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Reverse Electrowetting-on-Dielectric Energy Harvesting Using 3D Printed Flexible Electrodes for Self-Powered Wearable Sensors

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Abstract— Reverse electrowetting-on-dielectric (REWOD) presents a unique low-frequency motion energy harvesting method to self-power wearable sensors for human health monitoring in real-time. However, previous studies in REWOD energy harvesting have mainly focused on enhancing power density using rigid electrodes, which due to their rigidity, are not ideal to be implemented as wearable energy harvesting or motion sensing applications from human motion activities. Self-powered wearable sensors should operate continuously and sustainably in any kind of bending motion of electrodes and without an external power source to be considered as the next generation self-powered wearable sensors. Herein, we demonstrate AC current generation by repeatedly modulating a liquid droplet of microliter volume on an elastomer-based 3D printed flexible electrode without any external bias source as a potential power source for the next generation self-powered wearable sensors. Flexible electrodes were fabricated by deposition of ~200 nm of Titanium (Ti) layer and an additional ~200 nm of Aluminum Oxide (Al_2O_3) dielectric layer along with ~50 nm of Chromium (Cr) as an interlayer between the metal and the dielectric layers on a flexible Polydimethylsiloxane (PDMS) substrate. Using a 50 µL electrolyte droplet and 2.5 mm of electrode displacement at a low-frequency motion of 1-2 Hz, a maximum peak-to-peak AC current of ~340 nA was measured. Although significant progress is yet to be made towards implementing REWOD energy harvesting as a reliable source of power for wearable self-powered systems, this work signifies the proof of concept in implementing flexible electrodes in REWOD energy harvesting.

Index Terms—REWOD energy harvesting, Self-powered wearable sensors, Flexible electrodes, 3D printing.

I. INTRODUCTION

In recent years, wearable sensors and portable electronic devices have been in a stage of rapid development [1-5]. Traditionally, wearable sensors are powered using batteries that limit the longevity of the device due to the need for frequent battery replacement and device maintenance. For the next generation self-powered wearable sensors to reliably monitor human health in real- time, they need to operate continuously and sustainably without any external bias source. There are many existing energy harvesting technologies that can produce an ample amount of power that is required to self-power these sensors [6-9]. However, many of these technologies can efficiently operate only at a high- frequency range and also require the resonance of solid structures. In the last decade, reverse electrowetting-on-dielectric (REWOD) energy harvesting has emerged as an efficient energy harvesting technology that can generate high power output at low modulation frequency and does not require resonance of solid structures. [10-12]. Although much progress has been made in enhancing power density from REWOD energy harvesting, much of the work in REWOD thus far has used rigid electrodes such as; glass and silicon substrates, which due to their fragile nature, are not ideal to be implemented in human motion sensing applications [13-16]. Therefore, in this work, as a proof of concept, we have successfully generated high magnitude AC current from a very low-frequency modulation (1-2 Hz) using Polydimethylsiloxane (PDMS)-based three dimensional (3D) printed flexible electrodes. The working mechanism of REWOD energy harvesting is illustrated in Fig. 1. A liquid droplet of microliter volume is sandwiched between two electrodes and repeatedly squeezed due to electrode oscillation thereby mechanically varying electrical double layer (EDL) capacitance across electrodes and as a result generating AC current.

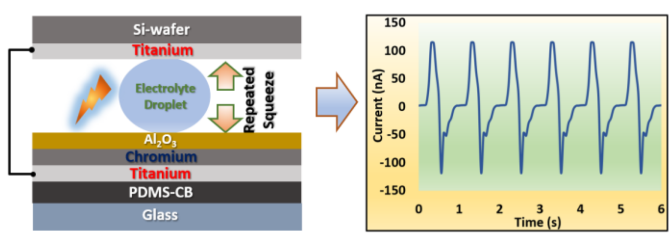

Fig. 1. Working mechanism of REWOD energy harvesting (left). Repeatedly squeezing a droplet between two electrodes induces modulating capacitance at the electrolyte-dielectric interface to generate alternating current signal (right).

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Table 1. Ink composition by percentage

SE1700	SE1700 crosslinker	Sylgard 184	Sylgard 184 crosslinker	Carbon black
75	7.5	11.3	1.2	5

In wearable sensors for human motion sensing applications, electrodes fabricated on a flexible substrate are ideal due to their flexibility, lightweight, and conformity to the curvilinear body shape. However, the insulating nature of different polymer-based substrates, such as the one used in this work, require thin film deposition of conductive and dielectric materials to render interactive functionality to substrates in REWOD energy harvesting. In addition, the porous nature of 3D-printed flexible substrates for REWOD electrode fabrication is another challenge. To overcome these challenges, as a novel approach, we have successfully implemented conformal thin film deposition of both the conductive and dielectric materials with an additional thin metal adhesion layer in between to help create a stronger adhesion between the metal and the dielectric layer such that it provides required flexibility and prevents the metal and dielectric layers from fracturing due to bending and stretching. Unlike prior research work on REWOD that heavily relied on rigid electrodes, the novelty of this work also lies on the feasibility of implementing REWOD energy harvester to self-power wearable sensors from multiple bending of various human motion activities.

II. MATERIALS AND METHODS

A. Ink Formation

We have developed a 3D-printable ink for a direct ink writing (DIW) additive manufacturing technique to fabricate flexible electrode substrates for REWOD energy harvesting using PDMS and carbon black (PDMS-CB). We formulated the base PDMS with two types of PDMS (Dowsil SE1700® and Sylgard 184®) and their corresponding curing agents with a ratio provided in Table 1. Thicker Dowsil SE1700® and thinner Sylgard 184® were used together to adjust the rheological properties of the ink for 3D printing [17-18]. Next, the CB powder was added to the base of PDMS formulation to provide some mechanical strength to the flexible electrodes. The PDMS print without CB was extremely flexible than what was required and was very difficult to handle during further fabrication.

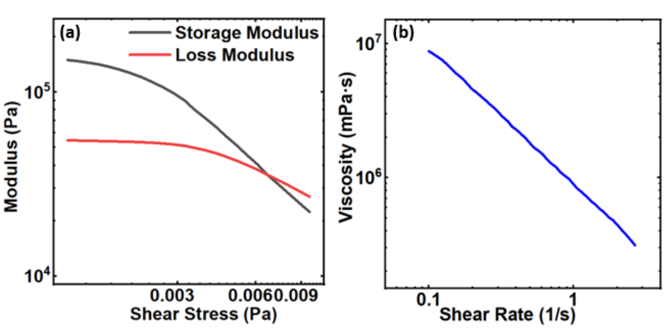

Fig. 2. Measurement of rheological properties for the PDMS-CB ink: (a) Modulus as a function of shear-stress. (b) Viscosity as a function of shear rate.

Finally, the composite was mixed in a Flacktek® DAC 400.2 VAC Speedmixer at 2000 rpm for 3 minutes to make the mixture ready to be used for 3D printing.

B. 3D Printing

After mixing, the ink was transferred into a Nordson® 10-cc syringe and was centrifuged (Ohaus FC5706) at 3000 rpm for 3 min to remove air bubbles and condensate the ink. Then the syringe tip was connected with a 610 µm nozzle by Luer lock and sealed with a piston. Afterwards, the syringe was mounted on a customized DIW 3D printer (MakerGear M2). The flexible electrode substrates were 3D printed using the following printing conditions: 0.002 cc s^{-1} material extrusion rate and 15 mm s^{-1} printing speed. The electrodes were cured in an oven at 100°C for 1 hour after printing.

C. Ink Characterization

The rheological properties of the ink are crucial as they determine how well the ink prints in DIW method. Using a rotational rheometer (MCR 72, Anton Paar®) with a 24.9 mm diameter flat plate, the rheological properties of the PDMS-CB ink were measured as shown in Fig. 2. The yielding and shear thinning behaviors indicate that the ink is 3D printable via DIW. Fig. 2(a) shows shear thinning behavior in relation to the storage and loss modulus with shear stress. Storage modulus dominates loss modulus before crossover, and ink shows a solid like behavior. Upon cross-over, ink behaves like viscoelastic gels as the loss modulus dominates the storage modulus. Flow curve in Fig. 2(b) shows the shear-thinning response of the PDMS-CB ink. With shear strain, the ink viscosity decreases and it flows easily through the nozzle.

III. DEVICE FABRICATION AND CHARACTERIZATION

A. Thin Film Deposition

A 3D printed PDMS-CB flexible substrate was used for the bottom REWOD electrode. The printed substrate and its bending capability is shown in Fig. 3(a) and 3(b), respectively. The flexible substrate was first deposited with ~200 nm of Ti conductive layer and an additional adhesion bilayer of Cr before depositing with ~200 nm of Al_2O_3 dielectric layer. A very thin adhesion layer (~50 nm) of Cr in between Ti and Al_2O_3 was added to provide a stronger bond between the Ti and the Al_2O_3. It has been shown that an adhesion layer of Cr between Ti or other softer metals and dielectric strengthens the overall material properties [19-20]. Before the deposition of dielectric material over the Ti and Cr layers, a small portion of the flexible substrate was covered with Kapton tape to block the dielectric insulation and was later removed to enable electrical measurements. A completed flexible electrode is shown in Fig. 3(c). Generally, a hydrophobic layer is also deposited over the dielectric layer by spin coating in REWOD energy harvesting for surface hydrophobicity. However, the CYTOP solvent requires curing the electrode at over 185°C to completely evaporate the solvent, which is not feasible with PDMS since it is not thermally stable at that temperature. Nonetheless, metal oxide dielectrics, such as the one used in this work are polar in nature

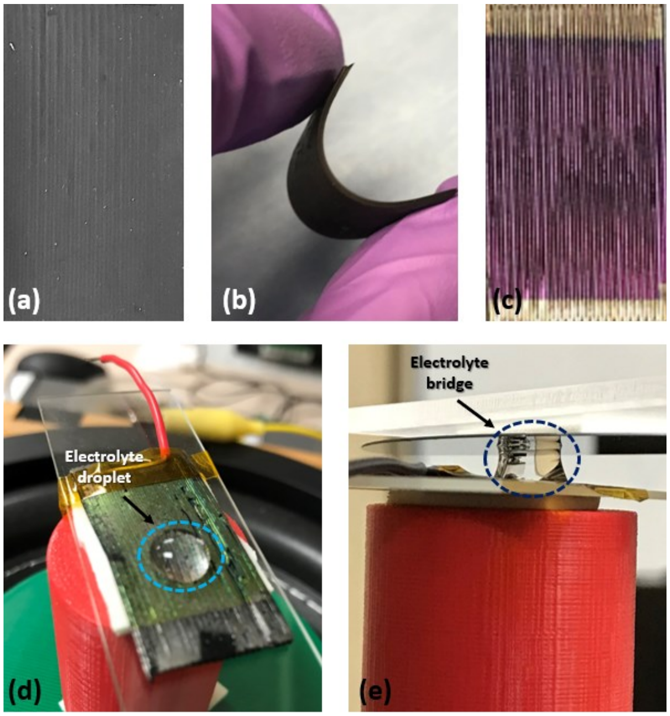

Fig. 3. Flexible electrodes from 3D printing to AC current generation: (a) 3D printed flexible substrate. (b) 3D printed flexible substrate showing its bending capability. (c) Fully fabricated flexible electrode with all metal and dielectric layers. (d) Electrolyte droplet over the dielectric layer on the electrode surface. (e) A bridge of the liquid droplet between top and bottom electrodes.

and therefore hydrophobic. The hydrophobicity of the Al_2O_3 surface was sufficient for the droplet modulation to generate AC current. The liquid droplet is visually observed to have formed a contact angle greater than 90° showing the hydrophobic surface suitable for REWOD energy harvesting as shown in Fig. 3(d). AC current was measured using a similar test set- up as used in our prior works [13, 21]. A bridge of the liquid droplet was created upon making the droplet contact both top and bottom electrodes as shown in Fig 3(e). The top conductive electrode was a doped Si wafer with a thin deposited layer (~100 nm) of Ti. Si wafer used as the top electrode in this work was for current conduction purpose only and will eventually require a smoother metal coated flexible electrode for a fully flexible and self-powered wearable sensor as the future work.

All thin films were deposited using the NEE-400 dual e-beam evaporator (Nanomaster Inc.). After each deposition, the layer thicknesses were measured and verified using the Alpha-Step D-300 Stylus Profiler (KLA Corporation). Low resistance laboratory-grade deionized (DI) water was used as an electrolyte. Many REWOD experiments in the past have used electrolytes that are either expensive such as Galinstan or toxic such as mercury. Semi-pure DI water was chosen electrolyte because it is safe, convenient, and cost-effective.

B. Surface Characterization

In order to implement flexible polymer-based electrodes as a REWOD-based energy harvester and a wearable sensor, they need to

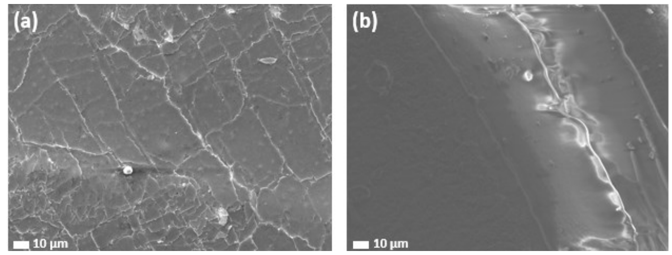

Fig. 4. SEM images of flexible electrodes after thin layer deposition of metal and dielectric layers: (a) Without Cr as an interlayer. (b) With Cr as an interlayer.

be easily deformed, bent, and stretched under strain without being damaged. Since PDMS-CB electrode fabricated in this work requires thin film deposition of a metal layer for conduction and dielectric layer for EDL formation to generate AC current, it requires conformal and adhesive deposition of these thin films and a strong adhesion between the Ti, and Al_2O_3 layers. SEM images were taken to study the surface condition and its morphology before and after each deposition layer. As shown in Fig. 4(a), the surface after Ti and Al_2O_3 layer deposition had many cracks. As discussed in the previous section, Cr metal has been shown to create an efficient adhesion between Ti and Al_2O_3 layers. As shown in Fig 4(b), the surface condition after Ti, Cr, and Al_2O_3 layer deposition was significantly improved. It is essential to ensure that there are minimal cracks on the surface for efficient REWOD energy harvesting. The presence of cracks may allow liquid electrolyte to penetrate through the cracks onto the metal layer, which can potentially short the electric circuit and cause experimental failure.

IV. MEASUREMENTS AND RESULTS

A. AC Current Measurements

AC current measurement set-up used in this work was similar to the one used in our prior works on REWOD energy harvesting [13]. During the electrolyte modulation between the electrodes, the generated AC current was measured using a Keithley 2400 Sourcemeter and the measurement results were acquired using the Keithley data acquisition software, Kickstart 2.0. The measured peak-to-peak AC current at 1 Hz modulation frequency and 2.5 mm of electrode displacement from a 50 µL of electrolyte droplet was ~40

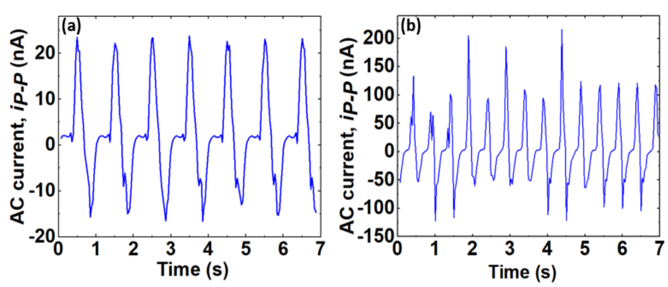

Fig. 5. AC current generation using REWOD energy harvester. (a) Low scale peak-to-peak AC current at 1 Hz modulation frequency. (b) peak-to-peak AC current at 2 Hz modulation frequency.

nA, which increased to as high as ~340 nA for 2 Hz modulation frequency. Note that no bias source was applied in this experiment. These magnitudes of AC currents for 1 Hz and 2 Hz modulation frequencies in terms of current density are 122 nA/cm^2 and over 1μA/cm^2 respectively. The AC signals for 1 Hz and 2 Hz frequencies are given in Fig. 5(a) and 5(b), respectively. The variation in AC signal magnitudes at both the frequencies of modulation (larger variation at 2 Hz) could be attributed to various external factors such as vibration of the measurement system and uneven spreading of the electrolyte droplet on the rough surface of the flexible electrode at different time intervals. The REWOD signals achieved in this work should be sufficient for detecting whether a person is at rest, walking, or running and integrate the harvester in wearable sensors to power them without requiring an external power source [21].

B. Computation of AC Voltage

Considering a parallel arrangement, the resistance (R_P) and capacitance (C_P) were measured during modulation using an impedance and electrochemical front end (AD5940) by Analog Devices. This measurement provided the total impedance of the system and phase angle for the frequencies of oscillation. For R_P and C_P in parallel, the equivalent impedance is given by Equation (1). The resistance, R_P, is obtained by rearranging the equation for phase angle (Equation 2).

$$|Z| = \frac{1}{\sqrt{\left(\frac{1}{R_P}\right)^2 + (\omega C_P)^2}} \tag{1}$$

$$R_P = \frac{\tan(\varphi)}{-\omega C_P} \tag{2}$$

In the above equations, |Z| is the absolute impedance, φ is the phase angle, and $\omega=2\pi f$ is the angular frequency of the AC signal where f is the applied frequency of oscillation. R_P for both the frequencies was computed from the measured impedance and phase angle. The impedance for both the frequencies was ~87MΩ. AC voltage was computed from the measured values of AC current (I_{AC}) and impedance ($|Z|$) using Ohm's law ($V_{AC} = I_{AC} * |Z|$). The AC voltage for 1 and 2 Hz frequencies were computed to be ~3.5 V and 29.5 V, respectively.

V. CONCLUSION

3D printed PDMS-based flexible electrodes were implemented for REWOD energy harvesting with an objective to self-power wearable sensors without any external bias source. Using a 50 µL of electrolyte droplet and 2.5 mm of electrode displacement at a low-frequency motion of 1-2 Hz, a maximum peak-to-peak AC current of ~340 nA was measured, which can be used to self-power wearable sensor and reliably monitor human health in real-time. Although significant progress is yet to be made towards implementing REWOD energy harvesting as a reliable source of power for wearable self-powered systems, this work signifies the proof of concept and paves the way towards implementing flexible electrodes in REWOD energy harvesting.

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