



Electrical energy harvesting from water droplets passing a hydrophobic polymer with a metal film on its back side



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ABSTRACT

Recent research has demonstrated that electrical energy can be harvested when water droplets move over a hydrophobic polymer covered by a single electrode on its back-side. Here we study the charge dynamics as water droplets pass the polymer. We also investigate how the charging of an external capacitor changes with water flow volume rate, and present a model to understand the results.

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1. Introduction

Electrification of water may occur when it undergoes phase changes or is contacted with other species (gas, liquid or solid) [1–6], and one of the most well-known examples utilizing this effect is the Kelvin water drop generator [8]. A hydrophobic surface coming into contact with water may develop a measurable negative charge. Much research has been undertaken to investigate this phenomenon, both from an experimental and a theoretical point of view [1,9–15]. Of particular interest in recent years has been the large negative charge developed on neutral hydrophobic fluoropolymers on contact with water, since such polymers have found widespread use and their properties therefore should be better understood. Although no universally accepted model can be said to exist, there is considerable evidence pointing to the negative charge as a result of preferential adsorption and/or orientation of O–H groups near the hydrophobic polymer surface [7,9–14]. In addition to more comprehensive molecular modelling, systematic and well-defined experimental studies of the contact electrification between water and a larger range of polymers are needed to obtain a better understanding of the underlying mechanisms [16].

When water is removed from the polymer, the resulting charge separation can be measured by utilizing an electrode on the back-surface of the polymer. Such investigations have revealed that the separation of charge depends on several parameters, including the

type of polymer and the conductivity of the liquid [15]. It has also been noted that while the surface charge density of the monolayer might be high (-50 mC/m^2 , see e.g. Ref. [14]), the charge density participating in charge transport is orders of magnitude lower than the total charge density of the double layer. Recent research has demonstrated that the charge separated when water droplets move over the hydrophobic polymer covered by a single electrode on its dry back-side can be used to power small electronics [17–28]. The main idea in several of these studies is to first electrify the hydrophobic polymer by contact with water. Subsequent water droplets will aid the formation of an electrical double layer at the polymer surface, thus resulting in current flow through an external circuit when water droplets pass the edges of the metal electrode. The qualitative features of the charge separation appear to be understood, although a first-principle quantitative estimate of the charges participating in the charge transport seems to be lacking. Also lacking is an understanding of which modes are responsible for the electrical current. Water droplets may either move over the metal electrode, or bounce directly on top of it. Here it is showed that these two mechanisms give different contributions to the current.

Of even larger practical importance is knowledge of how the electrical energy harvested by an external circuit can be related to the water volume rate. Sun et al. reported that the power generated by electrified water drops collected in a Faraday cup increases with volume flow rate as long as individual droplets form, but decreases with flow rate when a continuous water film forms [29]. However, no quantitative model to explain this observation was reported. We

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believe that the feature observed in Ref. [29] is a general one that should also be observed in the charging rate of an energy harvesting system. In the system presented in the current work, a metal electrode is placed on the back-side of the hydrophobic polymer. The contact electrification properties of this particular geometry were reported in Ref. [15], and its application to energy harvesting for powering electronic systems in Ref. [20]. In the current work it is demonstrated that the charging rate of an external capacitor connected to the metal electrode through a rectifying bridge will be charged at a rate that depends strongly on the water volume rate over the polymer. At the transition from droplet motion to a continuous stream of water, the charging rate changes radically. A model is developed, which might be expected to be of importance when designing electrical energy harvesting systems based on water droplet flow on hydrophobic polymers.

2. Experimental methods

A fluorinated ethylene propylene (FEP) film of thickness 75 μm (DuPont) of lateral dimensions 29 cm \times 20 cm was glued to aluminium tape of lateral dimensions $L = 29$ cm by $w = 15$ cm and thickness about 0.1 mm. The aluminum film was resting on a polymethylmethacrylate plate. Single droplets of ultrapure water (resistivity 18.2 M Ωcm , Millipore) or tap water (resistivity 7 k Ωcm) were pipetted through a grounded metal cone connected to a polyethylene pipette, while larger volume flow rates were provided by a faucet fed through a metal nozzle in a garden hose. The nozzle consisted of a circular metal plate of diameter 5 cm with 194 holes of diameter 0.5 mm. For small volume rates (below 10 mL/s) the garden hose produced larger droplets of diameter up to 5 mm (volume up to 65 μL), whereas for larger volume rates the droplets typically had a diameter of about 1 mm corresponding to smaller droplet volume of the order of 1 μL . Although different nozzles were tried, tests indicated that the different droplet size distributions at different volume rates had little on the charging properties of the energy harvester, for the simple reason that there is no one-to-one correspondence between droplet size in air and that passing the lower edge of the metal electrode on the polymer. That is, upon impacting the polymer, the droplets would change size due to coalescence or separation in a more or less random manner. There was no way to control this factor experimentally.

The amount of charge as well as the current induced in the metal electrode as water droplets passed its edge were measured using a Keithley 6514 electrometer. In order to store the charge induced in the metal electrode in a simple energy harvesting system, the electrode was connected to a bridge rectifier and a 33 μF electrolyte capacitor as shown in Fig. 1. As bridge rectifier, we used a Fairchild Semiconductor DF005M, with a reported maximum root mean square bridge input voltage 35 V and maximum repetitive reverse voltage of 50 V. The open circuit voltages measured upon contact electrification (<20 V) were much smaller than the limiting values of the bridge rectifier.

3. Current generated by a single drop

Contact between water and polymer generates charge on the polymer surface, which can be measured by measuring the change in surface potential. Using a Digital Static Field meter from DescoEMIT, we measured typically up to -1 kV, which should be compared to the nearly zero surface potential found for dried unused polymer. The magnitude and sign of the observed surface potential (and surface charge) is in agreement with results found previously for Teflon [15]. Small amounts of water remain on the surface for some time. When the water is removed (due to evaporation, etc), the surface potential becomes smaller, and is further

removed by ions in the air. In the current study, measurements were done on a recently wetted surface to ensure that this factor did not obscure the results.

Let us first consider the situation that occurs when the droplets roll/slide over the surface as shown in Fig. 2 a) and b). Drops moving over the polymer surface will form an electrical double layer at the polymer surface, as shown in Fig. 2 a). The surface charge density in the electrical double layer can be large (about -50 mC/m 2 , see e.g. Ref. [14]), but the electret charge density forming on the surface of the polymer (red color in Fig. 2) is only a fraction of the total charge density. The black charges in Fig. 2 illustrate the additional charge participating in the double layer. Although one expects the total electrical double layer charge to be orders of magnitude larger than the net electret charge (red color), the two different charges (black and red) have similar magnitudes in the figure for clarity. When the droplet moves over the edge of metal electrode, a net negative charge remains on the polymer surface, and net positive charge moves into the metal electrode to compensate for this. Thus, a current will run in the external circuit as shown in Fig. 2 b).

The charge measured as individual water drops of volume 50 μL is displayed in Fig. 3 a). It is found that each charge step has a negative sign (i.e. the water droplet is positively charged) and magnitude between 0.5 nC and 1 nC. The variability is probably due to variations in how the droplets move down the incline, i.e. whether there is rolling, sliding, fluctuations or air-induced charging, such that it is picking up additional charge on its way down the incline. The contact area between a water drop of diameter D and the hydrophobic polymer beneath depends on the three-phase contact angle θ as $A_t \approx (1/4)\pi D^2 \sin^2\theta$. Thus, the largest contact area occurs when the contact angle is $\theta = 90^\circ$, and the smallest when the contact angle is $\theta = 180^\circ$. Here we consider FEP which has been found to have a three-phase contact angle $\theta \approx 109^\circ$ [28].

For the largest droplets of volume 50 μL , we observe that the contact area between the droplet and the FEP polymer is $A_t \approx 1.2 \cdot 10^{-5}$ m 2 (corresponding to a diameter of about 4 mm) when the droplet is at rest. We observed this area by placing the transparent FEP film on glass slide, and then photographing the glass slide from below. Assuming, as in Ref. [28], a transferrable surface charge density $\sigma \approx 16$ $\mu\text{C}/\text{m}^2$ results in an estimated induced charge of $q \approx 0.2$ nC. This number is at least a factor of two smaller than the observed charge steps in Fig. 3 a). The explanation is either that the transferrable charge density is higher than 16 $\mu\text{C}/\text{m}^2$, or that the area during droplet movement is larger than for a droplet at rest. Knowing that splashing and motion of droplets through air causes additional charge to emerge, this observation might not be surprising [2,16]. The observation could also be explained if the droplet utilizes more than the apparent contact area given above to pick additional charge on its way down the polymer incline, an action which would depend strongly on the rolling and/or sliding motion on the way down.

Fig. 3 b) shows an example of current induced as the single droplet moves over the metal electrode edge when the polymer + metal electrode has an angle of 44° with the horizontal plane. Integrating the current over time gives a charge of the order of 0.7 nC, in agreement with the observations of Fig. 3 a). It should be noted that the solid line in Fig. 3 b) exhibits a sudden increase after about 0.06 s. The reason for this is unknown, but may be related to spatial charge accumulation and subsequent enhanced electrostatic attraction between the droplet and the metal as the droplet rolls of the electrode edge.

Current can also be generated when the water droplet falls directly onto the edge of the electrode generates a current as the droplet is flattened upon impact, see Fig. 2 c) and d) for schematic drawings. The current generated for such an event is shown in Fig. 3

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