

Ion-Boosting the Charge Density and Piezoelectric Response of Ferroelectrets to Significantly High Levels

Wang, Ningzhen; Van Turnhout, Jan; Daniels, Robert; Wu, Chao; Huo, Jindong; Gerhard, Reimund; Sotzing, Gregory; Cao, Yang

DOI

[10.1021/acsami.2c12185](https://doi.org/10.1021/acsami.2c12185)

Publication date

2022

Document Version

Final published version

Published in

ACS Applied Materials and Interfaces

Citation (APA)

Wang, N., Van Turnhout, J., Daniels, R., Wu, C., Huo, J., Gerhard, R., Sotzing, G., & Cao, Y. (2022). Ion-Boosting the Charge Density and Piezoelectric Response of Ferroelectrets to Significantly High Levels. *ACS Applied Materials and Interfaces*, 14(37), 42705-42712. <https://doi.org/10.1021/acsami.2c12185>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Green Open Access added to TU Delft Institutional Repository

'You share, we take care!' - Taverne project

<https://www.openaccess.nl/en/you-share-we-take-care>

Otherwise as indicated in the copyright section: the publisher is the copyright holder of this work and the author uses the Dutch legislation to make this work public.

Ion-Boosting the Charge Density and Piezoelectric Response of Ferroelectrets to Significantly High Levels

Ningzhen Wang, Jan van Turnhout,* Robert Daniels, Chao Wu, Jindong Huo, Reimund Gerhard, Gregory Sotzing, and Yang Cao*



Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 42705–42712



Read Online

ACCESS |



Metrics & More



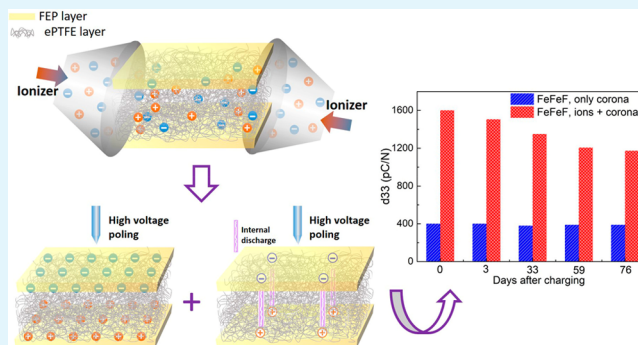
Article Recommendations



Supporting Information

ABSTRACT: In contrast to molecular-dipole polymers, such as PVDF, ferroelectrets are a new class of flexible spatially heterogeneous piezoelectric polymers with closed or open voids that act as deformable macro-dipoles after charging. With a spectrum of manufacturing processes being developed to engineer the heterogeneous structures, ferroelectrets are made with attractive piezoelectric properties well-suited for applications, such as pressure sensors, acoustic transducers, etc. However, the sources of the macro-dipole charges have usually been the same, microscopic dielectric barrier discharges within the voids, induced when the ferroelectrets are *poled* under a large electric field typically via a so-called corona poling, resulting in the separation and trapping of opposite charges into the interior walls of the voids. Such a process is inherently self-limiting, as the reverse internal field from the macro-dipoles eventually extinguishes the microdischarges, resulting in limited density of ions and not too high overall piezoelectric performance. Here, a new method to form ferroelectrets with gigantic electroactivity is proposed and demonstrated with the aid of an external ion booster. A laminate consisting of expanded polytetrafluoroethylene (ePTFE) and fluorinated-ethylene-propylene (FEP) was prefilled with bipolar ions produced externally by an ionizer and sequentially poled to force the separation of positive and negative ions into the open fibrous structure, rendering an impressive piezoelectric d_{33} coefficient of 1600 pC/N—an improvement by a factor of 4 in comparison with the d_{33} of a similar sandwich poled with nonenhanced corona poling. The (pre)filling clearly increases the ion density in the open voids significantly. The charges stored in the open-cell structure stays at a high level for at least 4 months. In addition, an all-organic nanogenerator was made from an ePTFE-based ferroelectret, with conducting poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) coated fabric electrodes. When poled with this ion-boosting process, it yielded an output power twice that of a similar sample poled in a conventional corona-only process. The doubling in output power is mainly brought about by the significantly higher charge density achieved with the aid of external booster. Furthermore, aside from the bipolar ions, extra monopolar ions can during the corona poling be blown into the open pores by using for instance a negative ionic hair dryer to produce a unipolar ePTFE-based ferroelectret with its d_{33} coefficient enhanced by a factor of 3. Ion-boosting poling thus unleashes a new route to produce bipolar or unipolar open-cell ferroelectrets with highly enhanced piezoelectric response.

KEYWORDS: ePTFE ferroelectret, corona charging, ion boost, bipolar and unipolar charging, piezoelectric response, wearable energy harvester



Such a process is inherently self-limiting, as the reverse internal field from the macro-dipoles eventually extinguishes the microdischarges, resulting in limited density of ions and not too high overall piezoelectric performance. Here, a new method to form ferroelectrets with gigantic electroactivity is proposed and demonstrated with the aid of an external ion booster. A laminate consisting of expanded polytetrafluoroethylene (ePTFE) and fluorinated-ethylene-propylene (FEP) was prefilled with bipolar ions produced externally by an ionizer and sequentially poled to force the separation of positive and negative ions into the open fibrous structure, rendering an impressive piezoelectric d_{33} coefficient of 1600 pC/N—an improvement by a factor of 4 in comparison with the d_{33} of a similar sandwich poled with nonenhanced corona poling. The (pre)filling clearly increases the ion density in the open voids significantly. The charges stored in the open-cell structure stays at a high level for at least 4 months. In addition, an all-organic nanogenerator was made from an ePTFE-based ferroelectret, with conducting poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) coated fabric electrodes. When poled with this ion-boosting process, it yielded an output power twice that of a similar sample poled in a conventional corona-only process. The doubling in output power is mainly brought about by the significantly higher charge density achieved with the aid of external booster. Furthermore, aside from the bipolar ions, extra monopolar ions can during the corona poling be blown into the open pores by using for instance a negative ionic hair dryer to produce a unipolar ePTFE-based ferroelectret with its d_{33} coefficient enhanced by a factor of 3. Ion-boosting poling thus unleashes a new route to produce bipolar or unipolar open-cell ferroelectrets with highly enhanced piezoelectric response.

1. INTRODUCTION

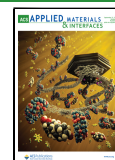
Ferroelectrets are made from polymers with a cellular structure that is polarized up to now by means of internal microplasma discharges. They can exhibit a very high piezoelectricity usually along their thickness direction.^{1,2} Ferroelectrets offer, compared to traditional piezoelectric ceramics like PZT³ and to piezoelectric polymers with molecular dipoles like PVDF and its copolymers,⁴ the advantages of a higher piezoelectricity and higher flexibility.² Ferroelectrets are, therefore, applied in wearable electronics like nanogenerators,^{5–7} sensors,⁸ microphones, and loudspeakers⁹ for building body sensor networks.

Polymers for ferroelectrets must have the ability to store charges for a long time. Cellular polypropylene (PP) with closed lens-shaped cavities has been studied the most widely. It is corona charged after undergoing biaxial stretching, gas diffusion expansion, sudden release of pressure, and heat

Received: July 8, 2022

Accepted: September 2, 2022

Published: September 13, 2022



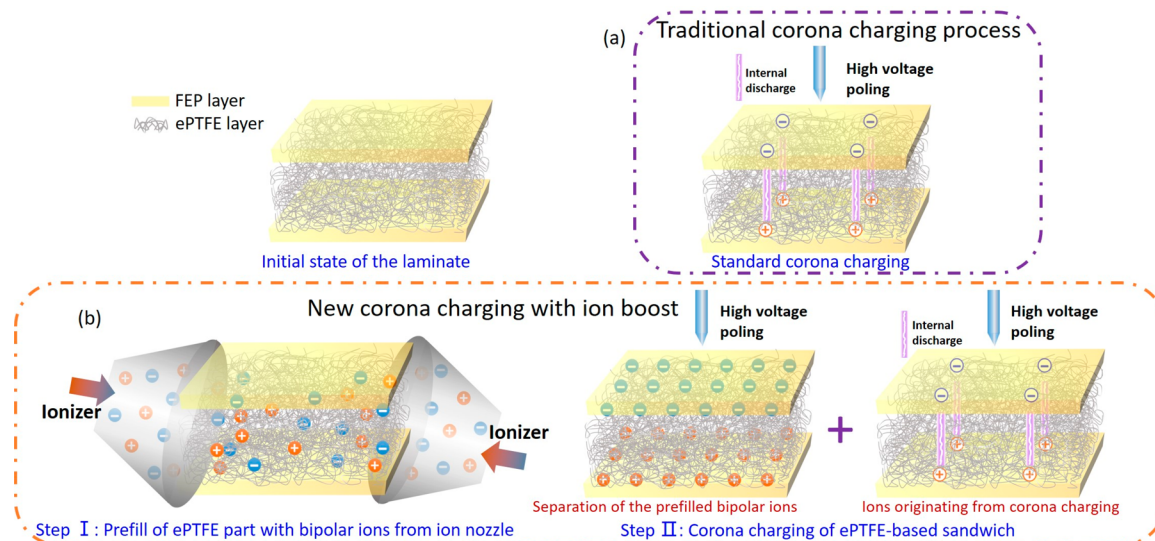


Figure 1. (a) Sketch of the standard corona poling process with a positive voltage. (b) Schematic view of the new corona poling enhanced by first blowing in extra positive and negative ions for making highly charged bipolar ferroelectrets.

treatment.¹ The d_{33} of PP ferroelectrets is about 400 pC/N for an optimized porous structure. PP electrets can only be applied for long periods of time if they are kept below 60 °C.² Ferroelectrets made of a fluorinated polymer show a much better thermal and long-term stability.^{10–12} Expanded PTFE foam with open cells is produced by heating PTFE rods that are next quickly stretched.¹³ The d_{33} of neat ePTFE is fairly low after charging.¹ By putting two FEP films on the top and bottom of an ePTFE layer, the piezoelectric coefficient of the sandwich can be increased to about 400 pC/N, due to added charges trapped at the upper and lower FEP–ePTFE interfaces. Hence, most ePTFE-based ferroelectrets are made as sandwiches with the ePTFE foam enclosed between FEP films.¹⁴ There are also other fluorinated polymer-based ferroelectrets with patterned pores made by laser cutting or with templates.^{12,15}

Apart from intrinsic properties such as the elastic modulus and the dielectric constant of the polymers, the piezoelectric activity of ferroelectrets is mainly determined by the total charge stored. The latter is related to the porous structure and the density of charges trapped at the pore interface.^{11,16} Usually, macro-dipoles inside pores are generated via microplasma discharges triggered by high electric fields from external corona or contact charging.^{15,17} Paschen breakdown is initiated at the threshold voltage, whereupon further discharges occur when the voltage increases. The reversed internal electric field matches up with the external field during the voltage ramp-down stage. After the external field is removed, the retained positive and negative charges form macro-dipoles across the pores.¹⁷ Von Seggern et al.^{11,16} studied the influence of porosity and film thickness on the remanent interface charges in ePTFE-based sandwich ferroelectrets. A very high poling field is required to increase the charge density, when porosity and porous-layer thickness are reduced. Hence, the window for optimization is quite limited. However, if the internal charges are supplemented by an external ion source, the piezoelectric performance can be improved substantially. An ePTFE-based ferroelectret is very suitable for external injection of positive or negative ions, owing to its open-porous structure.

Piezoelectric nanogenerators are indispensable in wearable electronics for harvesting the mechanical energy from human motion and for converting it into electricity for powering other devices.¹⁸ An all-organic ferroelectret nanogenerator (FENG) with poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) (PEDOT: PSS)-coated fabric as electrodes has been proposed previously.^{19,20} Fabric electrodes have not only the advantage of being flexible, soft, biocompatible, and skin-friendly^{7,21} but also of being porous and compliant; they may also form two charge-spring dipole layers^{22,23} in addition to—and in the same direction as—the inner ferroelectret charge-spring dipoles. The rather unexpected additional dipole moments might contribute considerably to the overall piezoelectric response.^{20,22,23} Therefore, the ePTFE-based ferroelectret polarized by the new charging method was assembled deliberately with fabric electrodes to build a high-performance ferroelectret nanogenerator and demonstrate its outstanding functionality.

It has been reported^{24–26} that FEP-based unipolar ferroelectrets also show significant piezoelectricity and high thermal stability. The unipolar ferroelectrets were produced in a straightforward way by charging artificial open tubular cavities in FEP negatively and covering them with an uncharged, one-sided metallized film. Negative corona charging should be applied,²⁷ as negative electret charges are usually more stable than positive charges in the fluorocarbon-based Teflon family of polymers. Obviously, ePTFE-based ferroelectrets with their inherent open cells are also attractive for monopolar or unipolar charging. Negative corona charging of ePTFE-based ferroelectrets can easily be combined with a simultaneous blow-in of negative ions. In this way, we have studied the feasibility of a fill-in of extra monopolar ions and explored the enhancement in piezoelectric activity.

In this paper, two ferroelectrets with a FEP–ePTFE–FEP–ePTFE–FEP 5-layer structure and different thicknesses were polarized by means of corona poling and through corona charging with an extra boost of external positive and negative ions. The beneficial effect of adding ions of both polarities on the piezoelectric activity shows up in the enhanced d_{33} coefficient. The rise in piezo-response has also been

demonstrated by assembling nanogenerators equipped with conducting fabric electrodes. The charging involving blow-in of extra ions was also extended to unipolar corona charging.

2. EXPERIMENTAL SECTION

2.1. Preparation of ePTFE-Based Sandwich Structures.

Expanded-PTFE (ePTFE) films with average pore sizes of 1 or 3 μm and a thickness of approximately 20 μm were provided by BHA Altair. 12.5 μm thick FEP films were supplied by Goodfellow Corp. According to our previous study on ferroelectret nanogenerators, an FEP–ePTFE–FEP–ePTFE–FEP stack with an ePTFE pore size of 3 μm yields the highest piezoelectric activity owing to the good trade-off between the number of macro-dipoles and the overall elastic modulus. Therefore, FEP–ePTFE–FEP–ePTFE–FEP (or FeFeF) stacks with an average pore size of 3 μm were fused together by means of a Carver Laboratory hot press. The sandwich was held at 285 $^{\circ}\text{C}$ for 0.5–1 h under an applied force of 5 kN. Bonding between the layers was achieved, as the FEP films melted slightly, while the pores in the ePTFE layers were kept intact.²⁸ Details of the procedure can be found in the literature.²⁰ Figure 1 shows the schematic of the laminate, and only a single ePTFE layer is shown in Figure 1a and b for simplification. Figure 2a and b shows scanning electron microscope (SEM) images of an ePTFE surface with 3 μm pore size and of an FeFeF laminate cross-section, respectively.

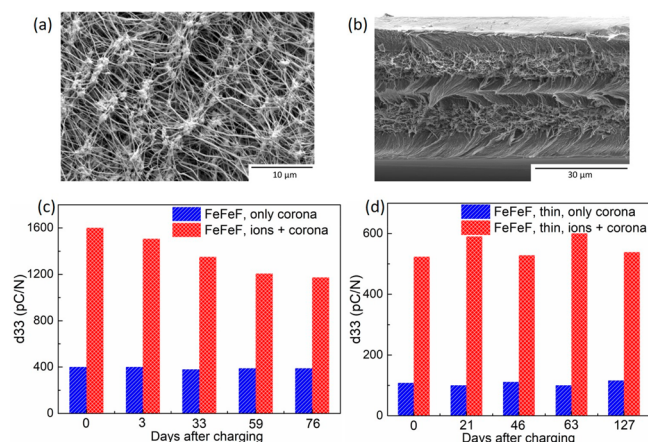


Figure 2. SEM images of (a) the surface of an ePTFE layer and (b) the cross-section of an FEP–ePTFE–FEP–ePTFE–FEP (FeFeF) laminate. Measured piezoelectric coefficient (d_{33}) of two FeFeF sandwiches with thicknesses of (c) 60 and (d) 40 μm , respectively, after poling either by means of a standard corona-charging setup (only corona) or via corona charging with a bipolar ion boost (ions + corona).

For fabricating unipolar ferroelectrets, the open pores of the laminate must first be exposed to a corona charging and then be closed by use of an uncharged nonporous film. To this end, four ePTFE layers with 1 μm pore size and two FEP layers were put together by hot pressing under the same conditions as above. Smaller pores and a thicker four-layer porous foam were employed to reduce the charge loss after poling. The FEP film at the bottom acts as a barrier that separates the positive charges at the bottom electrode and the negative charges inside the pores. Two FEP films were added to avoid detrimental effects from defects after hot pressing. Another FEP film was put on top of the 4ePTFE–2FEP stack after charging, and the resulting laminate is abbreviated as F–4e2F in the following.

2.2. Corona Charging Process. For bipolar charging, two sandwiches with the same final thickness were prepared from each type of FeFeF sandwich. One sandwich was poled in a normal corona charging setup at a corona-tip voltage of +20 kV for 5 min. The distance between the needle tip and the top surface of the sample was 5 cm. The sketch of the setup is shown in Figure 1a. Details of the

poling process are given in the literature.²⁰ The other FeFeF sandwich was poled with ion-enhanced corona poling. As depicted in step I of Figure 1b, dry clean air at a pressure of 20 psi (1.38 bar) was sent to an in-line ionizer (Ioncell from Simco-Ion) for ionization. The resulting ions of both polarities were injected from two sides into the layered sandwich, and two other ports were left open to let air flow out. The experimental process can be found in Figure S1. After the sandwich had been filled with ions of both polarities through the interconnected pores of ePTFE for around 5 min, it was moved quickly (within 1 min) to the corona charging rig for poling under +20 kV for 5 min. The accumulated ions could thus be separated and trapped in the ePTFE foam and at the interfaces between FEP and ePTFE, as depicted in step II of Figure 1b. Combined with the bipolar ions created during the dielectric barrier discharges (DBDs) caused by the high poling field, the total ion density and, thus, the trapped charge both increase significantly. Accordingly, the piezoelectric performance is markedly enhanced in comparison to that achieved via traditional poling. Hollow and solid filled symbols represent the charges obtained from corona poling and ions filling in Figure 1, respectively.

For monopolar charging, two similar 4e2F sandwiches had been prepared. One was poled with –20 kV for 5 min. Then, an uncharged FEP film was put on top. The poling process of the other sandwich can be found in Figure S2. A negative ionic hair dryer (Conair) was operated from above for blowing negative ions into the open pores during the negative corona charging. It can be assumed that due to DBDs, created near the bottom electrode, positive charges are trapped into the bottom of the FEP film of the sandwich. Negative ions collected in the interlinked pores of ePTFE come both from direct injection by means of the ion blower and the negative corona charging. Finally, an uncharged FEP film was used for sealing.

2.3. Fabrication of Ferroelectret Nanogenerators. Conductive PEDOT:PSS-coated fabrics made of 94% cotton and 6% Spandex were employed as electrodes in the nanogenerator. Details of the coating procedure are given in the literature.²⁰ SEM images of the surface and cross-section of the fabric coated with conductive PEDOT:PSS can be seen in Figures S3 and S4. The FeFeF ferroelectret was cut into pieces of 16 \times 16 mm^2 , and two PEDOT:PSS-coated conductive fabrics with an area of 13 \times 13 mm^2 were put on the top and the bottom as electrodes, each of which is extended in one direction for connecting to the external circuit. Kapton tape was used for protection and for insulation of the active nanogenerator area.

2.4. Characterization and Measurements. The morphology of the ePTFE and the laminated films was visualized with a ThermoFisher Verios SEM. The piezoelectric coefficient was measured with a PM3500 d_{33} meter from KCF Technologies at a force amplitude of 0.25 N and a frequency of 110 Hz. The tested film was placed between two aluminum sheets in order to avoid contact problems between hard probes and soft ferroelectrets. The ferroelectret nanogenerators were compressed by a cyclic force with a peak of 40 N at 1 Hz, which was provided through a self-designed linear motor system. The short-circuit current and the open-circuit voltage arising from the piezoelectric response were measured with a Keithley 6514 electrometer. A rough estimate of the ion density near the surface of the monocharged ferroelectret was obtained with a KT-401 mini air ion tester from Kilter Electronic Institute, Co.

3. RESULTS AND DISCUSSION

3.1. Enhancing Piezoelectricity by Means of Corona Poling with Ion Boost.

As shown in Figure 1b, an equal amount of positive and negative ions was injected into the porous layer from two outlets of the ionizer. These ions will survive for a while due to the intertwining of fibers in ePTFE and the relatively long recombination time. However, it would be unfavorable for ion injection if the open pores of ePTFE were too small. Sufficient porosity of the ePTFE layers is important for the injected ion density and the ion lifetime.

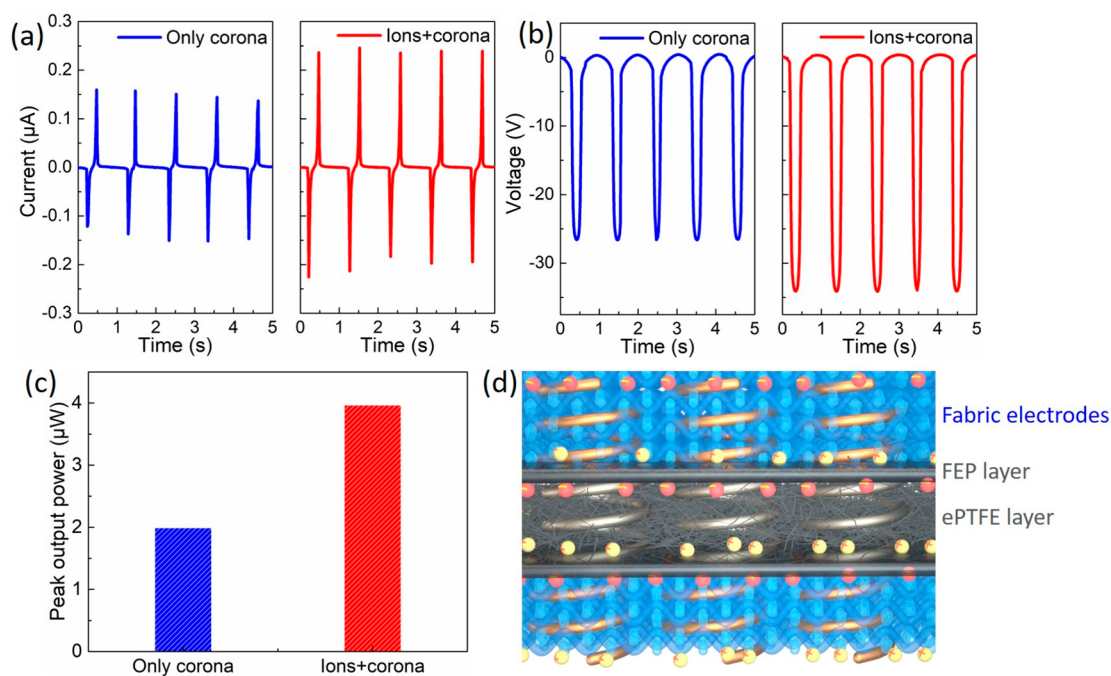


Figure 3. (a) Short-circuit current, (b) open-circuit voltage, and (c) peak output power of the ferroelectret nanogenerators made from an FeFeF sandwich and conductive fabric electrodes after corona poling without and with an ion boost. (d) The three charge-spring dipole-moment layers of the ferroelectret nanogenerator with two highly porous (air-filled) conductive-fabric electrodes.

Two FEP–ePTFE–FEP–ePTFE–FEP (FeFeF) sandwiches with overall thicknesses of about 60 and 40 μm , respectively, were investigated, prepared under different hot-pressing conditions. Obviously, the porosity of the thicker FeFeF sandwich is higher. Both were poled by means of corona charging with additional ion blowing and by use of corona charging without extra ions. The resulting d_{33} coefficients can be seen in Figure 2c and d, for different aging times.

Figure 2c shows that d_{33} of the thicker FeFeF film can be as high as 1600 pC/N just after poling by means of the corona charging with additional ions. This amounts to four times the response of a sample after standard corona poling (400 pC/N). Since d_{33} was measured dynamically, which usually yields a lower value than a quasistatic measurement,²⁹ a d_{33} value of 1600 pC/N is outstanding, when compared to the values of other ferroelectrets reported in the literature.^{2,30} Figure 2c further shows that the d_{33} value of the sample poled by blowing in ions first decreases with time and reaches a stable value of approximately 1200 pC/N two months after poling. Figure 2d presents the d_{33} results of the thinner (40 μm thick) FeFeF sample. The d_{33} of this sandwich poled with the ion-enhanced corona-charging process remains stable at 500 pC/N over time—i.e., up to five times the value of a sample that had been poled in a normal corona-charging setup. Therefore, filling with extra positive and negative ions before applying corona improves the piezoelectric coefficient by no less than a factor of 4–5 times for a FeFeF structure. The ePTFE foam ferroelectret with the higher porosity reaches a higher d_{33} , while the one with the lower porosity shows better stability. This will be discussed in the following.

Referring to the SEM images in Figure 2a and b, the blown-in ions in step I should be kept in the voids between the intertwined fibers of the ePTFE layers. The thicker laminate with higher porosity has larger pores across its thickness, which allows the bipolar ions to be injected more easily so that more

ions will be trapped at the same air pressure. The transfer to the corona setup will cause some leakage of ions, especially for the thicker film. The transfer time should thus be as short as possible. Interestingly, after the prefill, the positive corona poling in step II creates two additional macro-dipoles, since its high poling field assures that negative and positive charges are trapped at the upper (FEP–ePTFE) and lower (ePTFE–FEP) interfaces between the FEP and ePTFE layers, respectively. The charges that are finally trapped stem from two sources: (1) from the prefill of positive and negative ions in step I and (2) from ions that originate from the dielectric-barrier discharges (DBDs) excited by the +20 kV corona.

When only corona poling without additional ion injection is applied, the d_{33} value of the thicker sandwich is somewhat larger. In this case, the charges only arise from the second source. This means that the larger pore size of the thicker film is a bit more favorable for DBD inception. Since d_{33} of the sandwich poled by corona charging with ion boost increased no less than four times, it can be inferred that the charges from the first source, the ion prefill, contribute the most to the d_{33} value observed here. The exceptional piezoelectric coefficient of 1600 pC/N for the thicker FeFeF stack stems from the more efficient filling of ions in step I and the slightly more efficient DBD process in step II. It can be noticed from Figure 2c that the high charge level in the thicker sandwich is less stable. The injection pressure and the porosity of the ePTFE layers can undoubtedly be optimized to ensure a high amount of ion inflow and an increase in charges generated during the DBDs, along with a better charge stability. A higher porosity will moreover make the ePTFE foam more compliant. This will produce a higher d_{33} .

3.2. Performance Improvement of Ferroelectret Nanogenerators. After poling either with the novel ion-enhanced bipolar corona-charging process or with the standard one, the two FeFeF laminates of 60 μm thickness were both

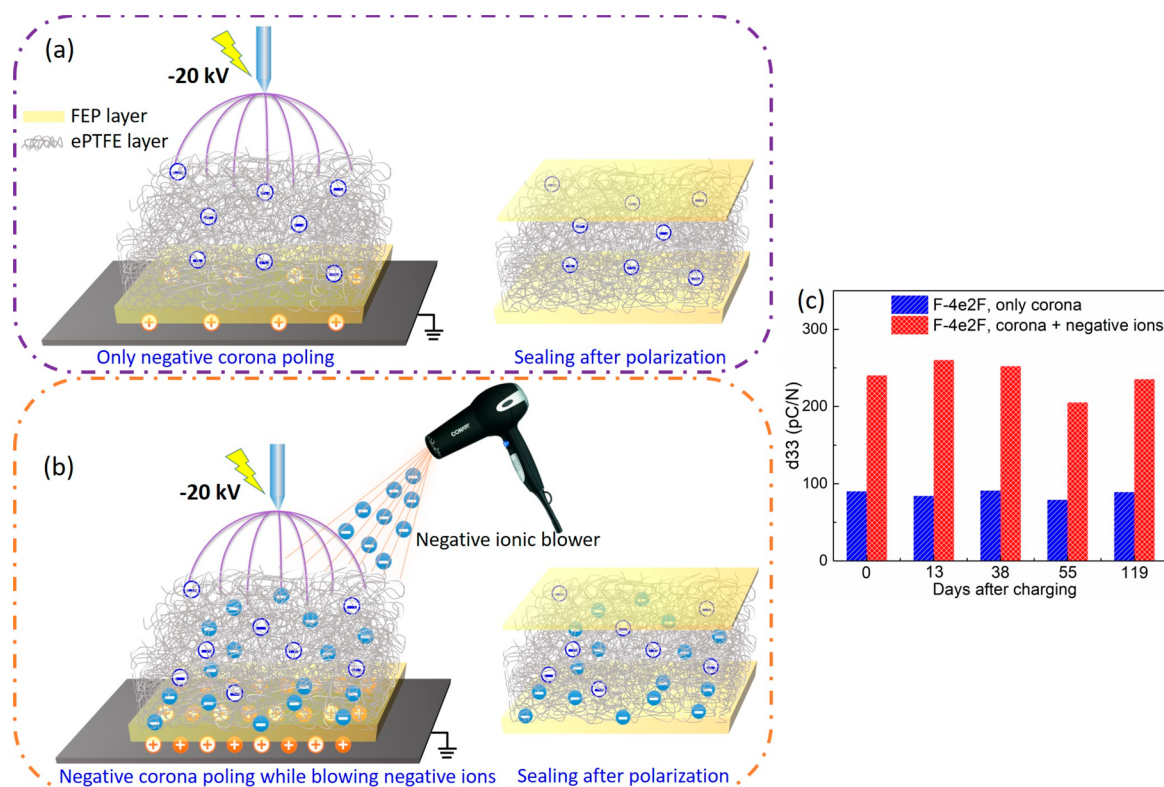


Figure 4. (a) Sketch of the common corona charging with a negative voltage. (b) Sketch of the corona-charging process enhanced by blowing in additional ions for making higher charged unipolar ferroelectrets. (c) Measured piezoelectric d_{33} coefficient of two F-4e2F structures after poling either via traditional corona charging (only corona) or via combined charging (corona + negative ions).

assembled into an all-organic ferroelectret nanogenerator. Figure 3a and b shows the short-circuit current and the open-circuit voltage responses of the two differently poled sandwiches under a cyclic force of 40 N at a frequency of 1 Hz. Both the current and the voltage output improve very significantly when the FeFeF samples were poled by means of the corona-charging process with a prefill of positive and negative ions. The peak-to-peak short-circuit current (I_{pp}) increases to 0.5 μ A and the peak-to-peak open-circuit voltage (V_{pp}) to 35 V, respectively. Assuming the nanogenerator drives a load with the same resistance as the ferroelectret sandwich, the peak output power can be calculated by multiplying $1/2 I_{pp}$ with $1/2 V_{pp}$. The result is shown in Figure 3c. The output power of the ferroelectret nanogenerator poled via the new charging method turns out to be twice of that from a similar device poled in a conventional corona-charging setup, whereas the d_{33} coefficient increases by a factor of 4. The factors determining the degree of output-power improvement should be discussed in detail, as they are the cause of this discrepancy.

Figure 3d schematically depicts the charge-spring dipole-layer arrangement proposed for the ePTFE-based ferroelectret nanogenerator with porous fabric electrodes at the top and at the bottom. Only a single PTFE layer is displayed for simplicity. As proposed earlier,²⁰ the two air-filled conductive fabric layers form two additional charge-spring dipole layers due to their image charges induced by the electric field from the nearby FEP and ePTFE electret charges. Therefore, the final total piezoelectric response stems from three charge-spring dipole layers connected in series and arranged in the same direction (the dipoles point upward). One of them derives from the charged ePTFE-layer sandwich. The other two dipole layers are formed by the macro-dipoles created by

the open-porous conducting fabrics. For the two nanogenerators made from similar ePTFE-based ferroelectrets but prepared with different charging methods, the contribution from the fabric electrodes to the overall output as shown in Figure 3c is the same. Hence, the final difference in the response of the nanogenerators will indeed be less than the difference in piezoelectricity of the two bare ePTFE-based ferroelectrets.

Another reason for the discrepancy in the performance enhancement may be the different testing conditions. Force and frequency (40 N, 1 Hz) applied to the nanogenerators differ from the values applied during the d_{33} measurement (0.25 N, 110 Hz). Ferroelectret sandwiches have specific resonances that are related to their elastic moduli and that can be used to determine their piezoelectric coefficients.^{31,32} The elastic modulus of the ePTFE-based ferroelectrets is low due to the soft nature of ePTFE, which might thus be more suitable for applications with a small cyclic force, such as biosensors. Force and higher frequency during d_{33} measurement could be more favorable for ePTFE-based ferroelectrets, so that the improvement of the poling with ion boost shows up more prominently in d_{33} .

3.3. Monocharging of Unipolar Ferroelectrets with Injection of Additional Ions. Figure 4 shows the sketch of the two monocharging processes for preparing unipolar ferroelectrets. Hollow and solid filled symbols represent the charges obtained from corona poling and ions filling, respectively. As shown in Figure 4b, negative ions were injected into the 4e2F laminate by means of an ionic hair dryer during corona charging. The ion density measured near the ePTFE surface was $17\text{--}19 \times 10^6$ ions/cm³, whereas the ion density of the laminate exposed solely to the negative corona

charging was only $8\text{--}9 \times 10^6$ ions/cm³. The ion densities are estimates because the results can be affected by changes in the testing distance and inaccuracies of the ion tester. However, the large difference in the ion densities nonetheless demonstrates the effect of the additional ions. Covering the ePTFE top surface with another uncharged FEP film right after the charging resulted in an F-4e2F sandwich. Figure 4c shows the d_{33} coefficients of the two different F-4e2F ferroelectrets measured after different aging times. The d_{33} value of the F-4e2F ferroelectret that was corona-charged with simultaneous injection of external ions reaches 240 pC/N, i.e., about three times the corresponding value for a sample poled only by means of standard corona charging. The piezoelectric coefficients of the two sandwiches remain quite stable over time periods of up to four months. Since only negative charges are trapped in monoferroelectrets, internal charge neutralization is impossible. Thus, the higher stability of negative charges on PTFE and FEP is further enhanced—a clear advantage of monocharging over bipolar charging.²⁵

The effect of blowing in *nonionized* air was also investigated. Could this also lead to a higher ion density? In a comparative experiment, one ePTFE–FEP laminate was poled unipolarly by means of the new method shown in Figure 4b, and another one was done just by use of a negative corona discharge with simultaneous injection of air from a small fan. After the top of the laminates was covered with a FEP film, the laminated stack charged with the ionic hair dryer exhibited a much higher d_{33} coefficient than the one obtained by means of air-flow-assisted corona charging via a simple fan. The comparison clearly demonstrates that the very significant increase of d_{33} that is visible in Figure 4c for the F-4e2F sandwiches charged with the novel method is mainly caused by the injection of additional negative ions. As illustrated in Figure 2, there are two concurrent sources of injected negative ions, one from the corona discharge, the other from the ionic hair dryer. The injected charges are trapped on the intertwined fibers of ePTFE by the high poling field of the negative corona.

In order to better understand the respective roles of the injected ions and of the corona charging itself, two additional experiments were carried out:

- (1) When the 4e2F laminate was just filled with the negative ions from the ionic hair dryer, the measured d_{33} coefficient was a mere 14 pC/N after putting an uncharged FEP film on top, i.e., a value that is well below the 240 pC/N in Figure 4c. This implies that it is the strong electric field of the electric charges deposited by the -20 kV corona that enforces the trapping of the ions collected inside the ePTFE matrix.
- (2) When the corona charging was only applied after prefilling the laminate with negative ions from the ionic blower, the d_{33} value of the F-4e2F sandwich was just around 120 pC/N. Apparently, the injected ions leak out quite easily from the open-porous ePTFE foam.

Therefore, performing the negative corona charging simultaneously with the injection of negative ions is the most effective way for producing highly active unipolar ePTFE-based ferroelectrets.

It was reported earlier that the piezoelectric coefficient of unipolar ferroelectrets is lower than that of bipolar ferroelectrets.²⁴ Along the same line, d_{33} of the F-4e2F poled by means of standard corona charging is not that high in Figure 4. However, the d_{33} coefficient of F-4e2F stacks can be

improved three times by blowing in extra negative ions from an external source. Such an ion-enhanced corona charging provides a significant boost to the monocharging process and paves the way for high piezoelectricity in ePTFE-based unipolar ferroelectrets. The piezoelectric properties of unipolar ferroelectrets may be further improved by an optimal design of the open-porous structure, by enhancing the ion density of the ionic hair dryer, or by applying a more sophisticated negative ionizer to further raise the injected ion density.

4. CONCLUSIONS

Corona charging with an additional ion boost for fabricating highly charged bipolar or unipolar ferroelectrets was reported and discussed. A significant charge-level and piezoelectric-coefficient enhancement is achieved by blowing in extra positive and negative ions before corona poling. The rise in performance has been demonstrated by preparing and assessing all-organic ferroelectret nanogenerators. Highly piezo-active unipolar ePTFE-based ferroelectrets were prepared successfully in a similar way by adding a negative-ion boost during corona charging.

- (1) After applying the enhanced corona poling with injection of additional positive and negative ions, the piezoelectric coefficient (d_{33}) of an ePTFE-based ferroelectret with a FeFeF stack sequence reached 1600 pC/N, which exceeds the d_{33} value of a similar stack poled by means of traditional corona poling by a factor of 4. The piezoelectric performance stays at a high level for at least three months. The structure with the lower porosity showed a better charge stability.
- (2) Two FeFeF ferroelectrets poled either with the new or with the standard corona-poling method were turned into ferroelectret nanogenerators equipped with conducting fabric electrodes. The peak output power was found to be doubled due to the application of the 2-step charging with a prefill of bipolar ions. The gain was not 4-fold because the air-filled conducting fabric electrodes contributed to the overall output in both nanogenerators as well.
- (3) By combining corona charging with a simultaneous inflow of additional negative ions for monocharging, d_{33} could be increased 3-fold. The ion-enhanced charging works well for fabricating highly charged unipolar ferroelectrets with good charge stability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c12185>.

Photograph of the experimental setup and microstructures of the conductive fabric (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jan van Turnhout – Department of Materials Science and Engineering, Delft University of Technology, 2628CD Delft, The Netherlands; Email: j.vanturnhout@tudelft.nl

Yang Cao – Electrical Insulation Research Center, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States; orcid.org/0000-0001-7034-2792; Email: yang.cao@uconn.edu

Authors

Ningzhen Wang – Electrical Insulation Research Center, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States; orcid.org/0000-0002-1263-7266

Robert Daniels – Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, United States; orcid.org/0000-0003-1114-5515

Chao Wu – Electrical Insulation Research Center, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States; orcid.org/0000-0002-4565-8231

Jindong Huo – Electrical Insulation Research Center, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269, United States

Reimund Gerhard – Institute of Physics and Astronomy, Faculty of Science, University of Potsdam, 14476 Potsdam-Golm, Germany

Gregory Sotzing – Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269, United States

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsami.2c12185>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to gratefully acknowledge Prof. George Rossetti for providing the PM3500 d_{33} meter and suggestions for the measurement.

REFERENCES

- (1) Qiu, X. Polymer Electrets and Ferroelectrets as EAPs: Materials. In *Electromechanically Active Polymers. A Concise Reference*; Carpi, F., Ed.; Springer, 2016; Chapter 30, pp 561–589. DOI: 10.1007/978-3-319-315300_25.
- (2) Zhang, Y.; Bowen, C. R.; Ghosh, S. K.; Mandal, D.; Khanbareh, H.; Arafa, M.; Wan, C. Ferroelectret Materials and Devices for Energy Harvesting Applications. *Nano Energy* **2019**, *57*, 118–140.
- (3) Qi, Y.; McAlpine, M. C. Nanotechnology-enabled Flexible and Biocompatible Energy Harvesting. *Energy Environ. Sci.* **2010**, *3*, 1275–1285.
- (4) Lu, L.; Ding, W.; Liu, J.; Yang, B. Flexible PVDF Based Piezoelectric Nanogenerators. *Nano Energy* **2020**, *78*, 105251.
- (5) Li, W.; Torres, D.; Wang, T.; Wang, C.; Sepúlveda, N. Flexible and Biocompatible Polypropylene Ferroelectret Nanogenerator (FENG): On the Path Toward Wearable Devices Powered by Human Motion. *Nano Energy* **2016**, *30*, 649–657.
- (6) Cao, Y.; Figueroa, J.; Pastrana, J. J.; Li, W.; Chen, Z.; Wang, Z. L.; Sepúlveda, N. Flexible Ferroelectret Polymer for Self-Powering Devices and Energy Storage Systems. *ACS Appl. Mater. Interfaces* **2019**, *11*, 17400–17409.
- (7) Pastrana, J.; Dsouza, H.; Cao, Y.; Figueroa, J.; González, I.; Vilatela, J. J.; Sepúlveda, N. Electrode Effects on Flexible and Robust Polypropylene Ferroelectret Devices for Fully Integrated Energy Harvesters. *ACS Appl. Mater. Interfaces* **2020**, *12*, 22815–22824.
- (8) Wu, N.; Cheng, X.; Zhong, Q.; Zhong, J.; Li, W.; Wang, B.; Hu, B.; Zhou, J. Cellular Polypropylene Piezoelectret for Human Body Energy Harvesting and Health Monitoring. *Adv. Funct. Mater.* **2015**, *25*, 4788–4794.
- (9) Li, W.; Torres, D.; Díaz, R.; Wang, Z.; Wu, C.; Wang, C.; Wang, Z. L.; Sepúlveda, N. Nanogenerator-based Dual-functional and Self-powered Thin Patch Loudspeaker or Microphone for Flexible Electronics. *Nat. Commun.* **2017**, *8*, 15310.
- (10) Kacprzyk, R.; Motyl, E.; Gajewski, J. B.; Pasternak, A. Piezoelectric Properties of Nonuniform Electrets. *J. Electrostatics* **1995**, *35*, 161–166.
- (11) Zhukov, S.; Fedosov, S.; von Seggern, H. Piezoelectrets from Sandwiched Porous Polytetrafluoroethylene (ePTFE) Films: Influence of Porosity and Geometry on Charging Properties. *J. Phys. D: Appl. Phys.* **2011**, *44*, 105501.
- (12) Altafim, R. A. P.; Qiu, X.; Wirges, W.; Gerhard, R.; Altafim, R. A. C.; Basso, H. C.; Jenninger, W.; Wagner, J. Template-based Fluoroethylenepropylene Piezoelectrets with Tubular Channels for Transducer Applications. *J. Appl. Phys.* **2009**, *106*, 014106.
- (13) <https://www.gore.com/about/technologies> (accessed 2021-03-11).
- (14) Hu, Z.; von Seggern, H. Breakdown-induced Polarization Buildup in Porous Fluoropolymer Sandwiches: A Thermally Stable Piezoelectret. *J. Appl. Phys.* **2006**, *99*, 024102.
- (15) Zhang, X.; Pondrom, P.; Sessler, G. M.; Ma, X. Ferroelectret Nanogenerator with Large Transverse Piezoelectric Activity. *Nano Energy* **2018**, *50*, 52–61.
- (16) von Seggern, H.; Zhukov, S.; Fedosov, S. Importance of Geometry and Breakdown Field on the Piezoelectric d_{33} Coefficient of Corona Charged Ferroelectret Sandwiches. *IEEE Trans. Dielect. Electr. Insul.* **2011**, *18*, 49–56.
- (17) Qiu, X.; Mellinger, A.; Wegener, M.; Wirges, W.; Gerhard, R. Barrier Discharges in Cellular Polypropylene Ferroelectrets: How Do They Influence the Electromechanical Properties? *J. Appl. Phys.* **2007**, *101*, 104112.
- (18) Fan, F. R.; Tang, W.; Wang, Z. L. Flexible Nanogenerators for Energy Harvesting and Self-powered Electronics. *Adv. Mater.* **2016**, *28*, 4283–4305.
- (19) Sinha, S. K.; Noh, Y.; Reljin, N.; Treich, G. M.; Hajeb-Mohammadalipour, S.; Guo, Y.; Chon, K. H.; Sotzing, G. A. Screen-Printed PEDOT:PSS Electrodes on Commercial Finished Textiles for Electrocardiography. *ACS Appl. Mater. Interfaces* **2017**, *9*, 37524–37528.
- (20) Wang, N.; Daniels, R.; Connelly, L.; Sotzing, M.; Wu, C.; Gerhard, R.; Sotzing, G. A.; Cao, Y. All-organic Flexible Ferroelectret Nanogenerator with Fabric-based Electrodes for Self-powered Body Area Networks. *Small* **2021**, *17*, 2103161.
- (21) Li, Z.; Sinha, S. K.; Treich, G. M.; Wang, Y.; Yang, Q.; Deshmukh, A. A.; Sotzing, G. A.; Cao, Y. All-organic Flexible Fabric Antenna for Wearable Electronics. *J. Mater. Chem. C* **2020**, *8*, 5662–5667.
- (22) Gerhard, R. A Matter of Attraction: Electric Charges Localized on Dielectric Polymers Enable Electromechanical Transduction. *IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)* **2014**, 1–10.
- (23) Gerhard, R.; Bauer, S.; Qiu, X. Charge-spring Model for Predicting the Piezoelectric Response of Dielectric Materials: Considering Tetragonality Extends Validity to Ferroelectric Crystals. *2016 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)* **2016**, 81–84.
- (24) Rychkov, D.; Altafim, R. A. P.; Gerhard, R. Unipolar Ferroelectrets—following the Example of the Electret Microphone More Closely. *2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)* **2014**, 860–862, DOI: 10.1109/CEIDP.2014.6995907.
- (25) Rychkov, D.; Wirges, W.; Gerhard, R.; Altafim, R. A. P. Unipolar Teflon-FEP Ferroelectrets—Choice of Negative Electret Charge Enhances Stability. *2015 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)* **2015**, 84–86, DOI: 10.1109/CEIDP.2015.7352088.
- (26) Ma, X.; Zhang, X.; Sessler, G. M.; Chen, L.; Yang, X.; Dai, Y.; He, P. Energy Harvesters Based on Fluorinated Ethylene Propylene Unipolar Ferroelectrets with Negative Charges. *AIP Adv.* **2019**, *9*, 125334.
- (27) Rychkov, D.; Rychkov, A.; Efimov, N.; Malygin, A.; Gerhard, R. Higher Stabilities of Positive and Negative Charge on Tetrafluoroethylene–hexafluoropropylene Copolymer (FEP) Electrets Treated

with Titanium-tetrachloride Vapor. *Appl. Phys. A: Mater. Sci. Process.* **2013**, *112*, 283–287.

(28) Wang, B.; Zhong, J.; Zhong, Q.; Wu, N.; Cheng, X.; Li, W.; Liu, K.; Huang, L.; Hu, B.; Zhou, J. Sandwiched Composite Fluorocarbon Film for Flexible Electret Generator. *Adv. Electron. Mater.* **2016**, *2*, 1500408.

(29) Zhang, X.; Hillenbrand, J.; Sessler, G. M. Thermally Stable Fluorocarbon Ferroelectrets with High Piezoelectric Coefficient. *Appl. Phys. A: Mater. Sci. Process.* **2006**, *84*, 139–142.

(30) Zhang, X.; von Seggern, H.; Sessler, G. M.; Kupnik, M. Mechanical Energy Harvesting with Ferroelectrets. *IEEE Electr. Insul. Mag.* **2020**, *36*, 47–58.

(31) Mellinger, A. Dielectric Resonance Spectroscopy: A Versatile Tool in the Quest for Better Piezoelectric Polymers. *IEEE Trans. Dielec. Electr. Insul.* **2003**, *10*, 842–861.

(32) Wegener, M.; Wirges, W.; Gerhard-Multhaupt, R.; Dansachmuller, M.; Schwodiauer, R.; Bauer-Gogonea, S.; Bauer, S.; Paajanen, M.; Minkinen, H.; Raukola, J. Controlled Inflation of Voids in Cellular Polymer Ferroelectrets: Optimizing Electro-mechanical Transducer Properties. *Appl. Phys. Lett.* **2004**, *84*, 392–394.

Recommended by ACS

C/H/O/F/Al ReaxFF Force Field Development and Application to Study the Condensed-Phase Poly(vinylidene fluoride) and Reaction Mechanisms with Aluminum

Yawei Gao, Adri. C. T. van Duin, *et al.*

JUNE 29, 2022

THE JOURNAL OF PHYSICAL CHEMISTRY C

READ 

Enhanced Piezoelectricity in Poly(vinylidene fluoride-co-trifluoroethylene-co-chlorotrifluoroethylene) Random Terpolymers with Mixed Ferroelectric Phases

Zhubing Han, Qing Wang, *et al.*

MARCH 22, 2022

MACROMOLECULES

READ 

Ionic Liquid Assisted α - γ ' Phase Transition of Poly(vinylidene fluoride) Thin Films

Zixiong Liu, Shouke Yan, *et al.*

MARCH 09, 2022

MACROMOLECULES

READ 

Enhanced Dielectric and Ferroelectric Properties of Poly(vinylidene fluoride) through Annealing Oriented Crystallites under High Pressure

Jia-Yi Ren, Zhong-Ming Li, *et al.*

MARCH 09, 2022

MACROMOLECULES

READ 

Get More Suggestions >