x 8 mm x 50 mm sized foam plug was used as one of the electrodes. A stainless steel electrode was the other electrode. The spacing between the thermocouple and the electrodes was 5 mm. Also, baseline electro-nucleation experiments were conducted with two stainless steel electrodes. The electrodes were connected to a DC power supply (Kepco) and an ammeter (Keithley).

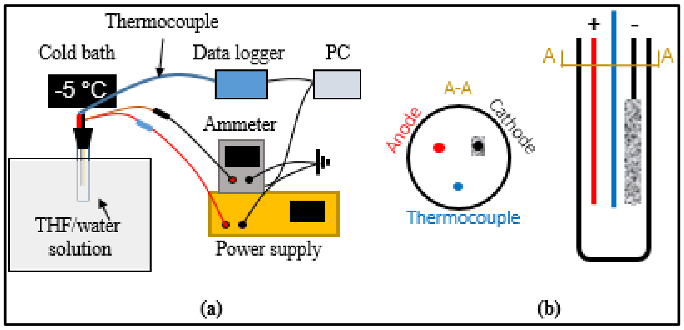


Figure 1. (a) Schematic of experimental setup, (b) Aluminum foam and stainless steel electrodes inside the tube.

A single tube was used in every experimental run. The tube contained the water-THF mixture was agitated (for complete mixing) and then degassed in a sonication bath (Branson) to remove air bubbles. The tube was immersed in the cooling bath set at 5 °C. After the tube reached steady state, the bath temperature was lowered to -5 °C. Once the water-THF mixture reached -5 °C, an electrical voltage (5, 10 or 20 V) was applied. The induction time was measured from this point to the time when hydrates nucleated.

To eliminate the possibility of contamination, all electrodes, the thermocouple and the glass tube were subjected to a rigorous cleaning treatment after every single experiment. The electrodes and the thermocouple were first cleaned with acetone, followed by ultrasonication in a bath. The electrodes, thermocouple and the tube underwent three such separate ultrasonication treatments, each lasting for 10 minutes, with the tube filled with acetone, isopropanol alcohol, and deionized water, successively. The electrodes, thermocouples and test tubes were dried and kept in a vacuum desiccator until the next experiment.

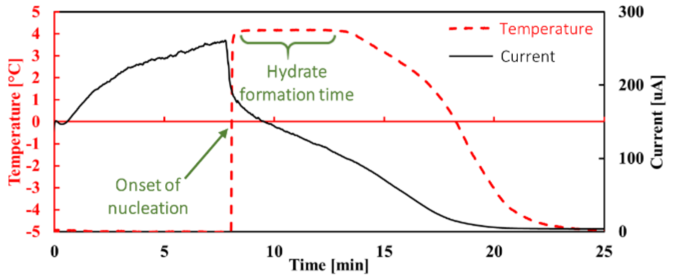


Figure 2. Detection of nucleation of hydrates by tracking the temperature and current flow in the hydrate forming solution.

Electronucleation was detected by tracking the temperature of the solution, as detailed in our previous study [12]. The heat released right at the onset of nucleation instantaneously raises the temperature of the entire solution to the equilibrium temperature of ~ 4 °C (Figure 2). Another indication [12] of hydrate nucleation is a sudden decrease in the electrical conductivity of the solution due to the formation of clathrate hydrates (Figure 2). These techniques have been used by several other researchers to infer the nucleation of THF hydrates [17] and ice [18, 19].

RESULTS

Figure 3 shows the induction time versus voltage for the baseline case and the cases with the aluminum foam acting as the cathode and anode. The baseline case (stainless steel electrodes), shows voltage-dependent reduction in the induction time. Aluminum foam as the cathode significantly reduces the induction time, eg. a 10X decrease at 20 V. This highlights the benefits of foams, with the high surface area of the porous foam enhancing nucleation. It is noted that each data point is the average of more than five measurements.

Induction time is further reduced, by switching polarity to make the foam electrode as the anode. Figure 3 shows that the induction time is reduced by 40X (at 5V) when compared to the foam as the cathode. Average induction times at 10 V and 20 V, were only 43 seconds and 20 seconds, respectively. This is very close to instantaneous nucleation. It is significant that no nucleation occurred in any experiment at 0 V even after twelve hours. Overall, these experiments reveal that appropriate polarity foams can enable a two order of magnitude reduction in induction times when compared to non-foam electrodes. To illustrate this point, the induction time decreases by 150X at 5 V, when a non-foam electrode is replaced with an aluminum foam anode.

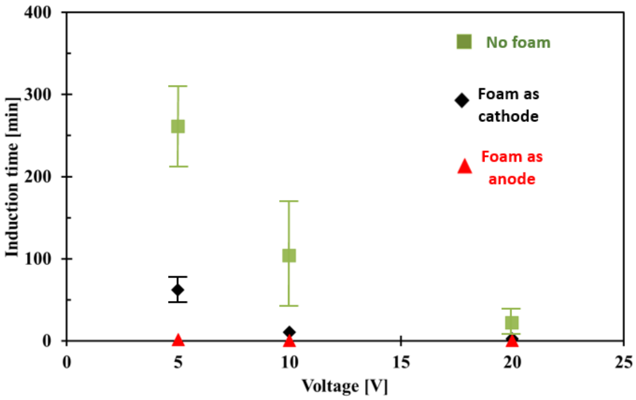


Figure 3. Electronucleation induction times for the baseline (non-foam) case, and the cases where the aluminum foam was the cathode and anode.

Interestingly, the scatter in the measurements is significantly reduced in the foam experiments, especially at higher voltages. The standard deviations in the induction times for non-foam experiments is ~ 60% of the mean value, at 10 and 20 V. The standard deviations for foam electrodes (both as cathode and anode), are only 13-25% of the mean value. This suggests that the foams can reduce the inherent stochastic nature of nucleation and convert nucleation to a deterministic phenomenon.

Table 1: Induction time (in minutes)

	Al foam as cathode				**Al foam as anode**			
Voltage (V)	**20**	**10**	**5**	**0**	**20**	**10**	**5**	**0**
Average	2.1	10.2	62	>12 hours	0.3	0.7	1.6	>12 hours
Standard Deviation	0.3	1.9	7	-	0.1	0.16	0.3	-

	Non-foam electrodes			
Voltage (V)	**20**	**10**	**5**	**0**
Average	21.8	103.6	280.9	>12 hours
Standard Deviation	13.8	65.7	27.9	-

The influence of polarity is significant, with the induction time reduced by an order of magnitude by switching the foam polarity from negative to positive. This also suggests that multiple physical phenomena influence electronucleation. One electronucleation mechanism is bubble generation at the electrodes, resulting from hydrolysis reactions. Current flow in the solution leads to localized electrolysis; this generates hydrogen bubbles at the cathode. These bubbles act as nucleation sites to increase the nucleation probability. Furthermore, these bubbles grow and detach from the electrode. The convection and the pressure fluctuations associated with bubble growth and detachment can provide the energy to initiate nucleation in a quiescent fluid. Bubble generation on the foam electrode was observed as described ahead. However, this mechanism cannot explain the polarity-dependent results.

Another mechanism is at play, which affects nucleation more strongly than bubble-related effects, and is polarity dependent. This can be understood by examining the results of Hozumi and Shichiri & Nagata who conducted studies to determine the influence of electrode material on the electrofreezing of pure water [21, 22]. Freezing was enhanced [21] with aluminum electrodes, when compared to more inert metals like platinum and gold. This enhancement was attributed to the formation of aluminum-based coordination compounds. The physical structure of these compounds is similar to the crystal structure of ice [21]. Other studies [23, 24], have also acknowledged the role of such ion complexes in promoting nucleation. A similar mechanism is responsible in the current work and explains the rapid hydrate formation with the aluminum foam anode.

The above mechanisms are further elaborated by analyzing the chemical reactions at the two electrodes. For the foam electrode cathode, water is reduced to hydroxyl ions and hydrogen gas is generated ($4H_2O + 4e^- \rightarrow 4OH^- + 2H_2\uparrow$). This is responsible for the bubbles at the cathode (Figure 4a). The high surface area and surface irregularities provide a large number of nucleation sites for bubble generation, which explains the faster electronucleation when compared with the bare electrode. At the stainless steel anode hydroxyl ions are oxidized to generate oxygen ($4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^-$).

The influence of polarity is explained by a different reaction occurring with a foam anode. Oxidation of aluminum is favored [21] over oxidation of hydroxyl ions, due to the high ionization tendency of aluminum ($Al \rightarrow Al^{3+} + 3e^-$). Al^{3+} ions enter the electrolyte solution and are surrounded by water molecules to form a coordination compound $[Al(H_2O)_6]^{3+}$. OH^- ions form bridges between the coordination compound. This results in an octahedral polynuclear complex [21] (Figure 3b). The similarity of this structure to the structure of the hydrate promotes nucleation. While direct measurements of such metal-ion complexes is challenging, the formation of such complexes is a strong mechanism for the accelerated nucleation of hydrates.

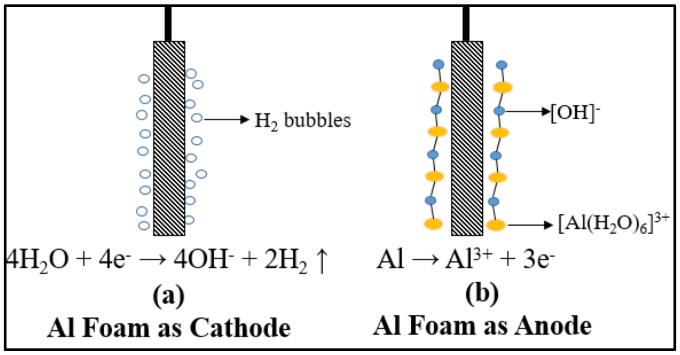
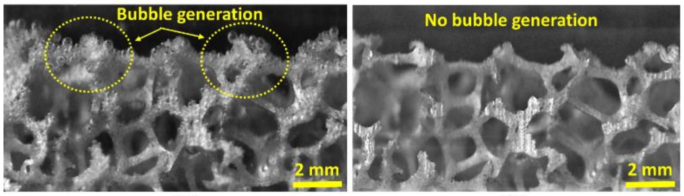


Figure 4. Mechanisms influencing electronucleation (a) Bubble-related effects with aluminum foam cathode (b) Coordination compound formation-based nucleation with aluminum foam anode.

These observations were validated by visualization of bubbles in the foam electrode during experiments. Figure 5 shows the foam electrode as the cathode and as the anode. The visualization experiments were carried out with higher voltages of 200 V to obtain a perceivable visualization of bubble generation. When the foam is the cathode (Figure 5(a)), significant bubble generation and departures are seen on the foam surface. In contrast, there is no bubble generation when the foam is the anode (Figure 5(b)). This indicates that electrolysis is not occurring at the foam anode, and that an alternative electrochemical reaction is responsible for nucleation enhancement. Aluminum-based coordination compound formation offers a logical explanation, in the absence of bubbles. Importantly, the induction time measurements suggest that coordination compound formation-based mechanism influences nucleation more strongly than any bubble-related effects. Future work can isolate more specifics of the details involved in these mechanisms.

It is important to note that the magnitude of Joule heating is very low in the present experiments. The maximum current in all these experiments was 86 µA, 211 µA and 803 µA at 5, 10 and 20V, respectively. This will generate less than 16 milliwatts at 20 V. Also, stoichiometric calculations suggest that less than 0.001 % of water is hydrolyzed during the experiments. Electro-nucleation will therefore not affect the chemical composition significantly, which increases the benefits of this concept.



(a) (b)

Figure 5. Aluminum foams as the (a) cathode, with leads to bubble generation, and (b) anode, where no bubbling is observed.

Importantly, metal foams also accelerate the rate at which the hydrate formation front progresses. This is due to the high thermal conductivity of the aluminum foam-solution network (11 W/mK). The conductivity of the water-THF mixture would have been much lower (0.6 W/mK). Higher thermal conductivity aids removal of the heat released during hydrate formation. The decreased hydrate formation time can be quantified by measuring the phase change propagation time. This is the time to convert the entire tube to a hydrate. This time can be measured from the temperature-time curve in Figure 2, and is summarized for various experiments in Table 2. The propagation time for the -5°C experiments is reduced from 7.5 minutes in the absence of foams to 5.1 minutes with the foam (average of 5 experiments each with the foam as the cathode and anode). It is noted that the foam polarity and the voltage magnitude did not influence the propagation time. Repeating the experiments in a -10°C bath reduced the propagation time from 4.8 minutes to 1.9 minutes upon using foams. The -10°C experiment was carried out without an applied voltage, since the additional supercooling leads to fast nucleation. Furthermore, it can be seen that the phase propagation time for hydrate formation exhibits an inverse dependence on the degree of supercooling of the solution which is in accordance with previous studies on electrofreezing [23,24]. It is important to understand that hydrate formation rates are influenced by all available pathways for heat rejection. The present results apply only to this particular geometry. However, the electronucleation benefits of foams, together with the heat transfer enhancement clearly shows the benefits of foam-assisted electronucleation of hydrates.

Table 2. Time taken for hydrates to form in the entire tube (minutes).

Bath temperature	With foam electrode	Without foam electrode
-5°C	5.1	7.5
-10°C	1.9	4.8

CONCLUSIONS

Overall, this study introduces a new approach to promote and control hydrate nucleation, in addition to the current techniques of chemical promotion and mechanical stirring. It is seen that foam-based electronucleation is a powerful tool to accelerate nucleation by many orders of magnitude. The induction time can be fundamentally eliminated by instantaneous nucleation. Bubble-based effects and electrochemistry-based mechanisms influence the nucleation kinetics. While this study was about THF hydrates, similar benefits can be expected for other hydrates such as methane hydrates, which form from a water-gas mixture. Electronucleation can also aid the nucleation of hydrates which form from immiscible liquids, eg. cyclopentane.

ACKNOWLEDGEMENTS

The authors acknowledge American Chemical Society Petroleum Research Fund PRF 54706- DNI5 and Welch Foundation Grant # F-1837 for support of this work.

REFERENCES

[1] Koh, C. A.; Sloan, E. D. Clathrate Hydrates of Natural Gases. 3rd edition, CRC Press, **2008**.

[2] Sum, A. K.; Koh, C. A.; Sloan, E. D. Clathrate Hydrates: From Laboratory Science to Engineering Practice. *Ind. Eng. Chem. Res.* **2009**, *48* [16], 7457–7465.

[3] Chatti, I.; Delahaye, A.; Fournaison, L.; Petitet, J. P. Benefits and Drawbacks of Clathrate Hydrates: A Review of Their Areas of Interest. *Energy Convers. Manage.* **2005**, *46*, 1333−1343.

[4] Sloan, D.; Koh, C. Clathrate Hydrates of Natural Gases, Third ed.; CRC Press, Taylor & Francis Group: New York, **2008**.

[5] Chatti, I.; Delahaye, A.; Fournaison, L.; Petitet, J. P. Benefits and Drawbacks of Clathrate Hydrates: A Review of Their Areas of Interest. *Energy Convers. Manag.* **2004**, *46*, 1333–134.

[6] Kashchiev, D.; Firoozabadi, A. Induction Time in Crystallization of Gas Hydrates. *J. Cryst. Growth* **2003**, *250*, 499–515.

[7] Zhong, Y.; Rogers, R. E. Surfactant Effects on Gas Hydrate Formation. *Chem. Eng. Sci.* **2000**, *55*, 4175–4187.

[8] Zhang, J. S.; Lee, S.; Lee, J. W. Kinetics of Methane Hydrate Formation from SDS Solution. Ind. Eng. Chem. Res. **2007**, 46, 6353−6359.

[9] Zhang, J. S.; Lo, C.; Somasundaran, P.; Lu, S.; Couzis, A.; Lee, J. W. Adsorption of Sodium Dodecyl Sulfate at THF Hydrate / Liquid Interface. *J. Phys. Chem.* **2008**, *112*, 12381–12385.

[10] Ganji, H.; Manteghian, M.; Sadaghiani zadeh, K.; Omidkhah, M. R.; Rahimi Mofrad, H. Effect of Different Surfactants on Methane Hydrate Formation Rate, Stability and Storage Capacity. *Fuel,* **2007**, *86*, 434−441.

[11] Yoslim, J.; Linga, P.; Englezos, P. Enhanced growth of methane-propane clathrate hydrate crystals with sodium dodecyl sulfate, sodium tetradecyl sulfate, and sodium hexadecyl sulfate surfactants. *J. Cryst. Growth,* **2010**, *313*, 68–80.

[12] Carpenter K.; Bahadur V.; Electronucleation for rapid and controlled formation of hydrates. *J. Phys. Chem. Lett.*, **2016** , *7[13]* , 2465-2469

[13] Yang L.; Fan S.S.; Wang Y.H.; Lang X.M; Xie D.L. Accelerated formation of methane hydrate in aluminium foam. *Ind. Eng. Chem.*, **2011** , *50* , 11563-11569.

[14] Fan, S., Yang, L., Lang, X., Wang, Y., and Xie, D., 2012, "Kinetics and thermal analysis of methane hydrate formation in aluminum foam," Chem. Eng. Sci., **82**, pp. 185–193

[15] Wilson, P. W.; Lester, D.; Haymet, a. D. J. Heterogeneous Nucleation of Clathrates from Supercooled Tetrahydrofuran [THF]/water Mixtures, and the Effect of an Added Catalyst. *Chem. Eng. Sci.* **2005**, *60*, 2937–2941.

[16] Liu, W.; Wang, S.; Yang, M.; Song, Y.; Wang, S.; Zhao, J. Investigation of the Induction Time for THF Hydrate Formation in Porous Media. *J. Nat. Gas Sci. Eng.* **2015**, *24*, 357–364.

[17] Dai, S.; Lee, J. Y.; Santamarina, J. C. Hydrate Nucleation in Quiescent and Dynamic Conditions. *Fluid Phase Equilib.* **2014**, *378*, 107−112.

[18] Bauerecker, S.; Ulbig, P.; Buch, V.; Vrbka, L.; Jungwirth, P. Monitoring Ice Nucleation in Pure and Salty Water via High-Speed Imaging and Computer Simulations. *J. Phys. Chem. C* **2008**, *167*, 7631−7636._

[19] Alizadeh, A.; Yamada, M.; Li, R.; Shang, W.; Otta, S.; Zhong, S.; Ge, L.; Dhinojwala, A.; Conway, K. R.; Bahadur, V.; et al. Dynamics of Ice Nucleation on Water Repellent Surfaces. *Langmuir* **2012**, *28* , 3180−3186.

[20] Carpenter, K.; Bahadur, V. Electrofreezing of Water Droplets under Electrowetting Fields. *Langmuir* **2015**, *31*, 2243–2248.

[21] Hozumi T.; Saito A.; Okawa S.; Watanabe K. Effects of electrode materials on freezing of supercooled water in electric freeze control. *Int. J. Refrig.*, **2003** , *26* , 537-542.

[22] Shichiri T.; Nagata T. Effect of Electric currents on the nucleation of ice crystals in the melt. *J. Cryst. Growth*, **1981,** *54* ,207-210

[23] Orlowska M.; Havet M; Le-Bail A. Controlled ice nucleation under high voltage DC Electrostatic field conditions. *FoodRes. Int.*, **2009** , *42[7]*, 879-884.

[24] Wei S.; Xiaobin X.; Hong Z,; Chuanxiang X. Effect of dipole polarization of water molecules on ice formation under an electrostatic field. *Cryobiology,* **2008,** *56,* 93-99.