Condensed droplet-based electricity generation via water-phase change

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ABSTRACT

Water electrification mechanism is gradually being identified, and utilized to harvest various types of water-based energy. However, a lack of understanding of the complementary characteristics of water in real environment, such as the complex dynamics of droplet flow, phase change, high temperature, and humid conditions, continues to limit the realization of water-based energy harvesting. Here, we demonstrated the mechanism of condensed droplet-based electricity generation via water-phase change for the first time. The various characteristic electrical outputs were observed in a series of condensation processes (nucleation, growth, shedding, sweeping, separation, drop off). Furthermore, the correlation among the electrical outputs, heat flux, and condensation rate were identified. The distinct changes in the electrical outputs depending on changes in the heat flux can be utilized to detect sudden failures of heat exchanges and coolers.

1. Introduction

Water is one of the most useful and valuable resources for producing renewable energy. Recently, several research studies on contact electrification of water have been conducted to harvest various types of water-based energy [1–8]. In addition, researchers have overcome the barriers that limit the output of conventional water-based energy harvesters by realizing a continuous output of 50.1 W/m² [9]. However, the lack of understanding of the complementary mechanical and electrical characteristics of water continues to hinder the realization of water-based energy harvesting in real environments. Over the past few centuries, the mechanical properties of water, such as its high heat capacity, have been utilized mainly to control the temperature of machinery, systems, or engines in industries [10,11]. Such temperature control processes induce condensation phenomena that accompany heat exchange; moreover, the dynamics of droplet flow are complex. Although a water electrification phenomenon under controlled conditions has recently been identified [12–14], the complex dynamics of droplet flow, phase change, high temperatures, and humid conditions, which often occur in actual environments, have not been studied thus far. This makes it difficult to analyze an electrical energy generation mechanism from the real flow of water, eventually hindering the realization of water-based energy harvesting. Thus, to realize water-based energy harvesting, the complex environmental conditions accompanying condensation and heat exchange should be considered simultaneously.

Herein, we propose a condensed-droplet-based electricity generator (CDEG) for the first time. The electricity generation mechanism occurring within a series of condensation processes (nucleation, growth, shedding, sweeping, separation, and drop off) is identified by analyzing the correlation between the flow and electrical output of condensed droplets. Each specific phenomenon in the condensation process generates various characteristic electrical outputs that can be divided into four regions (A: t3, t13; B: t1–t2, t13; C: t4; and D: t5–t7, t9) depending on the period and polarity of the outputs. All of these outputs show distinct changes with changes in the heat flux within the heat exchanger, and the effects of the heat flux on the condensation rate and outputs are identified. The results imply that the CDEG can be applied to detect...
sudden failures of heat exchangers or coolers in real industrial environments. Moreover, the CDEG can expand the versatility of water-based energy-related research and be applied to detect critical situations and prevent large accidents in real industrial applications.

2. Electrification in condensation process

The condensation process involves several steps. First, when hot steam skims a cooled and hydrophobic surface, water clusters in the steam are adsorbed on the virgin hydrophobic [15,16] surface due to the temperature difference between the vapor and the surface (Fig. 1a. i). The mechanism of charge transfer through contact electrification between liquids and solid surfaces remains somewhat controversial, but recent studies have demonstrated that an electron moves from a water molecule to the solid surface, which can be negatively charged (Fig. 1a. ii) [12–14,17]. In this respect, the water molecule that loses an electron becomes a positive ion (positive charge), and the solid surface becomes negatively charged due to the transferred electron (negative charge) (Fig. 1a. iii). This pair of charges housed in the solid surface and the water molecules form an electrical double layer (EDL) that offsets the electric potential of the charges [18–20]. The cluster of water starts to grow by coalescing with other clusters within an area where the clusters are nucleated (Fig. 1b. i–iii). The EDL between the droplet and the solid surface is maintained and still has no electrical effect on the surrounding area if the droplet and the solid surface are not separated (x₁ and x₂ denote the left and right sides of the water droplet, respectively). Finally, when the droplet has grown to a considerably large size, droplet shedding occurs because the driving force overcomes the surface tension between the droplet and the surface (Fig. 1c. i). After the droplet has moved (x₁* and x₂* denote the left and right sides of the water droplet after it has moved, respectively), the area in which the droplet is separated (x₁*–x₂*) has a negative potential due to the remaining electrons, and the droplet has a positive potential due to the surplus cations, which can exceed the influence of the EDL (Fig. 1c. ii). By contrast, contact electrification occurs in the newly contacting area (x₂–x₂*), but the potential is offset by the EDL, as shown in Fig. 1a [14]. When the solid temperature increases, the surface charge escapes from the surface by thermal excitation [21]. Moreover, in condensations process, there are numerous water molecules, which can act as a natural conductor, so the discharge occurs faster and continuously [17,22–24]. In this manner, this sequential mechanism occurs repeatedly.

3. Design of CDEG structure

To mimic the industrial environment, we created a normalized CDEG structure (Fig. S1). A copper plate (area: 10,000 mm², thickness: 0.2 mm), with thermal conductivity, was used to prepare a heat sink with an external cooling fan (JS TECH, XH-X351). A cylinder made of polymethylmethacrylate (PMMA) (diameter: 100 mm, height: 200 mm) was used as the surface of the industrial equipment. Two aluminum electrodes (width: 25 mm) were attached inside the PMMA cylinder. The two electrodes were connected in the freestanding mode, which is...
one of the connection modes used in triboelectric nanogenerators (TENGs) to harvest energy from a fixed position [25]. Moreover, a polytetrafluoroethylene (PTFE) film (thickness: 0.08 mm) was used to cover the aluminum electrodes and the inner surface of the cylinder. The contact angle of the PTFE film was 112°, and the film surface was observed using a field emission scanning electron microscope (FE-SEM) (Fig. S2). The inside of the cylinder was filled with a continuous supply of steam obtained by boiling water. According to the design of the proposed CDEG, heat exchange and electric energy generation occur through the following sequential energy conversion process: the heat energy of the steam is converted into kinetic energy through phase change due to coalescence and gravity force, and the kinetic energy of the condensed water droplets is converted into electrical energy through contact electrification and electrostatic induction. By means of this complex phenomenon, the CDEG can generate electrical energy during condensation of water droplets.

4. Generation mechanism I: nucleation, growth, and shedding

Vapor molecules generated from hot steam form clusters on the PTFE surface (Fig. 2a). After the clusters evenly cover the entire surface, hydrogen bonds induced by attractive forces between clusters lead to the formation of a single large droplet due to the coalescing of nearby clusters. The volume of this droplet grows uniformly in the beginning. As the droplet size increases with repeated coalescence, the lower part of the droplet becomes thicker than the upper part. Then, the driving force increases in the downward direction. When the driving force is greater than the surface tension (friction force), the initial droplet begins to move downward. To clarify the electrical outputs from the complex flow of condensed droplets, we measured the voltages at the electrodes (Ψ1: upper electrode, Ψ2: bottom electrode) by using the non-grounded method; this method utilizes the difference in the outputs of the electrodes grounded to each other [25]. As described previously, it can be assumed that the area in which the droplet is separated is negatively charged, and the droplet itself is positively charged, where the magnitude of the positive charge is the same as the magnitude of the negative charge in the separated area. Before the droplet reaches the upper electrode (t1–t2), the electric potential of the droplet has no effect on the two electrodes (Fig. 2b and c). Because the surplus cations are closer to the negative charged surface than electrode, they cannot affect the electrodes. However, when the droplet reaches the upper electrode (t3), the electrode is affected by the accumulated surplus cations of the

Fig. 2. Electricity generation mechanism I: Nucleation, growth, and shedding. (a) Schematic of droplet flow in nucleation, growth, and shedding. (b) Induced voltage of electrodes measured using the non-grounded method. t1–t2, before the droplet reaches the upper electrode. t3, droplet reaches the upper electrode. Ψ1 and Ψ2 denote the upper electrode and bottom electrode, respectively. (c) Photos of droplet flow in nucleation, growth, and shedding. The regions in which the upper (Ψ1, gray dashed line) and bottom (Ψ2, blue dashed line) electrodes are indicated by black and blue tapes. (d) Schematic of generation mechanism during nucleation, growth, and shedding.
droplet (Fig. 2d). That is, the potential of the upper electrode increases, and consequently, negative free charges are induced in it (positive voltage). Unlike the conventional TENGs based on freestanding mode, the induction of free charges occurs only in upper electrode because each electrode is grounded. In this process, the output is always positive, and it always has a period of less than 5 ms because the surplus cations and the negative free charges are instantaneously equilibrated by electrostatic induction (Fig. S3).

5. Generation mechanism II: shedding, sweeping, and separation

The droplet flows along the surface, and it sweeps and coalesces with other clusters and droplets (Fig. 3a). During this process, the droplet volume increases, and its velocity changes over time. The force generated by the interaction of gravitational force and surface tension affects the droplet flow by repeatedly accelerating and decelerating its downward velocity. Finally, the liquid–vapor surface tension causes the elongation and even separation of the droplet. As the droplet is shedding...
and sweeping on the upper electrode \((t_4)\), no outputs are generated because the negatively charged surface and the surplus cations cancel each other’s potential (Fig. 3b, c, and d). However, when the droplet reaches the bottom electrode \((t_5)\), the potential of the surplus cations affects both of the electrodes. Thus, voltages of opposite polarities are induced in the electrodes, and the outputs are always negative and positive in the upper and bottom electrodes, respectively.

The droplet is separated irregularly during shedding and sweeping. When the droplet is separated and remains on the electrodes, some of the cations are retained in the separated droplets due to the electrostatic induction of free charges in the electrodes and fixed charges in the negatively charged surface \((t_6-t_8)\). Thus, as the droplet flows over the bottom electrode \((t_5-t_7)\) without droplet separation between the upper and bottom electrodes, a relatively small output is continuously generated in the same direction as \(t_5\) because the droplet containing the surplus cations gradually flows toward the bottom electrode. This output has a period of more than 5 ms, which is longer than the output at \(t_3\), because the droplet gradually moves over to the bottom electrode.

Fig. 4. Electricity generation mechanism III: separation and drop off. (a) Schematic of droplet flow in separation and drop off. (b) Induced voltage of electrodes measured using the non-grounded method. \(t_9\), before droplet reaches the remaining droplet. \(t_{10}\), droplet touches the remaining droplet. \(t_{11}-t_{13}\), droplet flows downward. \(t_{13}\), droplet completely drops off the surface. (c) Photos of droplet flow in separation and drop off. (d) Schematic of generation mechanism in separation and drop off.
6. Generation mechanism III: drop off

When the droplet drops off from the surface or when the clusters coalesce with each other at the bottom of the cylinder, some droplets remain at the edge of the cylinder because of surface tension (Fig. 4a). If the next droplet flows toward the remaining droplet, it will sweep the remaining droplet and drop off the edge. From the viewpoint of electrification, the potential of the droplet does not affect the electrodes until it reaches the remaining droplet ($t_9$) (Fig. 4b, c, and d). This is similar to the phenomenon in $t_1$–$t_2$ that does not affect the electrodes until the droplet reaches the upper electrode (Figs. 2b, c, and d). However, as soon as the droplet touches the remaining droplet, the positive charges in the remaining droplet increase the potential of the bottom electrode instantaneously ($t_{10}$). Then, the potential of the bottom electrode gradually decreases as the droplet containing the positive charges flows down ($t_{11}$–$t_{12}$). Eventually, when the droplet completely drops off the surface, a large negative potential is induced in the bottom electrode ($t_{13}$). The output before the drop off is positive in the bottom electrode ($t_{11}$–$t_{12}$), and its period is longer than 5 ms (Fig. S4). Meanwhile, the output generated when the droplet completely drops off ($t_{13}$) has the same polarity as $t_{11}$–$t_{12}$ and a period of 0–10 ms. As described previously, these phenomena occur completely below the electrodes, so all outputs are observed on at the bottom electrode.

7. Output profile of condensed water droplet and sensor application

In a series of condensation processes, various profiles of the electrical outputs with their intrinsic polarities and periods were identified. Each of these profiles was divided into four regions ($A$: $t_3$, $t_5$–$t_7$, $t_8$, $t_{11}$–$t_{12}$, $t_{13}$; $B$: $t_9$, $D$: $t_5$–$t_7$, $t_8$) based on polarity and specific period (5 ms), as shown in Fig. 5a. These divided outputs can be used to more accurately detect specific situations that occur when the condensation environment changes, such as cooler failure. Fig. 5b shows the differences between the outputs according to the temperature difference between both surfaces of the heat sink (copper plate). When the temperature difference increases (cooler on), the condensation rate of the clusters on the surface increases, which shortens the growth time until the droplets are able to start shedding. As the growth cycle of the droplets becomes shorter, more droplets start shedding. Because there are more tiny droplets and clusters that can be coalesced, the size of the droplets increases exponentially as they flow toward the bottom. Eventually, the generation frequency and magnitude of the electrical outputs increase. In contrast, when the temperature difference is small (cooler off), the condensation rate of the clusters decreases. Therefore, the growth time and the number of electrical outputs decrease. In addition, the droplet size decreases exponentially because the amount of condensation decreases. Therefore, the difference in the temperature of the surface causes differences in the heat flux and the condensation rate, leading to a

![Fig. 5. Correlation among heat flux, condensation rate, and electrical outputs of condensed water droplet. (a) Various output profiles (non-grounded method, $\Psi_1$ - $\Psi_2$) in series of condensation processes. $A$ ($t_3$, $t_{13}$), positive and less than 5 ms. $B$ ($t_{11}$–$t_{12}$, $t_{13}$), positive and more than 5 ms. $C$ ($t_9$), negative and less than 5 ms. $D$ ($t_5$–$t_7$, $t_8$), negative and more than 5 ms. (b) Voltage outputs depending on the presence and absence of cooler. (c) Correlation between heat flux and condensation rate. The heat flux and the condensation rate are approximately 2.4 and 1.4 times larger, respectively, when the cooler is on. (d) Number of outputs in four regions ($A$, $B$, $C$, $D$) depending on the presence and absence of cooler.](image-url)
difference in the output. The voltage, current, and rectified voltage outputs are illustrated in Figs S5–7. When the cooler is on, the total heat flux is 3286 W/m², and the condensation rate is 1.46 ml/min (Fig. 5c, see Section 9). Meanwhile, when the cooler is off, the total heat flux is 1383 W/m², and the condensation rate is 1.05 ml/min. Thus, the heat flux is approximately 2.4 times larger, and the condensation rate is approximately 1.4 times higher when the cooler is on. Fig. 5d indicates the number of outputs in the four regions depending on the presence or absence of the cooler. The heat flux directly affects the condensation rate, so the number of outputs decreases in all regions when the cooler is off. Specifically, the number of outputs generated in region B when the droplets drop off after passing through the electrodes (t₁–t₁₂) decreases significantly when the cooler is off because the droplet size decreases exponentially. These results prove that the CDEG can be applied as a sensor to detect heat exchanger failures.

8. Conclusion

We introduced the CDEG, which simultaneously considers the complex environmental conditions involving condensation and heat exchange, for the first time. We observed the characteristic outputs of droplets (t₁–t₂–t₃, t₄, t₁–t₁₂, and t₁₂) in a series of condensation processes and identified the effect of heat flux on the condensation rate and electrical outputs. Moreover, we confirmed that changes in heat flux can be clearly distinguished from the outputs of the droplets, which were classified based on the period and polarity of the outputs. These results indicate that the CDEG can detect abrupt failures of heat exchangers and coolers in real industrial environments. In summary, we analyzed the correlation between various electrical and mechanical mechanisms in a series of condensation processes, and we expect the results to advance the versatility and feasibility of water-related energy harvesting research.

9. Methods

9.1. Heat flux of PMMA surface

The length and diameter of the PMMA cylinder were 0.02 m and 0.01 m, respectively, and it was assumed that the cylinder was filled with 100 °C steam. The temperature of the inner wall surface was 100 °C under normal conditions. According to Fourier’s law, the heat transfer rate and Newton’s cooling law are as follows:

\[ q[W] = \frac{2\pi Lk_p(T_i - T_o)}{\ln(r_2/r_1)} \]  
\[ q[W] = h(A_o - T_o) \]  

where \( k_p \) [W/mK] denotes the thermal conductivity of PMMA; \( T_i \) and \( T_o \) [K] the inner and outer wall temperatures, respectively; \( T_w \) the ambient temperature; \( L \) [m] the cylinder length; and \( r_2 \) and \( r_1 \) the outer and inner radii of the cylinder, respectively. In addtion, \( h \) [W/m²K] is the heat transfer coefficient, and \( A_o \) is the outer surface area of the cylinder. According to the natural convection correlation equation in the vertical plate, the heat transfer coefficient can be expressed as follows:

\[ Nu = \frac{hD}{k_p} = 0.59Ra^{0.25}(10^4 < Ra < 10^6) \]  
\[ Ra = GrPr \]  

where \( Nu \), \( Ra \), \( Gr \), and \( Pr \) denote the Nusselt number, Rayleigh number, Grashof number, and Prandtl number, respectively, and \( g \), \( \beta \), \( L \), \( \nu \), and \( \alpha \) denote the gravitational acceleration, thermal expansion coefficient (for ideal gas 1/T[1/K]), characteristic length, kinematic viscosity, and thermal diffusivity. Eq. (3) was proposed for vertical plate flow, but it can be applied to a vertical cylinder with height \( L \) if the condition \( D/L > 35/Gr^{0.25} \) is satisfied, where \( D \) denotes the cylinder diameter.

The outlet temperature \( T_0 \) can be determined using the energy conservation law, and the values of \( T_0 \) and the average natural convection heat transfer coefficient, as determined using Eqs. (1–3), are 95.62 °C and 6.48 W/m²K, respectively. It also satisfies the range of \( Ra \) and cylindrical conditions. Therefore, the heat flux on the PMMA surface is 490 W/m².

9.2. Heat flux of side surface area of copper

When the heat flux [W/m²] is constant over the entire surface of the copper plate, the total amount of heat transferred \( (Q, [W]) \) is proportional to the area. Then, the upper and side surface areas are 78.54 cm² and 0.63 cm², respectively. Therefore, it is assumed to be negligible because the amount of heat transferred toward the side surface area is less than 0.8% of the total amount of heat transferred over the entire surface.

9.3. Heat flux through Peltier capacity (cooler on)

The heat transfer rate under the cooling condition can be measured based on the operating capacity of the Peltier device. In this study, a TEC1-12706 is used as the Peltier device for cooling, and it is operated at 2-V and 1.8-A. Its cooling capacity is 21.96 W. The heat flux of the Peltier device is 2796 W/m², which follows its operating capacity.

9.4. Heat flux of copper (cooler off)

The natural convection in the upper surface of the copper plate can be calculated using Eq. (3), which is based on Fourier’s law (Eq. 1). Here, the characteristic length \( L \) used in \( Ra \) in Eq. 4 is \( D/4 \) of the circle. In addition, the outside temperature and heat transfer rate can be obtained using Eqs. (2) and (3), and (5), as follows:

\[ q[W/m²] = k_p(T_o - T_w) \]  

where \( k_p \) is the latent heat of water, and it is 2,256,430 J/kg. -

9.5. Total heat transfer rate and condensation rate

To calculate the condensation rate, the total cooling capacity \( (Q, [W]) \) must be calculated. Assuming that all of the cooling capacity is used for condensation and the heat flux of the PMMA surface is the same under both the cooler on and off conditions, the condensation rate can be calculated as follows:

\[ \dot{m} = \frac{Q}{h_fg} \]  

where \( h_f \) [J/kg] is the latent heat of water, and it is 2,256,430 J/kg.

When the cooler is on, the total heat transfer rate is 52.75 W, which is the sum of the heat transferred through the PMMA (30.79 W) and the capacity of the Peltier device (21.96 W). In addition, the total condensation rate is 1.46 ml/min. Meanwhile, when the cooler is off, the total heat transfer rate is 37.81 W, which is the sum of the heat transferred through the PMMA (30.79 W) and the capacity of the copper plate (7.02 W). Moreover, the total condensation rate is 1.05 ml/min.

CRediT authorship contribution statement

Gunsob Shin: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. Hyungseok Yong:
Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. Jihoon Chung: Writing - original draft, Supervision. Eunho Cho: Formal analysis, Writing - original draft. Jihong Ju: Conceptualization, Methodology. Zong-Hong Lin: Supervision, Writing - review & editing. Dongseob Kim: Project administration, Writing - review & editing. Jihoon Chung: Writing - original draft, Supervision. Eunho Cho: Formal analysis, Writing - original draft. Jihong Ju: Conceptualization, Methodology. Zong-Hong Lin: Supervision, Writing - review & editing. Dongseob Kim: Project administration, Writing - review & editing. Hyungsoon Lee: Supervision, Resources, Project administration. Sangmin Lee: Conceptualization, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

G. S., H.Y., B.K., and S.L. discovered and conceptualized the phenomenon. G.S., H.Y., Z.H.L., and S.L. designed the project. G.S., H.Y., and J.J. conducted the experiments. E.C. and H.L. fabricated heat exchanger and analyze condensation process. D.K. and B.K. commented on the manuscript. All authors wrote the manuscript and analyzed the data. B.K., and S.L. supervised the whole project.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2020.105713.

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