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Microporous polyvinylidene fluoride film with dense surface enables efficient piezoelectric conversion

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We demonstrate that asymmetric porous polyvinylidene fluoride (PVDF) film, with pores mostly distributed in the bulk but not at the surfaces, can be used as a highly efficient piezoelectric energy generation device. For such microporous PVDF film with dense or pore-free surface, piezoelectric theory shows the efficiency of energy conversion by piezoelectric device depends upon the structure compressibility. Film mechanical properties can be controlled by dispersing micro-scale pores in a polymer matrix with a dense top layer. Piezoelectric output is enhanced by optimization of PVDF micro-structure and electromechanical coupling efficiency. The power output increased three folds with a designed three-dimensional asymmetric porous structure as compared to solid film. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4921007]

Polyvinylidene fluoride (PVDF) is an emerging piezoelectric polymer with unique features that include structural flexibility, ease of processing, and chemical resistance. Recent study has demonstrated its application in various transducers and harvesters to convert mechanical deformations into electrical charges. Wearable devices powered by transducers and harvesters are making great strides, with a focus on portable and flexible materials for biomedical sensing and power sources seamlessly integrated with the human body. The biocompatibility, high power density, and high flexibility of PVDF are desirable attributes for these exciting applications.

In order to produce enough power in a compact volume, more efficient PVDF structure design is required. Conventional thin film devices have been studied thoroughly but have not proved capable of achieving sufficiently high output for most projected applications. In contrast, nanostructures of piezoelectric material show enhanced piezoelectricity and numerous efforts seek to develop high-efficiency piezoelectric devices using micro/nano material structures.

In one promising approach, devices with porous structures have showed enhanced piezoelectric efficiency due to the optimized stress-strain response. However, current efforts on PVDF porous structure are limited due to the paucity of methods for nano fabrication of PVDF.

Currently, additive modeling and phase separation are two main methods for porous PVDF film preparation on large scale substrate. Both have drawbacks. For the additive method, metal salt and nanometer particles cannot be removed completely and the remainder in the film interferes with poling procedures. Moreover, pore size varies and large through holes exist in the films. PVDF phase separation has been investigated because it gives porous morphology with variable pore size and three dimensional structures. However, PVDF porous films are mostly used as passive materials in tissue engineering, separation membranes, mechanical damping, and packaging. Their potential as a soft active material for electromechanical transducers appears to have been neglected. Two main problems hinder the use of porous PVDF films in piezoelectric applications. First, most films obtained by immersion precipitation have non-uniform structure underneath the surface. Finger-like cavities will be suitable for filtering but not for sensors. Second, the film’s top surface comprises many defects and pinholes, possibly leading to short circuit between electrodes.

In this paper, we report a 3D porous PVDF film structure that overcomes these two obstacles. This work establishes the proof of concept that porous PVDF film manufactured by phase separation can be used as high-efficiency piezoelectric device. Asymmetric porous structure is developed to promote larger collecting area and aligned poling direction. Direct film deposition and pore-formation on electrode surface make this technology suitable for a wide range of devices. Both simulation data and test data confirm that porous structure can enhance power output in piezoelectric performance.

As volatile solvent evaporates, the polymer solution surface is cooled and water droplets condense on it (Fig. 1). Pores form within the developing film due to mixing of condensed water with polymer solution. The concentration variations following diffusive interchange between solvent and non-solvent lead to phase separation. The polymer-rich phase forms the porous matrix, while the polymer-poor phase gives rise to the pores. When the film returns to ambient temperature, the condensed water and residual solvent evaporate, leaving behind the 3D polymer scaffold, as shown in Fig. 1.

When PVDF porous film is prepared with Tetrahydrofuran–Dimethylformamide (THF-DMF) solvent in a humid environment, larger pores than those on the top surface are coexistent with smaller pores in the inner film. Larger pores originate from the coalescence of water droplets and small pores from the depletion by mixing of water droplets with the solution. However, as discussed in above, a dense surface and uniform structure are desired in piezoelectric device applications. A pre-evaporation procedure therefore is introduced to eliminate large pores on the surface. The cast solution is evaporated in a dry nitrogen environment for several minutes, thus...
guiding the formation of a dense top layer. After the sample is moved to a high-humidity environment, the water droplets penetrate the top surface and create non-solvent volumes beneath it. Most phase separation procedures are carried out by inversing polymer solution into non-solvent bath to induce porous structure. The film structure is formed immediately after submersion in the nonsolvent bath. Intensive phase separation induces finger-like cavities and large open cells within the film. In this work, precisely controlled phase inversion in a humid environment induces uniform cavity formation in the film structure. The volume of water penetrating the surface into the inner structure is much smaller and slower-moving than in conventional phase separation. The THF-DMF mixed solvent allows the minority presence of a non-solvent (water) to induce phase separation.

Polyvinylidenedifluoride–Trifluoroethylene (PVDF-TrFE) powder (molar ratio: 75/25) was dissolved in THF-DMF mixed solvent (5 ml) under magnetic stirring. THF and DMF solvent volume ratio were controlled at 1:2. Patterned copper bottom electrodes were deposited on Kapton film. 1 μl of the copolymer solution was cast on the substrate. The cast film was first evaporated in a dry nitrogen environment for 8 min. Then, the film was moved into a chamber with 90% relative humidity at room temperature (25°C) and kept for 6 h to allow complete phase separation between solvent and non-solvent. After solvent evaporation, 200 nm thickness top copper electrodes (2 × 0.5 cm) were deposited by E-Beam. Final film thickness was measured by using a surface profilometer (Dektak 6M) and found to be around 60 μm. The electrical polling process over the film was performed at 90°C with a 75 V/μm electrical field applied for 30 min.

By varying solvent ratio and humidity exposure, different pore morphologies can be achieved. Fig. 2 shows scanning electron microscopy (SEM) images of top surfaces and cross sections of PVDF-TrFE films. When pure THF is used as solvent, the top surface is smooth and the inner structure is solid, as shown in Fig. 2(a). All other films in Fig. 2 were prepared by cast-coating 16% weight concentration PVDF in THF-DMF mixed solvents at room temperature. In particular, a porous 3D film (Fig. 2(b)) was obtained by dip coating in a humid environment. As water droplets condense on the surface during most of the formation process, the result, as shown, is larger pores and an uneven top surface. When a solvent combining DMF and THF is used, solvent evaporation is slowed down, making it possible for the water droplets sink into the film. THF’s boiling point is 66°C, which encourages fast formation of a solid surface after dip coating. Water droplets are unable to pass through the surface and

![FIG. 1. Schematic cross section of porous PVDF film formation. (a) Evaporation of solvent in dry environment leads to a high PVDF concentration surface. (b) After dense surface is formed, film is moved into high-humidity environment. Solvent evaporation cools the PVDF surface and moisture begins to condense on the surface. (c) Larger-volume water droplets form below the surface. (d) More droplets sink into the solution creating a 3D porous structure. (e) Thermal treatment removes all residual solvent and water. (f) Illustration of porous PVDF structure with a dense top layer.](image-url)

![FIG. 2. Tilt-view SEM of three PVDF-TrFE film morphologies. (a) Solid film. (b) Porous film without dense surface. (c) Porous film with dense surface. (d) Closer view of porous film with dense surface. Scale bar: 10 μm.](image-url)
form pores. Figs. 2(c) and 2(d) show SEM images of porous PVDF films with dense surfaces. Evaporation in a dry environment creates a dense surface on the sample. Micro pores with 3–5 μm diameter can be observed in the image. In Fig. 2(d), it can be observed that small holes remain in the surface as paths for condensed water droplets sinking through.

The density of the solid PVDF films (e.g., Fig. 2(a)) was measured as $\rho_s = 1874 \text{ kg/m}^3$. This value is reasonable, given that a PVDF-TrFE (70/30) film having a density of 1917 kg/m$^3$. The density of the porous films prepared from 16% solution was calculated to be $\rho_p = 906 \text{ kg/m}^3$. The lower density of the porous films suggest a highly porous structure with a porosity of $\varphi = 52.7\%$. For the porous PVDF film with dense surface (Figs. 2(c) and 2(d)), the density was calculated as $\rho_p = 944 \text{ kg/m}^3$ indicating the dense top layer does not add much weight to the film. The minority presence of the nonsolvent was sufficient to induce the phase inversion of the polymer solution; therefore, liquid–liquid phase separation occurred at an early stage, and macrovoids could not develop.

In this experiment, 8%, 12%, and 16% concentrations of PVDF in THF-DMF are used. Increased polymer concentration hinders penetration of non-solvent during the separation step. In low PVDF concentration (8% and 12%), pore diameter ranges from 4 μm to 12 μm, as showed in Fig. S3. With 16% concentration, the solution reaches a balance between non-solvent penetration and pore formation.

The three dimension atomic force microscope (AFM) topography of the porous PVDF film with dense surface is shown in Fig. 3(a). AFM was accomplished using a Bruker MultiMode 8 operating in tapping mode at ambient conditions. Small cracks in the surface can be observed from the topography in agreement with the SEM image in Fig. 2(d). Fig. 3(b) is a Young’s modulus map of the dense surface film. The Young’s modulus is obtained by the retract curve using the Derjaguin, Muller, Toropov (DMT) model. The map reveals spots with obviously small Young’s modulus with dense surface (Figs. 2(c) and 2(d)), the density was calculated as $\rho_p = 944 \text{ kg/m}^3$ indicating the dense top layer does not add much weight to the film. The minority presence of the nonsolvent was sufficient to induce the phase inversion of the polymer solution; therefore, liquid–liquid phase separation occurred at an early stage, and macrovoids could not develop.

PVDF-TrFE copolymer has a high piezoelectric coefficient. Copolymers like TrFE can create artificial defects to decrease the energy to crystallize into the all-trans form without additional stretch processing. We used PVDF-TrFE to maintain high β-phase content without mechanical stretching in this porous structure. Fig. S1(a) shows XRD data for solid PVDF film and porous PVDF film. In the $10^\circ$–$40^\circ$, range of diffraction angle 2θ, we find a sharp peak at 20.08°. The peak at 2θ = 20.08 is assigned to (110) (200) reflection from ferroelectric polymer crystals. Fig. S1(b) shows the Differential Scanning Calorimetry (DSC) curves of PVDF films with different structures. All three samples showed two peaks, corresponding to the phase transition in crystallites (Tc) and paraelectric phase melting (Tm). According to these DSC results, the PVDF solid film and porous films, with or without dense surface, are piezoelectric due to the existence of β phase crystallites. Conventional film samples present a higher melting peak than porous film samples by about 6°C, reflecting a higher degree of crystallinity. The intensity increase indicated that the overall crystallinity of the material in the conventional films is slightly higher than porous film samples. Porous structure hinders the long-range order and the crystal structure of aligned arrays.

Generated piezoelectric charge (Q) can be calculated as

$$Q = \int_A D \, dA,$$  \hspace{1cm} (1)

where A is the surface area and D is the electric charge density displacement

$$D_i = \frac{\mu_i}{V}.$$  \hspace{1cm} (2)

$\mu$ is the total dipole moment and V is the volume of the porous film. By Eq. (1), a flat dense surface will collect more charges than a porous surface of equal overall size.

The piezoelectric charge coefficient (dij) is the electrical charge generated per unit of mechanical stress (T) applied to a piezoelectric material. It can be defined as

$$d_{ij} = \frac{\partial \epsilon_{ij}}{\partial T_j},$$  \hspace{1cm} (3)

Increasing piezoelectric charge coefficient will be another efficient way to enhance Q. According to Eqs. (2) and (3), the piezoelectric constant dij and film compressibility $\beta$ can be written as follows:

$$d_{ij} = \frac{\partial}{\partial T_j} \left( \frac{\mu_i}{V} \right) = \frac{1}{V} \frac{\partial \mu_i}{\partial T_j} - \frac{\mu_i}{V^2} \left( \frac{\partial V}{\partial T_j} \right),$$  \hspace{1cm} (4)

$$\beta = - \frac{1}{V} \frac{\partial V}{\partial T_j},$$  \hspace{1cm} (5)

where j = 3 for the pressure applied along the z-direction. Since $\partial V/\partial T_j$ is intrinsically negative, $\beta$ is a positive number proportional to piezoelectric constant. Young’s modulus (E) of porous film is related to its density through the relation

$$E = C \left( \frac{\rho_s}{\rho_p} \right)^n E_s,$$  \hspace{1cm} (6)

where $E_s$ and $\rho_s$ are the Young’s modulus and density of the solid film. The constants C and n depend on the
microstructure of the material. Experimental evidence suggests that \( n = 2 \) for open cells structure. As in Eqs. (5) and (6), in porous PVDF film, high compressibility can be achieved due to the smaller Young’s modulus. With larger deformation at identical pressure as compared to conventional solid films, higher piezoelectric output can be generated.

Finite element models have been developed to characterize the piezoelectric response of solid and porous materials. The potential of the fixed bottom part is grounded. After structural setup, constant pressure is applied to the top of the device, and the cross section potential profile is extracted. The porous piezoelectric structure used in the finite element model of a 0–3 piezocomposite membrane is shown in Figs. 4(b) and S5 in Ref. 19. This is chosen to be close to the practical structure of a foam-reticulated sample as described in the previous SEM section. The volume fraction of the piezocomposite film is taken as 47.3%. Fig. 4 shows the voltage response on sample top layers. The maximum output occurs in the porous film with dense surface. The simulation results show the porous structure potential is over two fold higher than solid film with the same strain.

To measure the piezoelectric performance of the film, the fabricated sample was installed on the bending machine with a rotation motor. During test, the sample buckled by the hitter on the rotation motor, as showed in Fig. S4.19 One edge of the sample was fixed with sliding clamp. The other side of film edge was periodically bent and unbent by a rotating motor with 1 Hz frequency. The buckling radius of the substrate in all tests was controlled at 35.7 mm. Fig. S2 (Ref. 19) showed a typical output from piezoelectric material. Fig. 5(a) shows measured variations of piezo voltage (electrical potential generated during deformation) and pressure over ten deformation cycles. The pressure sensitivities of solid PVDF film and porous PVDF film with and without a dense surface were tested. When pressure is applied to the film, piezoelectric charges are generated which build up the potential difference, and a corresponding peak is observed in the positive direction. When the pressure is released, a negative peak is observed. The positive and negative voltage peaks thus correspond to the compression and recovery, respectively, in the PVDF film. In the case of porous PVDF film (Fig. 5(b)), the generated peak to peak voltage reaches up to 3.4 V, whereas it is only 1.2 V for solid film (Fig. 5(a)).
Figs. 5(a) and 5(c), the pressure-induced electric charge of the film is consistent with the load pressure signal, whereas it varies unpredictably in Fig. 5(b). The consistent output is mainly contributed by the uniform surface electrode in charge collecting and high voltage poling procedure. With the much higher peak-to-peak voltage of the porous, dense surface film of Fig. 5(c) that the sensitivity of porous film to pressure is much higher than that of solid film. This remarkable output increase from porous structure can be attributed to the higher compressibility.

Notably, porous film can be directly coated on curved surface, making it easier to integrate with various devices other than other porous film preparation methods. A film based energy harvester has been demonstrated that exploits the piezoelectric property of a porous PVDF structure. The voltage generated by the porous film was used to charge a capacitor, and light a commercial red LED. A full wave bridge rectifier structure with dense surface an excellent option for piezoelectric electromechanical sensitivity, and low-cost make porous template-assistant manufacturing. Ease of manufacture, high performance characteristics, including output voltage and power density, exceeded values previously reported for PVDF energy harvesters. For practical use, processing costs for 3D porous piezocomposites will be considerably lower than for high density materials and template-assistant manufacturing. Ease of manufacture, high electromechanical sensitivity, and low-cost make porous structure with dense surface an excellent option for piezoelectric devices.

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19See supplementary material at http://dx.doi.org/10.1063/1.4921007 for thin film material characterization (Fig. S1) and polarity switching tests (Fig. S2).