Energy harvesters based on fluorinated ethylene propylene unipolar ferroelectrets with negative charges

Cite as: AIP Advances 9, 125334 (2019); https://doi.org/10.1063/1.5086113
Submitted: 26 June 2019 . Accepted: 08 December 2019 . Published Online: 27 December 2019

Xingchen Ma, Xiaoqing Zhang, Gerhard M. Sessler, Li Chen, Xiaoya Yang, Ying Dai, and Pengfei He
Energy harvesters based on fluorinated ethylene propylene unipolar ferroelectrets with negative charges

Xingchen Ma, Xiaoqing Zhang, Gerhard M. Sessler, Li Chen, Xiaoya Yang, Ying Dai, and Pengfei He

AFFILIATIONS
1 Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China
2 Institute for Telecommunications Technology, Merckstrasse 25, 64283 Darmstadt, Germany
3 School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, China
A) Authors to whom correspondence should be addressed: x.zhang@tongji.edu.cn and gerhard.sessler@tu-darmstadt.de

ABSTRACT
Energy harvesting devices can convert energy from various ambient sources (that are usually ignored) into electricity to power portable electronic devices and wireless sensor networks. Such devices have stimulated extensive interest in recent years. For the current study, we succeeded in designing and fabricating a new type of energy harvester using high performance unipolar ferroelectrets made from fluorinated ethylene propylene (FEP), consisting of a negatively charged and a noncharged wave-shaped FEP layer. Such materials are resistant to elevated temperatures owing to the thermally stable negative charges in this material. They also exhibit great stretchability due to the symmetric wave-shaped structure. By using a variety of test frequencies, seismic masses, external resistances, and wave-shaped FEP films with different surface potentials, we systematically investigated the energy harvesting performance of these devices. Typically, wave-shaped films with a material thickness of 12.5 μm and a maximum total thickness of the wavy structure (including the air thickness) of about 160 μm were employed. When charged to a surface potential of −500 V and operated with a seismic mass of 3 g fixed on the center of the band shaped unipolar ferroelectret sample, a power of 355 μW for an input acceleration of 1 g (g is the gravity of the Earth) was delivered to the optimal load resistance at the resonance frequency of 22 Hz. The relatively large power generated is due to the sizeable elasticity of the wave-shaped FEP film and the amplification of the force acting on the film in the specifically designed device.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5086113

I. INTRODUCTION

In the past two decades, accompanied by the development of miniature, low power consumption electronics, a new research field called energy harvesting has arisen and gained increasing attention from both academia and industry. Energy harvesting refers to collecting some of the surrounding energy resources, including solar, thermal, and mechanical energy, and converting it into electric energy. Numerous advantages of this technology exist, such as durable operation that is inexpensive and eco-friendly. In recent years, with the advent of the Internet of Things (IoT) and intelligent wearable electronics, energy harvesters were in great demand. For the operation of such harvesters, three working mechanisms are usually involved, namely, the piezoelectric, electromagnetic, and electrostatic principles.

For piezoelectric energy harvesting, the ceramic material lead zirconate titanate (PZT) and the ferroelectric polymer polyvinylidene fluoride (PVDF) are normally used. Recently, ferroelectrets were also employed to harvest vibrational and acoustic energy. Ferroelectrets, also known as piezoelectrets, are cellular materials with internally charged voids that can exhibit large piezoelectricity. Ferroelectrets can be divided into two categories, one being bipolar ferroelectrets with positive and negative charges located on opposite surfaces of the voids and the other being unipolar...
ferroelectrets with unipolar charges on only one surface. Bipolar ferroelectrets have been widely investigated, and their energy harvesting performance has been explored.\cite{17,18} Unipolar ferroelectrets are a relatively new concept.\cite{29,30} Previous work shows that they have great potential due to their increased thermal stability.\cite{31,32} Their energy harvesting performance was first investigated by using negatively charged polypropylene.\cite{26,27} However, the charge storage stability of polypropylene is relatively poor, and the charges will decay and even disappear completely when the devices are used at elevated temperatures.

In the present study, thermally stable unipolar ferroelectrets were realized with wavy fluorinated ethylene propylene (FEP) films having a negatively charged layer.\cite{26,28} The suggested harvesters incorporating such unipolar ferroelectret films are superior to those with bipolar ferroelectrets since in FEP negative charges are much more thermally stable than positive charges.\cite{27,33} It was found that a relatively large amount of power can be generated with such harvesting devices.

II. WORKING PRINCIPLE OF THE ENERGY HARVESTER

Figure 1 schematically illustrates the working mechanism of the energy harvester. In particular, Fig. 1(a) (inset) shows the schematic of the microstructure of a unipolar ferroelectret investigated in this study with a simplified model for calculating the induced charge on the sample electrodes. We assume that the lower surface of the upper FEP film is uniformly negatively charged. Thus, there are uniformly distributed induction charges on the electrodes. For simplicity, the wavy shape of the FEP film is not shown in the simplified model and it will also be ignored in the following calculations. This can be done without a significant loss in accuracy in the analytical results.

According to Gauss’ theorem and Kirchhoff’s second law in a short circuit, applied to the geometry shown in the inset of Fig. 1(a), the induction charge density on the top electrode is given by

\[
\sigma_T = \varepsilon_0 \varepsilon_1 E_1 = -\sigma_e \frac{\varepsilon_1 d_1 + \varepsilon_2 d_2}{1 + \varepsilon_1 \frac{d_1}{d} + \varepsilon_2 \frac{d_2}{d}},
\]

where \(\sigma_e\) is the surface charge density of the upper FEP electret film, \(\varepsilon_1\) and \(\varepsilon_2\) are the relative permittivity of upper FEP film and lower FEP film, respectively, \(d_0\), \(d_1\), and \(d_2\) are the thicknesses of the air layer, upper FEP film layer, and lower FEP film layer, respectively.

Figure 1(b) illustrates the relation between charge density on the top electrode and thickness of the air layer for the simplified model according to Eq. (1). The parameter values used in the calculation are a surface charge density of 0.42 mC/m\(^2\), a relative permittivity of 2.1, and a thickness of the FEP film of 12.5 \(\mu\)m. It is noted that when the thickness of the air layer varies from 1 to 100 \(\mu\)m, the corresponding charge density on the top electrode increases steadily. This means that large power can be generated by the energy harvester as it vibrates in this range. Therefore, the variation of the air gap thickness, which is associated with mechanical properties and size of FEP films, seismic mass, and vibration acceleration of the ambient energy, must be taken into account for designing an efficient energy harvester.

A variation of the air gap thickness may be obtained by stretching or releasing the wavy film. Since the film is under tension, this is a reversible process. Figure 1(c) illustrates how a sinusoidal thickness change of the air gap \(d_0\) during one cycle yields, with a phase shift (not shown), a sinusoidal change of charge density on the top electrode increases steadily. This variation is a surface charge density of 0.42 mC/m\(^2\), and a thickness of the air layer for the simplified model.

**FIG. 1.** Working mechanism of the energy harvester. (a) Schematic cross sectional view of the structure of the unipolar ferroelectret investigated in this study. The inset shows a simplified model for calculating the induced charge on electrodes in the sample. (b) Induced charge density of the top electrode vs the thickness of air layer for the simplified model. The charge density varies strongly in the area between the two blue marks. (c) Schematic diagram indicating the working principle of the energy harvester based on the FEP unipolar ferroelectret. For a short circuit, sinusoidal variations of the air-gap thickness cause the illustrated changes of charge density \(\sigma_T\) and current \(I\). Note: for finite values of \(R_L\), there is an additional phase shift between these quantities (not shown). (d) Setup for measuring output power of the energy harvester.
charge density of \(-\sigma_c\). The relationship between the induced charge densities and the charge density of the FEP electret is governed by

\[ -\sigma_c = \sigma_t + \sigma_B, \]

where \(\sigma_B\) is the induced charge density on the bottom electrode.

Figure 1(d) shows a photograph of the setup adopted for measuring the power generated by the harvester. This setup is similar to the device designed for energy harvesting with bipolar ferroelectrets utilizing a transverse piezoelectric \(d_{31}\) effect. \(^{27,28}\) It includes a unipolar ferroelectret sample, U-shaped support frame, cuboid seismic mass, shaker, vibration meter, and top and bottom electrode wires.

III. EXPERIMENTAL DETAILS

A. Fabrication process of unipolar ferroelectrets and the energy harvesters

For fabricating the unipolar FEP ferroelectrets, three steps are involved. These include preparation of the wavy FEP films by a template method, \(^{29,30}\) negative corona charging of a band-shaped wavy FEP film, and bonding a piece of negatively charged wavy FEP film with an uncharged wavy FEP film. Details of the preparation process of wavy FEP and polarization by corona charging may be obtained from the literature. \(^{29,30}\) The fabricated wavy FEP films had a length of 1 mm for the deformed (wavy) structure and a length of 0.5 mm for the nondeformed part. It should be noted that the bonding of the two films was different for different sections of the sample, as depicted in Fig. 1(a). Only the two terminals of the films were bonded with glue stick, while the other parts in between were attached by electrostatic force. The fabricated unipolar ferroelectrets are of a symmetric structure. The total length and width of the fabricated unipolar FEP ferroelectret sample were 30 mm and 10 mm, respectively, and the periodic repeat units can be estimated to be 20 in the length direction [axis x(1)].

For fabricating the energy harvester, the unipolar ferroelectret sample was fixed at two ends of a U-shape frame. A seismic mass was placed at the center of the sample, as shown in Fig. 1(d). \(^{17,24}\) The whole device was accelerated by an electrodynamic shaker, causing the periodic length variation of the ferroelectret shown in Fig. 1(c).

B. Experimental characterization of unipolar ferroelectrets and their application in energy harvesting

The mechanical properties of the unipolar ferroelectrets were characterized via tensile tests performed with a Tensile Tester (KJ-1065A), from which the stretchability of the samples can be determined. Charge storage capability of the unipolar FEP electret films was investigated by measuring surface potential decay and thermally stimulated discharge (TSD) current spectrum. Weatherability tests were carried out to assess the charge storage stability of the fabricated unipolar FEP films in high humidity environments. Dielectric resonance spectra (DRSs) were used to obtain the electromechanical properties of the unipolar ferroelectrets.

In energy harvesting applications, two ends of a unipolar ferroelectret film sample were fixed on a U-shaped frame and a seismic mass was placed at the center of it to form the transduction element of the energy harvester. The whole transduction element was stimulated by an electrodynamic shaker at various frequencies. In this study, the influence of frequency, load resistances, seismic mass, and surface potential of the negatively charged wavy FEP films on the energy output performance was investigated. The reliability of the energy harvesters was assessed by operating the devices for a long time. In addition, the application of the unipolar ferroelectret energy harvester sample in powering low energy consumption electronic devices was demonstrated.

IV. MECHANICAL, THERMAL, AND DIELECTRIC RESULTS

The unipolar ferroelectrets investigated in this study were prepared with two pieces of wave-shape FEP layers and with a symmetric structure, as shown in Fig. 1(a), of which one layer was negatively corona charged to a given surface potential. In this section, results for the mechanical, thermal, and dielectric properties of the unipolar ferroelectrets are discussed, while the data for the energy production of the harvesters, in particular, for the harvested power, are described and analyzed in Sec. V.

A. Stretchability of the wave-shaped FEP films

Stress-strain curves of the wavy FEP films were measured by using a tensile tester (KJ-1065A) working in a Constant Rate Extension (CRE) mode. The tensile speed of 30 mm/min was chosen in this study. In order to make a comparison, the stretchability of a flat FEP film with a thickness of 12.5 \(\mu\)m was also tested under the same experimental conditions. Figure 2(a) shows the optical image of the measuring setup. As shown, the tensile tester stretches the sample in the longitudinal direction corresponding to the x(1)-direction of the coordinates with a static force \(F\) and the corresponding strain \(\varepsilon_1\) can therefore be recorded. For the flat FEP film sample, we calculated its stress \(T_1\) from the applied force \(F\) and its thickness, which is 12.5 \(\mu\)m. However, since the thickness of the wavy FEP films is not uniform, the stress \(T_1\) was determined here by taking its maximal thickness \(t_{\text{max}}\) (about 160 \(\mu\)m), as shown in Fig. 2(a). The waviness is actually one dimensional such that the wavy structure is only in the length direction x(1). The apparent wavy structure in the y(2) direction may be due to some wrinkling on the tunnel surface during the fabrication process. Figure 2(b) presents the stress-strain curves for the two film samples. Young’s moduli are given by \(Y_{\text{y1}} = \Delta T_1/\Delta S_1\), \(Y_{\text{y1}}\) meaning that the stress and strain are in the direction x(1). In the strain range from 2 to 4%, Young’s moduli are 272 and 3 MPa for the flat and wavy FEP film samples, respectively. Obviously, the wavy FEP film sample shows much smaller Young’s modulus as compared with the flat FEP film sample. In practical energy harvesting applications, this is beneficial since the wavy films can deform more easily when exposed to ambient vibrations, as will be discussed later.

B. Charge storage performance of negatively charged unipolar FEP films

To investigate the thermal stability of the negatively charged wavy FEP films at room temperature, measurements of the surface potential decay were conducted with an electrostatic voltmeter (Trek Model 370). Normalized surface potential decay curves of three wavy FEP film samples are shown in Fig. 3(a). The tested samples
FIG. 2. (a) Optical image of the setup for the measurement of the stretchability of flat and wavy FEP film samples. The illustration above depicts the cross section of the wavy FEP film marked with its minimum and maximum thickness. (b) Stress-strain curves of the two films.

were charged and stored at room temperature without preageing. As will be noticed, with the increase in time, the decay of the surface potentials becomes gradually slower. After 8 days of storage at room temperature, about 76, 79, and 88% of the initial values were retained.

For further study of the thermal stability of charges and investigation of the distribution of charge traps in the fabricated wavy FEP films, the thermally stimulated discharge (TSD) current spectrum was measured in an open-circuit arrangement. Samples of 50 mm diameter were heated in a thermal chamber where the temperature rose from about 20°C (lab temperature) to 270°C with a heating rate of 3°C/min. During heating, the current curves were recorded with an electrometer (Keithley 6514). The temperatures of the TSD peaks provide us with the information on the charge drift in the discharge process. A typical open circuit TSD current spectrum for a wavy FEP film sample and a schematic diagram of the measurement setup are shown in Fig. 3(b). The surface potential of the tested sample was −592 V before TSD measurement. The TSD curve shows a relatively broad positive current peak at around 202°C (high temperature peak). The result demonstrates that the charge storage capability of the wavy FEP film is superior to that of flat FEP.

C. Humidity sustainability of negatively charged wavy FEP films

To explore the stability of the surface potential of unipolar FEP films in different humid environments, we created three storage conditions. The first test group was stored in a container with desiccant to create a completely dry environment. The second test group was kept in a lab environment where the average humidity was about 60%. The third test group was also put in a container but with a high humanity of 99%. The surface potentials were measured following preageing at 120°C for 30 min just after corona charging. The initial surface potentials for the three representative samples were −540, −504, and −605 V, respectively. The normalized surface potential decay curves are shown in Fig. 4. For the first two groups, the surface potentials are relatively stable during the entire testing period. Due to the preageing, the slight decay shown in Fig. 3(a) is not observed. For the test sample stored in high humidity environments, the surface potential decreases to about 75% of the initial value after 10 days. These results confirm that wavy FEP films fabricated in this study are promising candidates for devices working in high humidity environments.

D. Dielectric resonance spectra and electromechanical properties of unipolar ferroelectrets

The dielectric resonance spectrum (DRS) in a frequency range from 0.1 to 100 kHz for a fabricated unipolar ferroelectret

FIG. 3. (a) Normalized surface potential decay at room temperature for three wavy FEP film samples not preaged. (b) Typical open circuit TSD current spectrum for a wavy FEP film sample. The inset schematically shows the measurement setup.
sample was measured with a precision impedance analyzer (Agilent 4294A). The tested sample was bonded with glue to a frame at the two ends, as shown in Fig. 1(d), while the other parts of the sample were mechanically free. A schematic diagram of the sample is shown in the inset of Fig. 5. In this measurement, no seismic mass was put at the center of the sample. The upper wavy FEP electret film used to fabricate this sample had a surface potential of −376 V. In Fig. 5, three resonances, namely, length, width, and thickness resonances can be observed and the resonance frequencies occur at 2, 20, and 47 kHz, respectively. The difference of the three resonance frequencies means that the sound velocities in the three directions are quite unequal because of the anisotropy of the samples, which was also found in bipolar ferroelectrets. From Fig. 5, it may be noted that the real part of the capacitance is between 30 and 40 pF and the value at 1 kHz is 36 pF (with this value, the optimal load resistance is determined in the energy harvesting application in this study), while the imaginary part is below 2 pF in the measured frequency range. Hence, the imaginary part is one to two orders of magnitude lower than the real part. We can conclude that the losses are little larger than those of parallel-tunnel FEP bipolar ferroelectret samples. This may be due to the different charge distribution of the two kinds of samples.

V. RESULTS OF ENERGY HARvestING AND DISCUSSION

A. Operation and analysis of the unipolar film harvesters

The U-shaped frame mounted with the band-shaped energy convert element and a seismic mass fixed on the center of it was placed on an electrodynamic shaker (B&K, Type 4809). A pulse analyzer (B&K PULSE Type 3560B) was used to generate the signal to drive the shaker after amplification with a power amplifier (B&K Power Amplifier Type 2706). The charge Q generated by the energy harvester was first amplified by a charge amplifier (B&K Charge Amplifier Type 2635) and then recorded by a data acquisition card (Virtins Technology DSO-2810H). During the measurement process, a static force \( m_g \) and a dynamic force \( m_a \) \( [a] \) is the root mean square (rms) value of the dynamic acceleration of the shaker] were acting on the sample simultaneously and the dynamic charge sensitivity is given by \( M = 9.81 Q_{rms}/a \), with \( Q_{rms} \) being the rms charge. To determine the output power, various resistances \( R_l \) were connected to the devices.

The resonance angular frequency \( \omega_0 \) of the harvester is given by the following formula:

\[
\omega_0 = \sqrt{\frac{k_m}{m_l}},
\]

where \( m_l \) is the seismic mass and \( k_m \) is the elastic modulus of the energy harvester. When a matching resistance is loaded, the maximum power can be generated. An optimal load resistance \( R_{opt} \) at the resonance frequency \( \omega_0 \) is given by

\[
R_{opt} = \frac{1}{\omega_0 C},
\]

where \( C \) represents the capacitance of the unipolar ferroelectret sample. After measurement of the AC charge across the resistance \( R_l \), the output power may be obtained from

\[
P_{out} = \frac{U_{rms}^2}{R_l} = R_I_{rms}^2 = R_m \omega^2 Q_{rms}^2,
\]

where \( U_{rms}, I_{rms}, \omega \), and \( Q_{rms} \) are the rms voltage, rms current, angular frequency of the shaker, and rms charge, respectively. Normally, \( P_{out} \) is normalized to the acceleration \( g = 9.81 \text{ m/s}^2 \) and is given by

\[
P_n = P_{out} \left( \frac{a}{g} \right)^2,
\]

with \( a \) being the actual rms acceleration.

Figure 6(a) shows the measured acceleration of the shaker as a function of frequency in this study. The measured charge sensitivity vs vibration frequency, referred to the gravity acceleration \( g \), is
plotted in Fig. 6(b). We note that the resonance frequency is about 20 Hz. Taking the sample capacitance of 42 pF, an optimal load resistance of about 200 MΩ is obtained. For the resistances of nonzero values, the frequency responses of the energy harvesters represent first order low-pass filters with a cutoff frequency of $\omega_0$, which is also found in other harvesters.\textsuperscript{19,37,38} When the frequency exceeds resonance, the sensitivity curves show a rapid decay as expected. For short-circuit condition, the sensitivity drops off proportional to $1/\omega^2$, while for finite load resistances, the sensitivity drops off proportional to $1/\omega^4$.\textsuperscript{37,38}

B. Generated power of the unipolar ferroelectret harvesters and discussion

The normalized output power as a function of vibration frequency for a unipolar ferroelectret sample [the same sample shown in Fig. 6(b)] at the optimal load resistance of 200 MΩ is shown in Fig. 7. The solid line is a theoretical prediction curve, and the output power is calculated by\textsuperscript{19}

$$P_{\text{out}} = \frac{4L^2 \left( \frac{d_{\text{eff}}}{R_c} \right)^2 m_t^2 a^2 R_c \omega_0^2}{\left( \frac{1}{\omega_0^2} - 1 \right)^2 + 4 \kappa_m^2 \left( \frac{a}{R_c} \right)^2 \left[ 1 + \left( \frac{1}{\omega_0^2} \right) \right]^2 \sin^2 \alpha},$$

(6)

where $L$ is the half length of the unipolar ferroelectret film, $t$ is the film thickness, $\alpha$ is the angle between the film and the plane perpendicular to the axis of vibration, and $\zeta_m$ is the mechanical damping ratio, as described in Ref. 24.

In the following, we introduce as an abbreviation an "effective" piezoelectric coefficient $d_{\text{eff}}$ equal to

$$d_{\text{eff}} = \frac{2L d_{31}}{\sin \alpha}.$$

(7)

This abbreviation will be frequently used in the following.

When choosing an optimal load resistance, $R_l = R_c = 1/\omega_0 C$, the maximum power output $P_m$ at the resonance frequency $\omega_0$ is given by\textsuperscript{24}

$$P_m = \frac{m_t^2 d_{\text{eff}}^2 a^2 \omega_0}{8 \kappa_m C}.$$

(8)

The theoretically predicted curve was obtained by fitting the logarithm of Eq. (6) to the logarithm of the experimental values to more equalize the magnitude of the squares of the differences, whose sum is minimized by the fit. We used the fixed experimental values of $m_t = 2$ g, $a = g = 9.81$ m/s$^2$, $C = 42$ pF, and $R_c = 200$ MΩ for the fit. As shown in Fig. 7, the theoretically calculated curve agrees pretty well with the experimental data. The power strongly depends on frequency below the resonance frequency. Above the resonance frequency, however, the output power is approximately proportional to $1/\omega^4$. At the optimum load resistance of 200 MΩ, the maximum output power of 114 $\mu$W was obtained at the resonance frequency. In addition, we fitted the experimental data for the other four load resistances (50 MΩ, 100 MΩ, 300 MΩ, and 400 MΩ) in the same way and fitted values for resonance frequency $f_0$, effective piezoelectric coefficients $d_{\text{eff}}$, and mechanical damping ratio $\zeta_m$, and their standard errors are indicated in Table I. This fitting process leads to relatively stable and consistent fitting parameters, especially for $d_{\text{eff}}$ and $\zeta_m$, which remain almost constant for different load resistances. The large $d_{\text{eff}}$ values are due to the small tensional modulus in the length direction of the wavy FEP films. To assess the rationality of the fitted results, we compared the fitted values with the experimental results. The fitted resonance frequency $f_0$ is very close to the measured value of 20 Hz. The effective piezoelectric coefficients $d_{\text{eff}}$ can be roughly estimated for different load resistors from the corresponding charge sensitivity shown in Fig. 6(b), at a frequency of
TABLE I. Values of the fitted parameters.

| R_l/Ω | f_0/Hz | d_eff/nC/N | ζ_m (fit quality factor) |
|-------|--------|------------|-------------------------|
| 50    | 21.4 ± 0.4 | 22.5 ± 2.1 | 0.031 ± 0.024 | 0.92 |
| 100   | 21.0 ± 0.2 | 23.2 ± 1.6 | 0.031 ± 0.022 | 0.96 |
| 200   | 20.8 ± 0.2 | 24.7 ± 1.7 | 0.031 ± 0.020 | 0.96 |
| 300   | 20.8 ± 0.2 | 24.2 ± 1.5 | 0.031 ± 0.018 | 0.97 |
| 400   | 20.9 ± 0.2 | 22.2 ± 1.4 | 0.031 ± 0.019 | 0.97 |

10 Hz utilizing equation \( d_{eff} = M / 9.81 \) m/s. Such estimates lead to values of about 25 nC/N, which are very close to the values obtained from the above fits (see Table I). The mechanical damping ratio \( ζ_m \) can be calculated from the experimental data shown in Fig. 7 and from similar data for the other terminating resistances (see above), utilizing the equation \( \Delta ω / 2ω_0 \), where \( Δω \) is the bandwidth between the half-power frequencies. The value of \( ζ_m \) so calculated is about 0.05. It was found to be independent of the terminating resistance, as is to be expected, and agrees reasonably well with the fitted value of 0.031, also assumed to be independent of \( R_l \).

Figure 8 presents the results of the normalized power as a function of the load resistances for the same unipolar harvester used in Fig. 7. All data were obtained at a resonance frequency of 20 Hz. The peak power of 114 µW was achieved for a matching impedance of 200 MΩ. A fit curve is also shown in this figure. It is found that using Eq. (6), the experimental data are in good agreement with the predicted values.

Figure 9 gives the results of the normalized output power as a function of the excitation frequency when the energy harvesters were loaded with different seismic masses between 0.2 and 3 g. As can be observed, the resonance frequencies change with the value of the seismic mass, as expected. In this experiment, we connected the harvester to a matched load resistor for each seismic mass. These resistances are 50, 70, 110, 120, and 150 MΩ.

Theoretically, according to Eqs. (8) and (3), the maximum output power increases with \( m^{-3/2} \), while the resonance frequency decreases with \( m^{-1/2} \) when \( ζ_m \) is seen as a constant. Comparative analysis for the theoretical dependencies and experimental results is plotted in Fig. 10. Experimentally, as the seismic mass varied from 0.2 to 3 g, by a factor of 15, the resonance frequencies of the harvester had a corresponding variation from 65 to 22 Hz. This result is in agreement with the theoretical prediction. When it comes to the maximum output power, the value increases from 2.3 µW for 0.2 g to 355 µW for 3 g. The increase in the output power is somewhat larger than calculated. This could be due to a slight variation of the damping ratio with seismic mass. To verify this point, we calculated the 3dB relative bandwidth for each seismic mass. The damping ratio can be obtained thereafter by \( \Delta ω / 2ω_0 \), where \( Δω \) is the bandwidth between the half-power frequencies. The calculated damping ratios from experimental results in Fig. 9 are 0.04, 0.03, 0.03, 0.02, and 0.01 for seismic masses of 0.2, 0.4, 1, 2, and 3 g, respectively. The damping ratios thus change somewhat with seismic mass. Our preliminary results show that the preloaded stress and surface potential of the FEP films influence the damping ratio of the devices. More work has to be done to further understand the influence factors.

The fitted parameters for elastic modulus \( k_m \), effective piezoelectric coefficient \( d_{eff} \), and mechanical damping ratio \( ζ_m \) of the
tested energy harvester are 34 Pa, 52.9 nC/N, and 0.05, respectively. The fitted values for $k_m$ and $d_{eff}$ are comparable to the experimental results. For example, taking the measured resonance frequency of 30 Hz and the seismic mass of 1 g fixed on the sample, the calculated $k_m$ is 35 Pa according to Eq. (3), and the evaluated $d_{eff}$ is 41.8 nC/N, obtained by using the measured charge sensitivity and the seismic mass of 1 g. The fitted value of 0.05 for the mechanical damping ratio is also reasonable.

Besides the seismic mass, the surface potential of the wavy FEP films is also an important parameter influencing the output power of the unipolar energy harvester. Figure 11(a) shows the results of the normalized power at the resonance frequency of 20 Hz generated by unipolar harvesters with various surface potentials obtained by controlling the charging conditions. In this experiment, we found that the resonance frequency is independent of the surface potential of the wavy FEP electrets. In order to avoid electric breakdown in the air gap of the unipolar ferroelectret sample, the surface potential of the upper FEP film was limited to $-500$ V in the study. The theoretical calculations were performed according to $P_n = \frac{1}{2} \left( \frac{\Delta CV_s^2}{s} \right) f$, where $\Delta C$ is the capacitance variation in a vibration cycle when a matching load resistance is used. In this study, the fitted value for $\Delta C$ is 2.7 pF. The measured relationship between the generated power and the electret voltage $V_s$ agrees comparatively well with the calculated theoretical square relationship. Figure 11(b) presents the Paschen curve and gap voltage of the energy harvesters as a function of the thickness of the air gap. This figure indicates that the surface potential of $-500$ V is below the breakdown voltage of the air gap and may be safely applied in this study.

To assess the fatigue behavior of the fabricated harvesters, a device was excited to vibrations at its resonance frequency and then its output power was measured after certain excitation times. The resulting output power decay for the harvester is shown in Fig. 12. The used seismic mass was 2 g. It is seen that the output power decreased with vibration time and the decay was fast in the first 30 min and then became very slow. After about 240 min vibration at resonance frequency, the output power decreased to about 80% of the initial value. As shown in Fig. 3, the charge of the wavy FEP films not preaged decreased relatively fast in the first day. For the tested energy harvester in Fig. 12, the wavy FEP film used to build up the device was not preaged, and thus the fast decay at the initial phase could be partly due to the decay of surface potential and partly to the variation of the mechanical properties of the wavy film structure under dynamic force resulting from the vibration of the seismic mass during the measuring period.

C. Demonstration of a unipolar energy harvester sample in powering electronic devices

The energy harvester sample described in this study may be implemented in self-powered portable electronic devices. Figure 13 shows a prototype for a self-sufficient electronic device. The AC/DC rectifier bridge (KBP206) and a Light Emitting Diode (LED) diode with an operating voltage in the range of 3.1–3.6 V and an operating current in the range of 5–17.5 mA were utilized. As can be seen, a blue LED diode was lit when the harvester was excited at...
a frequency of 20 Hz with an acceleration of 0.1 g and a seismic mass of 2 g.

VI. SUMMARY

To sum up, energy harvesters built up with unipolar ferroelectret films are successfully fabricated in this study. Using FEP unipolar ferroelectret films including a FEP layer of a surface potential of ~500 V, the harvesters whose length and width are 30 mm and 10 mm, respectively, can output a power of 355 μW at 22 Hz for a seismic mass of 3 g, normalized to an acceleration of 1 g. If normalized to a seismic mass of 1 g, this result is comparable to the generated power from the best energy harvesters with bipolar ferroelectrets utilizing the transverse piezoelectric effect, but achieved with a simpler fabrication process and, especially, the simple method to improve the thermal stability by just using unipolar FEP ferroelectrets with negative charges. The generated power from the harvester is fully capable of driving low power consumption electronic devices.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Sergey Zhukov for stimulating discussions. Financial support from the Natural Science Foundation of China (NSFC, Grant No. 61761136004) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, Projekt No. 392020380) is also gratefully acknowledged.

REFERENCES

1. Z. Wang, J. Chen, and L. Lin, Energy Environ. Sci. 8(8), 2250–2282 (2015).
2. K. Tao, J. Wu, L. Tang, and L. Hu, J. Micromech. Microeng. 27(4), 44002 (2017).
3. Y. Zhang, L. Wu, and G. M. Sessler, AIP Adv. 5(7), 077185 (2015).
4. W. Chen, K. Tao, J. Zhong, Q. Zhong, X. Yao, W. Wang, and X. Yao, Ceramic Int. 38(SI), S271–S274 (2012).
5. S. Roundy, J. Intell. Mater. Syst. Struct. 16, 809–823 (2005).
6. C. Sun, J. Shi, and X. Wang, J. Appl. Phys. 108(3), 034309 (2010).
7. M. Jian, C. Wang, Q. Wang, H. Wang, K. Xia, Z. Yin, M. Zhang, X. Liang, and Y. Zhang, Sci. China Mater. 60(11), 1026–1062 (2017).
8. S. J. Rupitsch, Piezoelectric Sensors and Actuators, Physical Basics: Fundamentals and Applications (Springer, Berlin, Heidelberg, 2019).
9. K. Murotani and Y. Suzuki, J. Micromech. Microeng. 28, 104001 (2018).
10. W. Li, D. Torres, T. Wang, C. Wang, and N. Sepulveda, Nano Energy 30, 649–657 (2016).
11. K. Tao, J. Wu, L. Tang, X. Xia, S. W. Lye, J. Miao, and X. Hu, J. Micromech. Microeng. 26(3), 035020 (2016).
12. Energy Harvesting Technologies, edited by S. Priya and D. J. Inman (Springer, 2009).
13. A. Erturk and D. J. Inman, Piezoelectric Energy Harvesting (Wiley, 2011).
14. X. Zhang, P. Pondrom, G. M. Sessler, and X. Ma, Nano Energy 50, 52–61 (2018).
15. S. R. Anton and K. M. Farinholt, Proc. SPIE 8341, 83410G (2012).
16. P. Pondrom, J. Hillenbrand, G. M. Sessler, J. Bös, and T. Melz, Appl. Phys. Lett. 104, 125334 (2019).
17. X. Zhang, G. M. Sessler, and Y. Wang, J. Appl. Phys. 116(7), 074109 (2014).
18. X. Zhang, L. Wu, and G. M. Sessler, AIP Adv. 5(7), 077185 (2015).
19. W. Li, N. Wu, J. Zhong, Q. Zhong, S. Zhao, B. Wang, X. Cheng, S. Li, K. Liu, B. Hu, and J. Zhou, Adv. Funct. Mater. 26, 1964–1974 (2016).
20. X. Yu, J. Zhao, X. Zhang, G. Sessler, and M. Kupnik, Phys. Scr. 94, 095002 (2019).
21. X. Zhang, P. Pondrom, L. Wu, and G. M. Sessler, Appl. Phys. Lett. 108(19), 193903 (2016).
22. S. Bauer, R. Gerhard-Multhaupt, and G. M. Sessler, Phys. Today 57(2), 37–43 (2004).
23. D. Rychkov, R. A. P. Altafini, and R. Gerhard, in Conference on electrical insulation & dielectric phenomena (CEIDP) IEEE, Annual Report (IEEE, 2014), pp. 860–862.
24. F. Emmerich and C. Thielemann, J. Phys.: Conf. Ser. 1052(1), 012058 (2018).
25. X. Ma and X. Zhang, Smart Mater. Struct. 26, 085001 (2017).
26. X. Zhang, G. M. Sessler, X. Ma, Y. Xue, and L. Wu, J. Micromech. Microeng. 28, 065012 (2018).
27. X. Ma and X. Zhang, in 2018 IEEE 2nd International Conference on Dielectrics (ICD) (IEEE, 2018).
28. H. V. Seggern, J. Appl. Phys. 50(4), 2817–2821 (1979).
29. H. V. Seggern, J. Appl. Phys. 52(6), 4081–4083 (1981).
30. S. Zhukov, D. Edergoy, S. Fedosov, B. Xu, and H. V. Seggern, Sci. Rep. 8(1), 4597 (2018).
31. H. V. Seggern, S. Zhukov, and S. N. Fedosov, IEEE Trans. Dielectr. Electr. Insul. 17(4), 1056–1065 (2010).
32. P. Pondrom, G. M. Sessler, J. Bös, and T. Melz, Appl. Phys. Lett. 109(5), 053906 (2016).
33. J. Hillenbrand, P. Pondrom, and G. M. Sessler, Appl. Phys. Lett. 106(18), 183902 (2015).
34. X. Zhang, L. Wu, and G. M. Sessler, in 2015 Joint IEEE International Symposium on the Applications of Ferroelectric (IEEE, 2015).
35. G. M. Sessler, P. Pondrom, and X. Zhang, Phase Transit 89, 667–677 (2016).
36. Z. Xiao, T. Yang, Y. Dong, and X. Wang, Appl. Phys. Lett. 104(22), 223904 (2014).
37. X. Chen, T. Yang, W. Wang, and X. Yao, Ceram. Int. 38, S271–S274 (2012).