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Filling the holes in piezopolymers with a solid electrolyte: a new paradigm of poling-free dynamic electrets for energy harvesting†

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We report the design and fabrication of a novel poling-free dynamic polymeric piezoelectret generator that has outstanding properties in kinetic energy harvesting. The piezoelectret, *i.e.* a solid polyelectrolyte filled cellular piezopolymer, was fabricated through solution casting of a poly(vinylidene fluoride) (PVDF)–Nafion blend followed by high pressure crystallization. The size and morphology of the Nafion-filled PVDF cells, together with their crystalline forms and substructures, were controlled at high pressure with the variation of PVDF–Nafion composition. Without any treatment of electrical poling, the open-circuit voltage output density of the PVDF–Nafion generator developed at the optimized conditions, stimulated under its dynamic deformation, reached 14.6 V cm^{-2}, exceeding that of most of the state-of-the-art piezoelectric polymers reported in the open literature. This was attributed to a synergistic action of "intrinsic" polarity and orientation of molecular dipoles of PVDF cells, formed during pressure crystallization, with "artificial" macroscopic dipoles of Nafion fillers on a scale of several micrometers, generated by their inner ionic motions during the cell wall deformation. Moreover, the PVDF–Nafion generator showed good stability and durability, and no decay of electrical output was observed for more than 100 000 continuous working cycles. Evidently, the study presented here may lead to a new paradigm of piezoelectrets, enabling the facile fabrication of a class of unique electret-transducer materials and their follow-up applications in electromechanical energy conversion.

Introduction

An energy harvesting technology capturing small amounts of ambient energy, such as wind, solar, thermal and vibration energy, with a multitude of transduction mechanisms and materials, and then converting them into electricity to operate autonomous electronic devices, has been recognized as very important for the realization of a sustainable society.[1–6] Among the environmental sources for energy harvesting, kinetic motions, prevalent with variable amplitudes and frequencies, may be converted into electrical energy by electromagnetic, electrostatic, or piezoelectric transduction.[3,6,7] Particularly, kinetic energy scavenging with piezoelectric generators has been attracting considerable attention because of their technical potential for application in self-powered systems.[3,7] Of the currently available materials for the fabrication of piezoelectric generators, piezopolymers, which include three main categories in terms of their operating principles and properties: bulk piezopolymers,[8–10] piezocomposites[11–15] and voided charged polymers,[16–30] showed more advantages over their inorganic counterparts, such as lower cost, less toxicity, and easier processing.[7]

Voided charged polymers, referred to as ferroelectrets or piezoelectrets, belong to a radically different type of piezoelectric polymer than bulk piezopolymers and piezocomposites.[7] For the conventional piezoelectric materials, piezoelectricity is derived from the rotations of intrinsic molecular dipoles, formed through a poling induced reorientation of crystallites.[7] The piezoelectric responses of the charged polymer foams stem from dimensional changes of man-made macroscopic dipoles, or charged voids, created during a high-voltage-induced microplasma discharge process in which Paschen breakdown occurs for the gas that fills the voids.[7,18,20,26] Since the cellular polypropylene piezoelectric material was first developed in the

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1980s, a significant amount of research has been conducted on such foamed piezoelectrets.[16–30] Several new or improved piezoelectret foam materials have been proposed, including cycloolefin polymers COP and copolymers COC,[18] fluorocarbon polymers,[19] poly(ethylene terephthalate) (PET),[20] polyethylene-naphthalate (PEN),[21] polycarbonate (PC),[22] and parylene.[23] Moreover, extensive studies have been carried out in electrostatic modeling, piezoelectric properties, fabrication optimization and industrial applications for the commercialized cellular PP electrets.[24–26] Very recently, the piezoelectret foams were also applied as vibration-based energy harvesters.[16,17,26–30] Nevertheless, the applications of voided charged polymers are still quite limited mainly because of their fabrication complexity. The piezoelectrets were manufactured by foam formation and an expansion process, using a chemical reaction process or mineral particles inside polymer matrixes for the initiation sites of the voids during stretching, or by bonding various layers of the same or different materials to introduce voids in between the fused areas.[7,16–30] The size, shape and density of the voids, as well as the type and pressure inside the holes, are the key factors affecting the piezoelectric responses of the electrets, and were optimized by a trial and error procedure.[7,16–30] Also, the poling process is always an inevitable step before they can become real piezoelectrets. The voids were charged through electrode, corona or soft X-ray poling in which a large potential is applied across the materials, causing void gas breakdown in the generation of charges of opposite polarity, permanently deposited at upper and lower internal surfaces of the cells to form artificial macro-dipoles.[7,16–30] Undesirable problems arose from the rigorous poling process, such as substantial additional power consumption, and sometimes electrical breakdown failure occurred in polymer matrixes, resulting in the discard of the whole samples.

Perfluorosulfonate ionomers, known as Nafion, are the most popular solid polyelectrolyte used in the purification of seawater, proton exchange membrane fuel cells, hydrogen fuel cells, photoelectrochemical cells, and other clean energy electrochemical devices, due to their high thermochemical stability and good proton conductivity in a wide humidity range.[31–38] Nafion consists of fluorocarbon macromolecular backbones with long pendant high acidic sulfonated groups covalently immobilized, and its proton transport is enabled by the dissociation and separation of cations (protons) and anions (sulfonic anions), even at very low water activity or anhydrous state.[31–38] When such an ionic polymer is stimulated by a very low DC/AC voltage, it undergoes a fast bending deformation toward the anode, due to the expansion of the cathode side by the migrations of mobile cations.[31,39–41] On the other hand, it can also generate electrical output responding to an external dynamic mechanical deformation, with the mechanism of ionic distribution, termed as the piezoionic effect.[6]

PVDF and its copolymers with trifluoroethylene are one of the limited known classes of bulk piezopolymers.[8–10,42–45] For PVDF, it exhibits a pronounced polymorphism, *i.e.* α, β, γ, δ and ε, transforming between several crystal forms under certain conditions.[8] Successful development of piezoelectric devices of the polymer depends on the effective fabrication of polar crystalline structures, such as β and γ.[8–10,42–45] PVDF-based nonwoven fiber fabrics promise applicability in stretchable generators with their chemical resistance, structural flexibility, processing simplicity, and large piezoelectric coefficients.[42–45] Furthermore, PVDF shows great attraction in the energy storage field, mainly due to its high safety and low cost, such as its application as gel polymer electrolytes (GPEs) in lithium or sodium ion batteries, supercapacitors, and solar cells.[46–55] The primary function for GPEs in lithium or sodium ion batteries is to keep the positive and negative electrodes apart to avoid electrical short circuit, and to allow rapid ion transport at the same time.[50] In a GPE, the PVDF matrix may trap a viscous electrolyte component of low volatility by physical or chemical bonds to form a hybrid system.[47] The absorbed liquid electrolyte determines the electrochemical performance of the GPE, and the polymer matrix ensures its mechanical properties, morphology and safety.[47] Particularly, the structures of GPEs have been found to play an important role in determining the measured cell performance by affecting the ion transportation between the electrodes.[50] Consequently, the composites of PVDF or its copolymer polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) with nonwoven fabrics,[50,54] glass fibers[51] or polyborate[52–55] were developed recently to improve the ionic conductivity and other critical performance of GPEs, such as electrolyte absorption capacity, wettability, thermal and electrochemical stability, mechanical and surface properties, flame retardancy, Al passivating ability, and so on.

To overcome the main shortcomings of voided charged polymers, being the same with some other state-of-the-art piezoelectric polymers, herein we propose the design and fabrication of a new, poling-free dynamic piezoelectret for the capturing of kinetic mechanical energy, and its composite structure and working mechanism are schematically described in Fig. 1. The piezoelectret is composed of a cellular piezopolymer, PVDF, with its voids filled by a solid polyelectrolyte, Nafion, fabricated through solution casting of a PVDF–Nafion blend followed by high pressure crystallization. Pressure treatment has been proven to be an effective route to promote the formation of new polymeric structures[56,57] and enhance the yielding and orientation of polar crystallites of β-form in PVDF,[58–60] which plays the same role as electrical poling and renders the cellular networks with high piezoelectric response. Initially, there is no charge on the surfaces of the PVDF–Nafion dynamic piezoelectret generator (PNDPG). Its working process is divided into two stages. The first stage is the self-generation of a real piezoelectret during a dynamic stimulation, with both intrinsic molecular dipoles and artificial macroscopic dipoles inside (Fig. 1, stage I). When a vertical compressive force is applied to the PNDPG, the polar crystalline PVDF cell network deforms, and voltage begins to generate on both sides, due to the piezoelectric response of PVDF. The generated potential enables the movement and distribution of the mobile ions in the embedded Nafion fillers, resulting in charges of opposite polarity accumulated on their lower and upper sides, respectively, and then the formation of desired solid macro-dipoles. The charges in Nafion fillers are opposite in polarity compared to the overall polarity of the outer layers of the generator, and

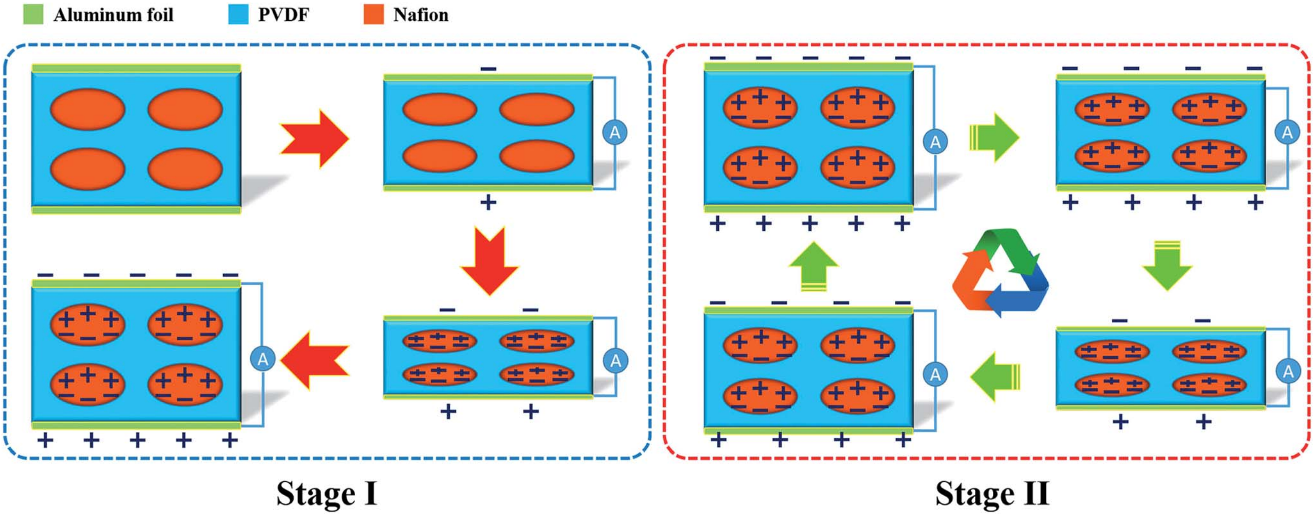

Fig. 1 Schematic drawing of the composite structure and working mechanism for a PVDF–Nafion dynamic piezoelectret generator (PNDPG).

dimensional changes or movements of such macro-dipoles will lead to rather strong electrical responses between generator electrodes. The second stage is a stable and durable power generation of the PNDPG in response to the succedent dynamic deformations and relaxations (Fig. 1, stage II). The compression of the PNDPG leads to a size reduction of Nafion macro-dipoles. Subsequently, the charge density on electrodes decreases until a new equilibrium is reached. This will result in a current flow from the bottom to the top electrode, corresponding to an instantaneous positive current signal output. On the other side, the size recovery of the macro-dipoles, resulting from the matrix relaxation of the PNDPG, increases the electrode charge density, which further induces a current flowing back from the top to the bottom electrode, corresponding to an output signal of negative current.

The synergistic action of intrinsic PVDF molecular dipoles and artificial Nafion macro-dipoles endowed the strategy guided as-fabricated PNDPGs with an outstanding efficiency together with long-term stability in mechanical-to-electrical conversion. Without any treatment of electrical poling, the open-circuit voltage of a PNDPG developed at the optimized conditions, stimulated by dynamic deformation, reached a peak value with 7.4 V, corresponding to an output density of 14.6 V cm^{-2}, exceeding that of most of the state-of-the-art piezoelectric polymers reported in the open literature (Table 1).

Experimental

Nafion® solution, 5 wt% Nafion® 117 in water and alcohol, was supplied by DuPont. PVDF powder, commercial-grade Solef 6010, was acquired from Solvay Co., Ltd., Belgium, and its weight-average molecular weight, M_w, was 322 000 g mol^{-1}. An analytical grade *N*,*N*-dimethylformamide (DMF) was provided by Chengdu Kelong Chemical Co., Ltd, and used as received. A schematic illustration for the mixing process of Nafion and PVDF is shown in Fig. S1, ESI.† Nafion solution was first heated up to evaporate the solvent at 70 °C, and then dissolved using DMF at 60 °C. Subsequently, PVDF powder was added in the reformed solution. With mechanical stirring for 2 h, homogeneously dispersed PVDF–Nafion solution was coated on glass substrates, and dried in a vacuum oven at 70 °C for 3 h to remove the DMF solvent. Finally, the dried blend films were detached and pelletized for the following high pressure crystallization.

Table 1 A comparison of PNDP with representative state-of-the-art piezoelectric polymers, including bulk piezopolymers, piezocomposites and voided charged polymers

Material	Designed size	Voltage output density	Poling process
PNDP	Φ 8.04 mm	14.6 V cm^{-2}	No
PVDF[9]	4.4 mm × 4.4 mm	0.71^a V cm^{-2}	Yes
PVDF-TrFE[10]	1.5 cm × 1.5 mm	0.6–1.0^a V cm^{-2}	No
PVDF–ZnO[11]	3 cm × 3 cm	0.76^a V cm^{-2}	No
$BaTiO_3$/PDMS[12]	1 cm × 1 cm	5.5^a V cm^{-2}	Yes
PZT/CNT/PDMS[13]	3 cm × 3 cm	1.1^a V cm^{-2}	Yes
$ZnSnO_3$: PDMS[14]	1 cm × 1 cm	12.0^a V cm^{-2}	No
$BaTiO_3$–PEBA[15]	12 mm × 30 mm	0.22^a V cm^{-2}	Yes
Cellular PP[16]	17.5 mm^2	13.7^a V cm^{-2}	Yes

^{a} Values calculated based on other parameters reported in the reference.

High-pressure experiments for the PVDF–Nafion composites, fabricated by the solution casting approach described above, were carried out with a self-made piston–cylinder apparatus, as schematically shown in Fig. 2a. The following procedure for crystallization was used. After loading the PVDF–Nafion granules, the temperature was increased to 200 °C to allow them to melt. Then a low pressure (150 MPa) was applied, and the temperature was raised to 260 °C. After equilibrium was established, the pressure was further raised to 400 MPa. These samples were kept under these conditions for 10 min, and then quenched down to ambient conditions. Six PNDP specimens, with a consistent column aspect, 8.04 mm in diameter and 0.50 mm in thickness, were prepared by varying the PVDF–Nafion composition (Fig. 2b).

Differential scanning calorimetry (DSC) measurements were conducted at atmospheric pressure by using a TA-Q20 instrument. The weight of the sample was around 5 mg. The melting behavior of the crystals was investigated through a heating scan with a heating rate of 10 °C min^{-1} under N_2 atmosphere. Wide-angle X-ray diffraction (WAXD) results were obtained at room temperature with a DX-1000 diffractometer. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) data were obtained using a Nicolet 5700 spectrometer in the range of 700–4000 cm^{-1}, with 32 scans conducted at a resolution of 4 cm^{-1}. After the WAXD and ATR-FTIR characterization, the sample surfaces were etched by using a method modified from that developed by Vaughan,[61] and then coated with gold for scanning electron microscopy (SEM) observations using a JSM-6330F apparatus.

The energy harvesting performance of the poling-free PNDPGs was evaluated by a periodic impacting test, with an experimental setup described in a recent publication.[60] A NTI AG HS01-37 × 166 linear motor was used as the impact source, and the simultaneously generated open-circuit voltage and short-circuit current were collected with a Keithley 6514 system electrometer and a Stanford Research SR570 low-noise current preamplifier, respectively.

Results and discussion

Fig. 3a–c show the DSC, WAXD and ATR-FTIR results of the PNDP samples with various Nafion concentrations, fabricated through crystallization at 400 MPa, 260 °C for 10 min. With the decrease of Nafion concentration, the area of the melting peaks generally increased, indicating more PVDF crystallites formed in the samples (Fig. 3a). Moreover, multiple melting arose, and the melting points of high-temperature peaks turned to shift to higher values, with a slight decrease for the sample with 50 wt% Nafion, and then remained more or less the same. This suggested that alterations of crystalline forms, morphologies and substructures occurred, tuned by the variation of the composite composition. Particularly, the relatively high melting points for the samples with or below 40 wt% Nafion indicated that PVDF crystallites with extended-chain lamellae as their substructures were crystallized internally. WAXD and IR data (Fig. 3b and c), used for the identification of the crystalline phases of PVDF, further confirmed a continuous increase in the content of the piezoelectric β phase when the Nafion concentration was decreased. This can be clearly observed by the intensity variation of the apparent single peak at 2θ angle 20.4–21.1° (WAXD), coming from the superposition of the (110)β and (200)β reflections, and those bands at 840 and 1280 cm^{-1} (IR), characteristic of the orthorhombic β phase of the polymer.[58,60] Crystallites with other crystalline forms, such as α and γ phases, were also

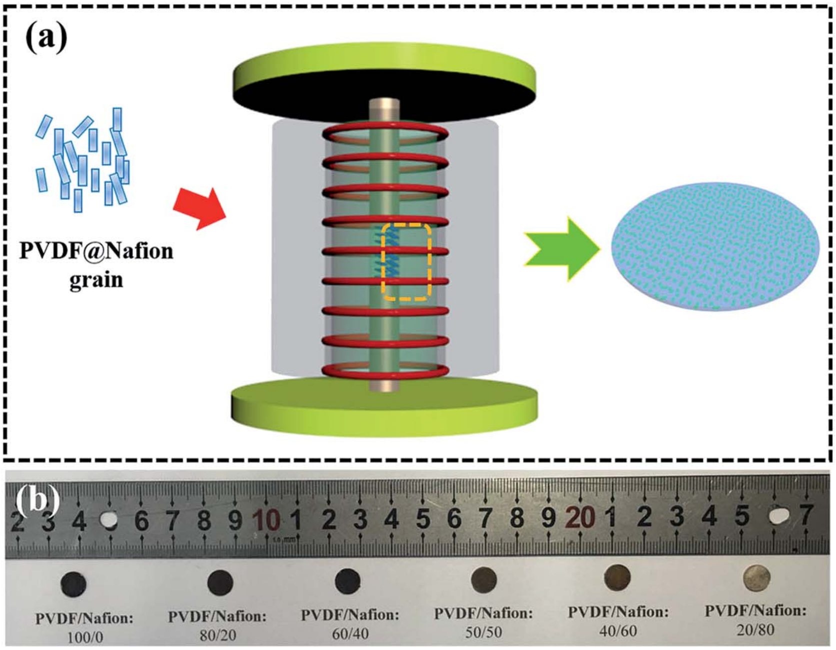

Fig. 2 Schematic diagram illustrating the fabrication process of the PVDF–Nafion dynamic piezoelectrets (PNDP) with a piston–cylinder high-pressure apparatus (a), and a digital picture showing the physical size and appearance of the as fabricated PNDP samples (b).

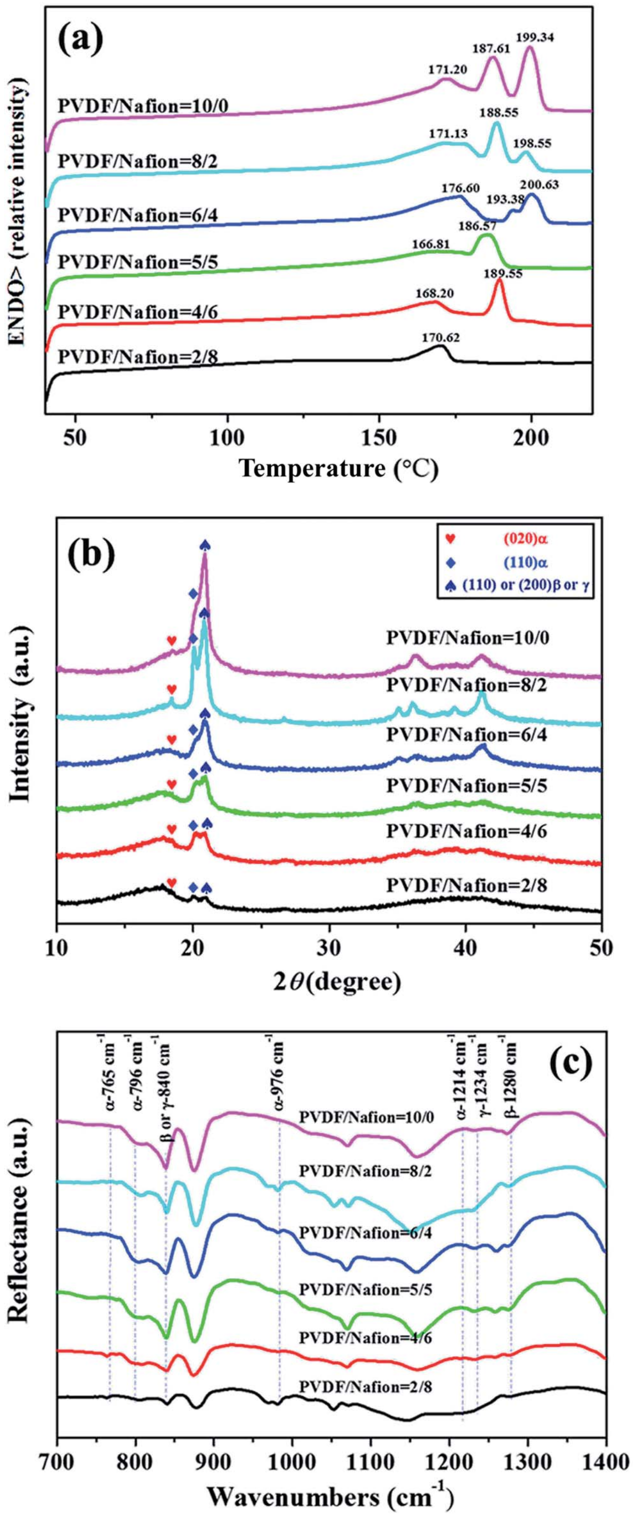

Fig. 3 DSC (a), WAXD (b) and ATR-FTIR (c) results of the PVDF–Nafion composite samples with different compounding ratios, crystallized at 400 MPa, 260 °C for 10 min.

detected in the PNDP samples, though the intensities of their characteristic reflections were relatively very weak, both in WAXD and IR spectra.

After the fabrication of a pressure treated pure Nafion sample (Fig. S2a, ESI†), a comparison experiment was conducted. The representative WAXD and IR results for the original neat PVDF and Nafion, both before and after the applied high pressure treatment at 400 MPa, 260 °C for 10 min, are shown in Fig. S2b and c, ESI,† respectively. As can be seen, no crystalline β phase crystal, essential in the creation of piezoelectricity, and the subsequent self-generation of a real piezoelectret by dynamic stimulation, was crystallized for both the pure Nafion samples, before and after the high pressure treatment. Also, WAXD and IR only detected non-polar α form crystals in the original PVDF sample if no high pressure treatment was applied. According to the proposed working mechanism (Fig. 1), original PVDF, prior to pressure crystallization, and pure Nafion, with or without pressure treatment, lack the necessary piezoelectric crystalline structures in the realization of a PNDPG for mechanical-to-electrical conversion.

Fig. 4a–f show the typical SEM micrographs of the fractured cross sections of the PNDP samples, with Nafion removed by the applied etching process. The removal of Nafion clearly revealed the size and morphology of the crystalline PVDF cells originally filled by this solid state polyelectrolyte. For the samples composed of pure PVDF (Fig. 4a) or with a relatively lower Nafion concentration (Fig. 4b), actually no void, crucial in the realization of a desired piezoelectret, was observed. SEM only disclosed featured α spherulites (Fig. 4a), embedded in β-phase fibrils, and extended-chain crystals with parallel striations (Fig. 4b), growing together with non-textured γ form crystallites. Crystalline PVDF cells, with smaller size and larger distribution density, began to emerge when the Nafion concentration was increased to 40 wt% (Fig. 4c), and the higher melting point (200.63 °C) of the sample (Fig. 3a) indicated that a large amount of their substructures were intrinsically with thermally stable extended-chain lamellae.[58] With the further increase of the Nafion concentration, the cell size became larger and larger, on the scale of several micrometers (Fig. 4d–f). Moreover, the originally closed cells (Fig. 4c and d) turned to be more and more open and interconnected (Fig. 4e and f).

Based on the above DSC, WAXD, IR and SEM results, it is concluded that piezoelectric cellular PVDF structures, with polyelectrolyte Nafion filled in the holes, were achieved in the PNDP samples with appropriate blending ratios. The density, size, morphology of the cells, as well as their crystalline form and substructures, which are the key factors in affecting the distribution of the final formed macro-dipoles, were able to be controlled at high pressure by a compositive variation, and optimized cellular structures may render the produced PNDPs good candidates for kinetic energy harvesting.

The electrical outputs of the poling-free PNDPG samples, fabricated with different Nafion concentrations, were measured under the stimulation of low frequency impacts. Fig. 5a and b show the generated open-circuit voltage and short-circuit current of various PNDPGs at a stimulated frequency of 5 Hz and applied force of 60 N. With the increase of Nafion concentration, both the voltage and current increased, and then decreased synchronously. Maximum peak values were attained for a PNDPG with 50 wt% Nafion, *i.e.* 110 nA and 7.4 V for short-circuit current and open-circuit voltage, respectively. According to a calculation, the voltage output density of this optimized

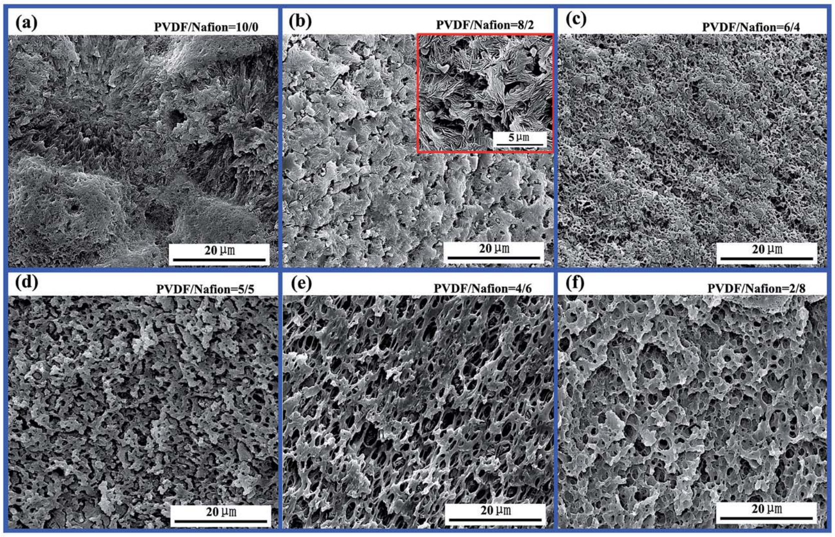

Fig. 4 Cross-sectional view of the SEM images of the PVDF–Nafion composite samples with different compounding ratios, crystallized at 400 MPa, 260 °C for 10 min. PVDF/Nafion: (a) 100/0, wt/wt; (b) 80/20, wt/wt; (c) 60/40, wt/wt; (d) 50/50, wt/wt; (e) 40/60, wt/wt; (f) 20/80, wt/wt. The inset in (b) is a more magnified view for the sample with 20 wt% Nafion. The cross sections of the high pressure crystallized PVDF–Nafion samples were etched before the SEM observations. The etching removed Nafion, and subsequently revealed the size and morphology of the voids, originally filled by this solid state polyelectrolyte in PVDF.

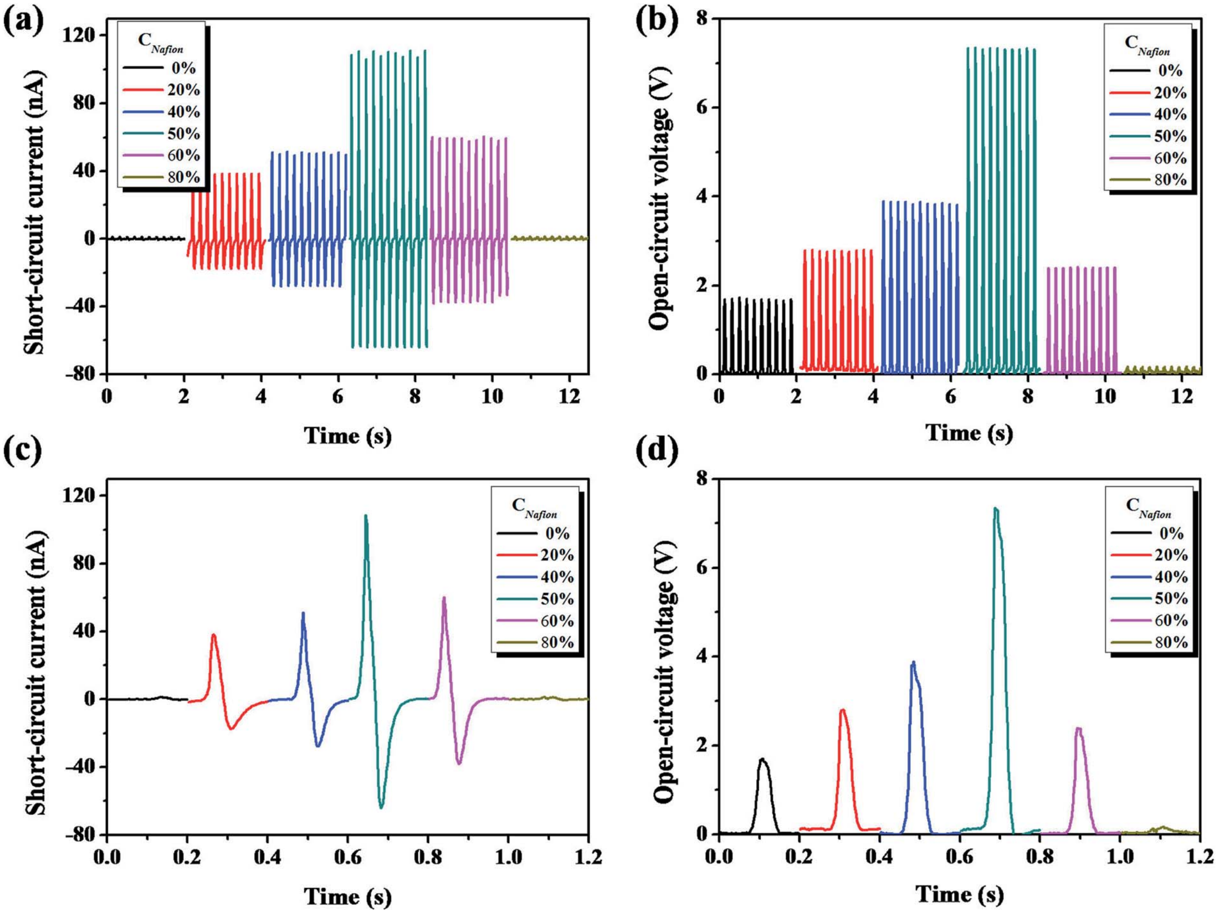

Fig. 5 Electrical potential and current outputs of the PNDPGs fabricated with a different percentage of Nafion: (a) short-circuit current and (b) corresponding open-circuit voltage, respectively, generated at a stimulated frequency of 5 Hz and applied force of 60 N; (c) short-circuit current and (d) related open-circuit voltage for one cycle with enlarged views, respectively.

PNDPG corresponded to 14.6 V cm^{-2}, which surpassed that of most of the state-of-the-art piezoelectric polymers reported in the open literature,[9–16] such as the piezocomposites based on piezoelectric materials $BaTiO_3$, PZT or $ZnSnO_3$ with elastomers PDMS[12–14] and PEBA,[15] as already shown in Table 1. Since the kinetic motions can be converted into electrical energy with various transduction forms,[3,4,6,7] the combination of electromagnetic, electrostatic or piezoelectric transductions may further improve the mechanical-to-electrical conversion of such PNDPGs. For example, $ZnSnO_3$/PDMS triboelectric nanogenerators (TENGs) showed a higher electrical output than its piezoelectric counterpart, mainly due to a synergistic action of electrostatic and piezoelectric effect.[4,14] However, the first-line purpose for the research presented here is to design and fabricate a piezoelectret with a new working mechanism so as to overcome the main shortcomings of the current piezoelectric polymeric generators, in terms of fabrication simplicity, energy conversion efficiency and performance stability and durability, as we discussed in the following text. Fig. 5c and d show the zoom-in views of the voltage and current curves for one cycle. As can be seen, the PNDPGs responded harmonically to the stimulation of low frequency impacts. The deformation and relaxation of the PNDPGs induced the generation of positive and negative current pulses, characteristics of an alternating current (AC), and the large positive peaks and almost negligible negative peaks of voltage mainly due to the capacitance effect of such piezomaterial.[62]

Combined with the DSC, WAXD, IR and SEM characterization (Fig. 3 and 4), the different electrical outputs for various PNDPGs in Fig. 5 could be attributed to the variation of the size, morphology, distribution, crystalline form and substructures of the Nafion-filled PVDF cells, tuned at high pressure by the variation of blend composition. Although no void was created in the sample of pure PVDF, a large amount of polar crystals, with oriented lamellar structures, were formed by high pressure crystallization. This also enabled the sample with piezoelectric response during the dynamic stimulation. A 20 wt% Nafion incorporation still had no direct effect on the formation of PVDF cells. However, this reduced the elastic stiffness of the sample, allowing large thickness deformation upon application of mechanical stresses, and then resulting in an improved electrical output. With the further continuous increase of the Nafion content, closed cells came into being, which initiated the synergistic action of molecular dipoles and macroscopic dipoles, and outstanding electrical generation was achieved in a PNDPG with an optimized cell geometry. The decrease of electrical output for the samples with higher Nafion concentrations was mainly due to the decreasing of polar crystals in PVDF cells, which rendered the co-working between micro- and macro-dipoles less effective. Moreover, the rather small electrical output of the 80 wt% Nafion sample suggested that a simplex piezoionic effect might be negligible in the power generation of such types of PNDPGs. Conclusively, PNDPGs, with an ideal electrical output, should be fabricated in a manner that optimizes the cooperation between intrinsic microscopic dipoles and artificial macroscopic dipoles.

The kinetic motions, existing with various amplitudes and frequencies, are quite diversified and irregular in a practical environment. So it is necessary to evaluate the power output performance of such PNDPGs under various conditions of stimulation. Fig. 6 shows the electrical output of a PNDFPG with 40 wt% Nafion by controlling the applied frequencies and input forces. The generated short-circuit current (Fig. 6a) and corresponding open-circuit voltage (Fig. 6b) of the stretch cycles obviously increased in accordance with the increase of the input forces as the frequency was fixed at 5 Hz. A negligible current output was observed for an applied force with 20 N amplitude. When the force reached 60 N, the short-circuit current was raised to ~50 nA, and can be further increased to ~60 nA, with the increase of the input force to 100 N. At the same time, the voltage was step by step increased from 2.5 V at 20 N to 6.0 V at 100 N, attributed to a higher piezoelectric response to a larger deformation of the polymeric matrix. On the other hand, for a constant stimulated force of 60 N, the short-circuit current was increased from ~50 to ~60 nA, and the open circuit voltage was increased correspondingly from ~4.0 to ~5.5 V, as the frequency was varied from 5 to 10 Hz (Fig. 6c and d). This phenomenon may possibly come from more charge accumulation on the PNDPG electrodes under higher frequency deformations of the viscoelastic polymeric matrix.[3] According to the above results, an appropriate increase of the stimulated force and frequency can lead to a larger electric output for such a type of PNDPG.

For the piezoelectric generators, their long-term stable and durable energy scavenging is very important in the operating of a sustainable, autonomous electronic device.[3,7,16] Herein, short-circuit current output was chosen as the main parameter to characterize the stability and durability of the as designed and fabricated PNDPGs. A just fabricated 40 wt% Nafion PNDPG sample was continuously hit for more than 100 000 cycles at a stimulated force of 60 N and frequency of 10 Hz, and its current outputs are shown in Fig. 7a. No performance decay was observed during the test cycles. Amazingly, the electrical outputs for different stimulated cycles kept increasing, with the increase of test time. The results are interesting and somewhat heart-stirring, which mean the energy harvesting performance of such PNDPGs can be improved by a self-activating process during its continuous working. The self-improvement on electrical output performance of the PNDPG may possibly be attributed to its unique internal composite structures. When the PNDPG is pressed and released constantly, mechanical energy is partially converted into heat energy, resulting in the increase of temperature in the composite matrix. Thus, the movement of the mobile ions in Nafion fillers is accelerated,[32] which in turn increases the overall macroscopic dipole movements and surface charges, and then makes the current output increasing continuously.

It is known that the performance of Nafion is well dependent upon the hydration of water. Hydration is directly related to the ionic conductivity of the polymer, which stems from the mobility of hydrated cations and water through the polymer matrix.[31–41,63–65] Nevertheless, the investigations by NASA and other researchers also demonstrated the workability of Nafion

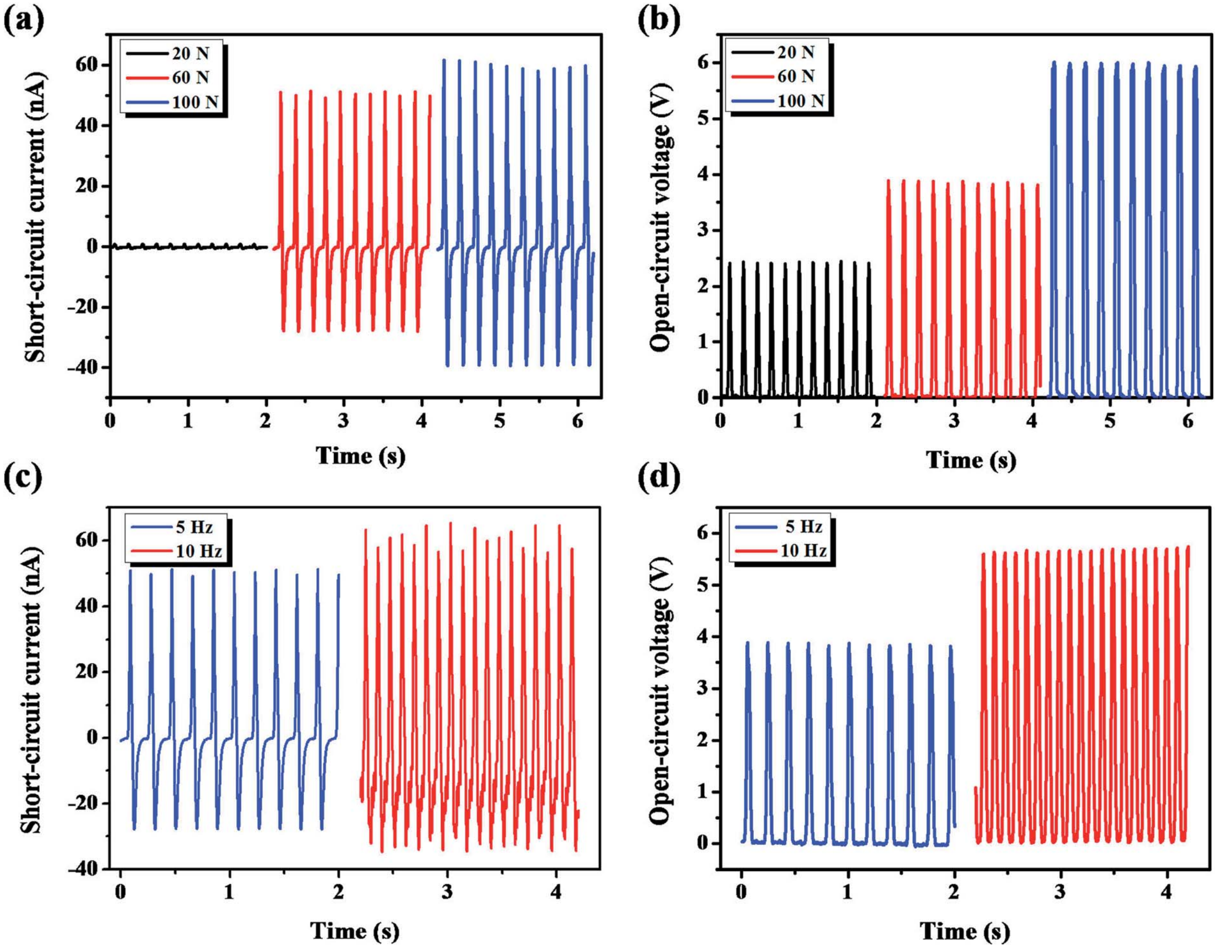

Fig. 6 Electrical outputs of a PNDPG (PVDF/Nafion: 60/40, wt/wt) under various input conditions: (a) short-circuit current and (b) corresponding open-circuit voltage, stimulated at different forces and a given frequency of 5 Hz; (c) short-circuit current and (d) relevant open-circuit voltage, stimulated at different frequencies and a given force of 60 N.

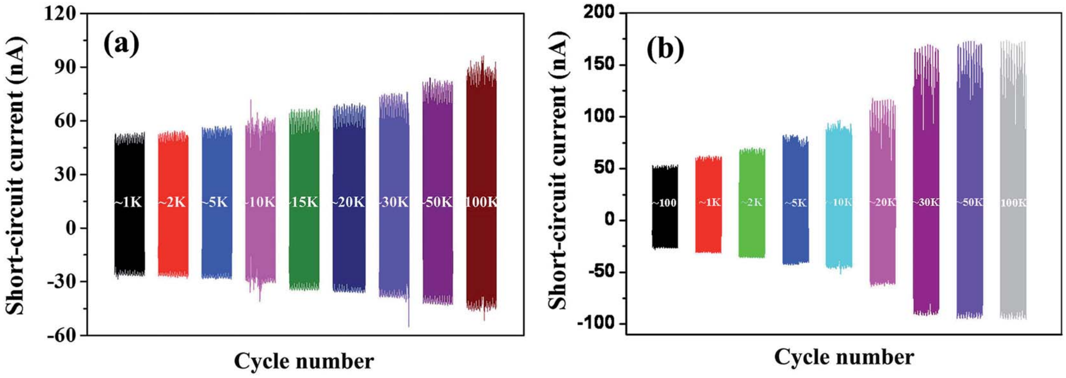

Fig. 7 Stability and durability test of a PNDPG (PVDF/Nafion: 60/40, wt/wt): (a) output current–time curves for ≈100 000 continuous working cycles just after the fabrication of the sample; (b) output current–time curves for additional ≈100 000 continuous working cycles of the same sample, which has already been exposed to open air for 240 days since the test in (a) was performed; whole signal.

even under very low water activity or anhydrous state.[39,64,65] For example, a harsh environment consisting of low temperature (−140 °C) and vacuum air conditions have a strong effect on the ion conductivity of Nafion by reducing its performance but not altogether eliminating it.[39,64,65] The fact that the PNDPG does exhibit a long-term stability and durability for energy harvesting, as shown in Fig. 7a, further confirmed the retention ability of Nafion for ionic conductivity, even though the sample was fabricated through a high temperature and high pressure process.

Fig. 7b shows the output current–time curves for additional ≈100 000 continuous working cycles of the same PNDPG sample, which has already been exposed to open air for 240 days since the test in Fig. 7a was performed. It can be observed that the electrical outputs still kept increasing until the hits reached ≈50 000 cycles. However, for each stimulated cycle, the electrical outputs of the sample exposed for a longer period are higher than those of its just fabricated counterpart without exposure. This may be attributed to the increase of water content in the PNDPG sample during its exposure. Compared with the high temperature and high temperature environment for sample fabrication, the open air environment for exposure has relatively higher humidity. Thus more water vapors were absorbed and then permeated in the PNDPG sample, which increased the ionic conductivity in the Nafion fillers and subsequently accelerated the overall macroscopic dipole movements.[39,63–65] We also noted that the PNDPG sample attained a stable state for electrical outputs when the hits exceeded ≈50 000 cycles, mainly due to a balance achieved for the diffusion of mobile cations as well as water through the nanosize pores and channels of Nafion fillers.[39,63–65] With excellent performance stability and repeatability, the PNDPG sample was operated for another ≈50 000 cycles under the above-mentioned experimental conditions. Still no electrical output decay was observed when the test was terminated.

The results in Fig. 7 revealed positive time-dependent behaviors of such PNDPGs for long-term stable and durable energy scavenging. Recently, more solid-state polymeric electrolytes were developed for anhydrous high temperature fuel cells.[32–34,36,66–69] By embedding such types of proton-conducting hybrid electrolytes in the host piezopolymers, with designable structures that permit water-free H^+ conductivity, the stability, durability as well as repeatability of the PNDPGs may be further improved when they work under harsh anhydrous or low humidity environments.

Conclusion

In summary, we have successfully demonstrated the design and fabrication of a new, poling-free dynamic piezoelectret by filling the holes in piezoelectric cellular PVDF with polyelectrolyte Nafion, achieved through solution casting and subsequent high pressure crystallization of their blends. The size, morphology, distribution, crystalline form and substructures of the internally pressure-crystallized Nafion-filled PVDF cells were tuned by the variation of blend composition, and the optimized cellular structures endowed the produced PNDPGs with outstanding performance in kinetic energy harvesting. Without any treatment of electrical poling, the open-circuit voltage output density of a PNDPG, stimulated by its dynamic deformation and relaxation, reached a value of 14.6 V cm^{-2}, which surpassed that of most of the state-of-the-art piezoelectric polymers. Moreover, the controllable electrical output of such PNDPGs was able to be realized by modulating the amplitude and frequency of the applied dynamic stimulation. Particularly, the energy capturing performance of such PNDPGs was found to be improved by a self-activating process during their long-term continuous working. The working mechanism of the developed PNDPGs was attributed to a synergistic action between intrinsic microscopic dipoles and man-made macroscopic dipoles. We believe that the void-filled piezoelectrets, based on PVDF and Nafion, may have some advantages over the most widely used traditional piezopolymers by diversifying niche applications in self-powered, autonomous systems, in terms of their fabrication simplicity and energy conversion efficiency, and the present study may possibly open up an avenue for the manufacturing of a new class of electret-transducer materials in energy scavenging.

Author contributions

Jun Lu conceived the idea, and initiated the study. Chenwen Xu, Lei Zhang, Yali Xu, Zhenzhong Yin, Qin Chen, Songyuan Ma, Huanhuan Zhang, Rui Huang, Chaoliang Zhang and Long Jin carried out the sample preparation and characterization. Jun Lu and Weiqing Yang organized the entire research. Jun Lu, Chenwen Xu, Lei Zhang and Weiqing Yang analysed and interpreted the data, and wrote the manuscript with the assistance of all other co-authors. All authors discussed the results and commented on the manuscript.

Competing financial interest

The authors declare no competing financial interest.

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