

Enhanced Piezoelectric Response in Nanostructured Ni/PVDF Films

Melilli G¹, Gorse D¹, Galifanova A¹, Oral O¹, Balanzat E², Doaré O³, Tabellout M⁴, Bechelany M⁵, Lairez D^{1,6}, Wegrowe JE¹ and Clochard MC^{1*}

¹Laboratoire des Solides Irradiés, CNRS-CEA-University Paris-Saclay, Ecole polytechnique, Palaiseau Cedex, France

²Center of Research on Ions Materials and Photonics (CIMAP), Boulevard Marechal Juin, France

³ENSTA ParisTech, Boulevard des Marechaux, France

⁴Le Mans University, Avenue Olivier Messiaen, France

⁵Institut Européen des Membranes, University of Montpellier, Montpellier, France

⁶Laboratoire Leon Brillouin, CNRS-CEA-Université Paris-Saclay, CEA-Saclay, Gif-sur-Yvette Cedex, France

Abstract

Poly(vinylidene fluoride) (PVDF) composites have recently emerged as excellent candidates to fabricate flexible and small piezoelectric generators for portable devices. Among various techniques used to nanostructure polarized PVDF, the track-etching represents a new route for manufacturing nanostructured composite thin films. The moderate influence of irradiation on the piezoelectric response of polarized PVDF makes possible the use of this technique. In this way, a nanostructured composite based on polarized thin PVDF films comprising embedded nickel nanowires (Ni NWs) was fabricated. The nanostructured PVDF/Ni NWs composites were tested under bending conditions using a homemade pressure cell. Due to the presence of NWs, an increase of five-fold the initial dielectric permittivity, in the low-frequency range, was observed. It suggested the presence of an interfacial polarization at the PVDF/Ni interface. With respect to the etched PVDF, the nanostructured PVDF/Ni NWs composites exhibited a non-negligible enhancement by 2.5 times the piezoelectric efficiency. This result was attributed to the increased Au/Ni NWs electrode surface.

Keywords: Track-etching; Swift heavy ion irradiation; Piezoelectric polymer; Nanowires; Composite; Nanostructuring

Introduction

Electric power generation exploiting the piezoelectricity of poly(vinylidene fluoride) (PVDF) is drawing growing interest recently owing to its prospective features of high robustness, high flexibility, and easy formability [1]. Various attractive methods of harvesting energy generated from human motion such as walking [2] or the use of wind and raindrops [3] have been demonstrated and industrial objectives are now evolved. Notably, the electric energy output can be increased by inducing a higher mechanical strain in PVDF [4]. Over the last few years, 1D- and 2D-nanostructured systems, such as semiconducting nanowires (NWs) presenting piezoelectric properties and multilayered piezoelectric PVDF composite have emerged as excellent candidates to fabricate novel ultra-compact and efficient piezoelectric generators [5-7].

The irradiation technology leads to large modifications in the physical and chemical properties of polymers [8]. It has been previously exploited to modify the piezoelectric properties of the most common ferroelectric polymers such as PVDF, and its copolymer with trifluoroethylene, P(VDF-TrFE). In particular, Zhang [9] reported an exceptionally high electrostrictive response after e-beam irradiation of P(VDF-TrFE) copolymer between 0.4 and 1 MGy [9]. The authors claimed that the breaking of polar regions into nanopolar ones was responsible for a slimmer polarization loop. Giegerich [10] have shown a large concentration of radicals and trapped electrons in PVDF after e-beam irradiation (1 per crystallite) and they registered an increase of electrical conductivity from 0.11 pS/m to 1.1 pS/m at 450 kGy. The same group also reported an interesting behavior: the creation of crosslinks upon irradiation allowed to slowdown the reduction of polarization with time or at elevated temperature.

Recently, Melilli et al. [11] have observed a remarkable resistance of the direct piezoelectric response of polarized irradiated PVDF. Two different radiation sources have been used such as electron beam (e-beam) and Swift Heavy Ions (SHI) in a range of doses between 0.1

and 100 kGy. Whatever the radiation source, a competitive mechanism was found. Whilst for low doses (<20 kGy) an increase of crystallinity was observed, at higher doses, crosslinking formation reduces the mobility of chains. The compensation of these two effects allows the conservation of the piezoelectric efficiency and output voltage.

One of the characteristics of SHI irradiation is the formation of tracks (cylindrical damaged zone) in the target polymer film [8]. The polymer tracks may be revealed by chemical etching creating rectilinear nanopores through the entire thickness of the initial polymer film. Combining track-etching technique and subsequent Ni electrodeposition in the resulting nanoporosity, our team has found that track formation at fluencies lower than 10^{10} cm⁻² does not affect the piezoelectric response of polarized PVDF [11,12]. Under these specific irradiation conditions, the track-etching technique opens new perspectives for the fabrication of novel nanostructured composite devices based on polarized PVDF membranes embedding inorganic nanowires or nanotubes as it is the case in the actual trend of developing piezoelectric hybrid nanogenerators [13-16].

The work, reported herein, provides an example of a track-etched polarized PVDF embedding nickel nanowires (Ni NWs). The fabrication process may be divided in three main steps: i) SHI irradiation is used to create tracks in the target PVDF film; ii) a specific chemical etching allows to reveal the tracks; iii) electrodeposition technique is exploited to grow Ni NWs arrays. A homemade device was realized to measure

***Corresponding author:** Mary-Claude Clochard, Laboratoire des Solides Irradiés, CNRS-CEA-University Paris-Saclay, Ecole polytechnique, Palaiseau Cedex, France, Tel: +33(0)169334526; Fax: +33(0)169334554; E-mail: marie-claude.clochard@polytechnique.edu

Received March 22, 2018; Accepted April 12, 2018; Published April 22, 2018

Citation: Melilli G, Gorse D, Galifanova A, Oral O, Balanzat E, et al. (2018) Enhanced Piezoelectric Response in Nanostructured Ni/PVDF Films. J Material Sci Eng 7: 444. doi: [10.4172/2169-0022.1000444](https://doi.org/10.4172/2169-0022.1000444)

Copyright: © 2018 Melilli G, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

the output voltage as a function of the bending deformation of the nano-composite material. Dielectric measurements were performed in order to investigate the interfacial polarization at low-frequency.

Materials and Methods

Irradiation

Bi-oriented and polarized PVDF films were purchased from PIEZOTECH SA (thickness: $h=9\ \mu\text{m}$). SHI irradiations were performed at GANIL, France. Films were irradiated at room temperature with Kr^{36+} at energies between 7.46 and 10.37 $\text{MeV}\cdot\text{amu}^{-1}$ under He atmosphere. Fluence was equal to $5 \times 10^8\ \text{cm}^{-2}$.

Track-etching

Chemical attack is performed at 65°C in a solution of KOH 10 N and KMnO_4 0.25 N. The final diameter depends of the etching time. To obtain a pore diameter of 50 nm, 30 minutes of etching were necessary. Afterwards, etched PVDF films were first washed in potassium disulfite solution (15%) and then 3 times rinsed with deionized water.

Electrodeposition

Ni(0) NWs are grown electrochemically by reduction of Ni(II) inside the porosity of etched PVDF films. The electrolyte solution consists of 65 g NiSO_4 and 15 g H_3BO_3 in 500 ml of water. The electrodeposition is performed using the potentiostat, HEKA PG310. The experimental set-up involved three electrodes connected with the potentiostat: a working electrode (WE), a reference electrode (RE) (Ag/AgCl, Calomel electrode), and a counter-electrode (CE). The CE is made of pure gold sheet. The WE consists in a thin layer of gold sputtered onto one side of the nanoporous track-etched PVDF membrane (WE thickness 200 nm). The WE is thick enough to block the nanopore entry on one side. The WE is contacted with a metallic support (dimension: $6.5 \times 3\ \text{cm} \times \text{cm}$) by conductive silver paint. Then, the support is sealed by Kapton tape to avoid its contact with the electrolyte. The other side of the nanoporous PVDF membrane, free of gold, is facing with the electrolyte solution. Electrodeposition potential is set to -1 V. The reduction occurs on the WE through the pores. The average length of the Ni NWs is proportional to the electrodeposition time. In this study, three different electrodeposition times were chosen: 50, 100 and 150 seconds. The volume fractions of Ni NWs, corresponding to the electrodeposition of 50, 100 and 150 seconds, are approximately equal to 1.6, 3.3 and 4.9% respectively. The determination of volume fractions is reported in "supplementary materials" section.

Atomic layer deposition (ALD)

All ALDs were carried out in a home-built reactor, described elsewhere [17,18]. ALD of Al_2O_3 was based on trimethylaluminum (TMA, $\text{Al}(\text{CH}_3)_3$) as precursor and water as co-reactant at a deposition temperature of 60°C . Briefly, the process consisted of 0.2 s pulse TMA, 30 s exposure, 40 s purge with Argon, 2 s water pulse, 30 s exposure and 40 s purge with Argon to finish the cycle. The selected pulse, exposure and purge times were chosen both to ensure completion of the ALD surface reactions and to prevent mixing of the reactive species. The growth rate was typically $2\ \text{\AA}/\text{cycle}$. For the deposition of 10 nm Al_2O_3 , 50 ALD cycles were used.

Piezoelectric measurement

As previously described [11], an experimental set-up was designed to measure the direct piezoelectric response of all PVDF samples, from untreated polarized PVDF films to the final nanostructured PVDF/Ni

NWs composites. All PVDF samples were sandwiched between two gold layers. The thickness of the bottom gold layer was 200 nm and the top gold layer 100 nm. These two gold layers serve as electrodes and are used to measure the produced piezo-potential of polarized PVDF part when a mechanical stress is applied. Golden PVDF samples were then clamped between the two parts of the device in contact with the pressure chamber (Figure 1a).

Metallic spheres, incorporated inside the cell housing, contact each gold electrode. The sensing area is $0.785\ \text{cm}^2$. The air arrival pressure was set by a 3-ways solenoid-valve SMC VDW250. The current was supplied by ISO-TECH DC power supply IPS 303DD. The pressure signal is a periodic square-wave, whose frequency and width are fixed by a KEITHLEY 3390 waveform generator. The pressure value is fixed directly by the compressed air cylinder (between 0.08 and 0.7 Bar; note that the pressure is expressed in terms of relative pressure). The pressure variation inside the cell was measured by a GEMS pressure sensor (output 0-5 V; range 0-2.5 bar). The pressure variation and the output voltage generated by the film deformation is recorded and displayed on a PicoScope 4000 series oscilloscope (input impedance=1 M Ω). The waveform generator and the oscilloscope were managed by computer using Matlab. A single cycle of the typical square-wave applied pressure and the output voltage response are shown in Figure 1b. All measured piezoelectric efficiencies were normalized by the etched PVDF films piezoelectric response.

Sample characterization

Field Emission Scanning Electron Microscopy (FESEM) (HITACHI S-4800 model) was used to measure the pores diameter and the average length of Ni NWs. The cross-section of the samples was realized by cryofracture. The PVDF nano-composite was immersed in liquid nitrogen for 5 minutes afterwards it was broken into two pieces. A following plasma cleaning cycle was performed to increase the contrast Ni NWs/PVDF matrix along the cross-section area.

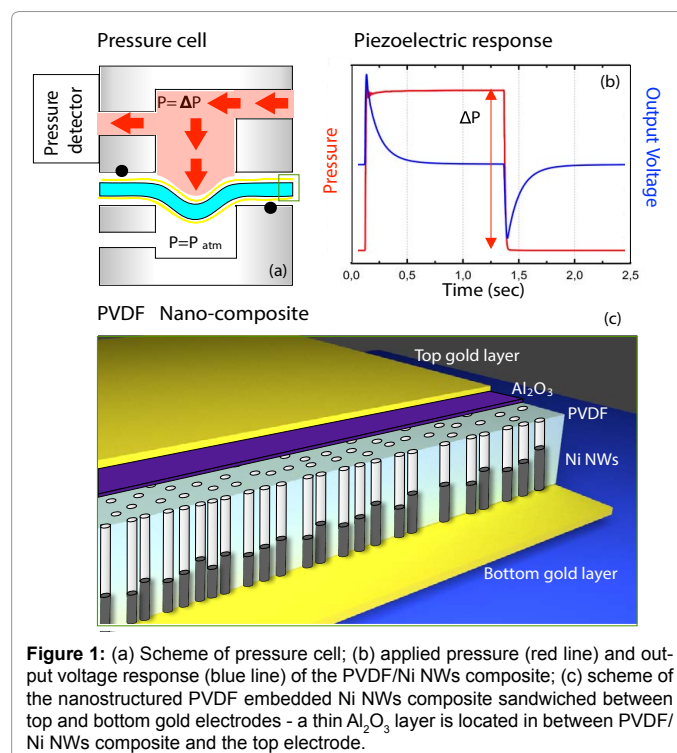


Figure 1: (a) Scheme of pressure cell; (b) applied pressure (red line) and output voltage response (blue line) of the PVDF/Ni NWs composite; (c) scheme of the nanostructured PVDF embedded Ni NWs composite sandwiched between top and bottom gold electrodes - a thin Al_2O_3 layer is located in between PVDF/Ni NWs composite and the top electrode.

Dielectric permittivity measurements

Dielectric characterizations were monitored by a Novocontrol broad band dielectric spectrometer. The samples were prepared with two concentric gold electrodes: one on the bottom (diameter=2 cm) and one on the top (diameter=1 cm) and then tested in frequency between 0.01 Hz and 10 MHz at room temperature.

Results and Discussion

An important step in the fabrication process is the chemical etching. During this step, the ion tracks created in the PVDF film during SHI bombardment are revealed to form an array of cylindrical nanopores. The evaluation of diameters was carried out by FESEM (Figure 2a). The density of pores corresponds to the ion fluence, whereas the final diameter depends of the etching time [19]. A cross-section of the etched PVDF is shown in Figure 2b. A complete opening of the nanopores is essential for a successful electrodeposition.

To fill these pores by Ni(0), an electrodeposition step was performed to reduce electrochemically Ni(II) from NiSO₄ aqueous solution inside the porosity of etched PVDF films. Due to the high hydrophobicity of PVDF, the electrodeposition of nickel becomes critical for a pore diameter smaller than 30 nm. Based on a reported correlation between the static permittivity and the nanometric size in PVDF-based nanocomposites [20], we have chosen to work with nanopore diameters of around 50 nm.

Three electrodeposition times were tested to partially fill the nanopores with Ni(0): 50, 100 and 150 seconds corresponding to 1.6, 3.3, and 4.9% volume fraction of nickel respectively. To prevent any risk of short-circuit between the top and bottom gold electrode in the final device, a layer of Al₂O₃ was deposited by ALD on top of the nanoporous PVDF surface (Figure 1c). The thickness of Al₂O₃ was set to 10 nm. Figure 3 shows the cross-section (treated by O₂ plasma) of the PVDF film with electrodeposited Ni NWs connected to the bottom Au electrode and the multi-layer Al₂O₃/Au forming the top electrode.

The presence of the Ni NWs on the left side of the Figure 3 allows to collocate the bottom gold layer at the extremity of the NWs. The electrodeposition time of 150 seconds permits to fill the nanopores as the half of the PVDF membrane thickness (9 μm) on average.

The final nanostructured PVDF/Ni NWs composite consists of a tracketched PVDF embedded Ni NWs covered by a thin Al₂O₃ layer and sandwiched between two gold layers. These gold layers serve as electrodes to measure the generated piezo-potential under applied mechanical stress. To measure the direct piezoelectric response of the nanostructured PVDF/Ni NWs composites, a homemade experimental set-up was built to periodically bend the samples via an air pressure system driven by a 3-ways solenoid-valve [11]. The piezoelectric

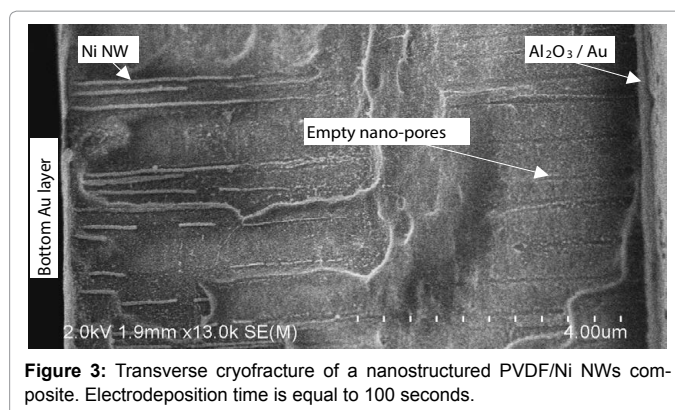


Figure 3: Transverse cryofracture of a nanostructured PVDF/Ni NWs composite. Electrodeposition time is equal to 100 seconds.

efficiency was defined as the ratio between the electrical energy (W_e) harvested by the system and the total mechanical energy (W_m). More details are reported in the supplementary materials section.

As shown in Figure 4, the etching of PVDF membranes results in a dramatic decrease of the piezoelectric efficiency.

Two parameters contribute to the decreasing of the piezoelectric efficiency. Firstly, the temperature partially affects the samples polarization as the samples were maintained at 65°C during the etching process for 30 minutes. A blank experiment was performed using only water to look at the temperature effect. In this case, it was shown that the temperature reduces the electrical efficiency by 20% (Figure 4). Secondly, the etching process removes parts of the piezoelectric material and simultaneously creates new interfaces which contribute to destabilize even further the dipole orientation. The resulting structural modification of the PVDF, due to the presence of the nanopores, interrupts the periodic arrangement of the dipoles in β-crystalline phase.

As shown in Figure 5, the presence of Ni NWs partially restores the drastic decrease of the efficiency due to the chemical etching. Respect to the etched PVDF sample, the presence of NWs increases the efficiency for all the considered volume fraction of Ni. Moreover, the maximum of efficiency is reached for a volume fraction of Ni NWs around 3.3%. A further increase of the volume fraction of Ni NWs leads to decrease the efficiency.

In order to investigate deeper the role of the Ni NWs and their contribution to the piezoelectric response, dielectric measurements were performed. In composite polymeric materials, relaxation phenomena in the low-frequency region are attributed to the heterogeneity of the systems. Etched PVDF and nanostructured PVDF/Ni NWs composite exhibit a dependence of the permittivity in the range between 0.1 and 10 Hz as shown in Figure 6.

The permittivity at 0.01 Hz frequency is reported as function of the volume Ni NWs fraction in Figure 5. It emphasizes the strong correlation between the permittivity and the registered piezoelectric response of the resulted nanostructured composites. Similar results have already been reported in several polymeric composites [21-23]. In particular, the low-frequency dependence of the permittivity is related with the interfacial polarization. The “electric modulus” formalism is proposed to investigate the relaxation properties related with the interfacial polarization in polymer composites. The electric modulus, M^* , is defined by the following equation [24]:

$$M^* = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + j \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} = M' + jM'' \quad (1)$$

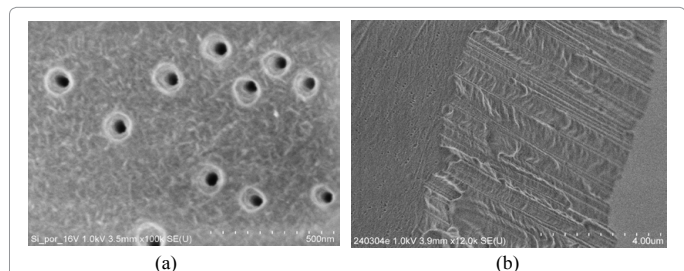


Figure 2: FESEM images of etched PVDF membrane: (a) PVDF surface with nanopores diameter around 50 nm (fluence=5.10⁸ cm⁻²); (b) transversal cryofracture showing rectilinear nanopores perpendicular to the PVDF surface.

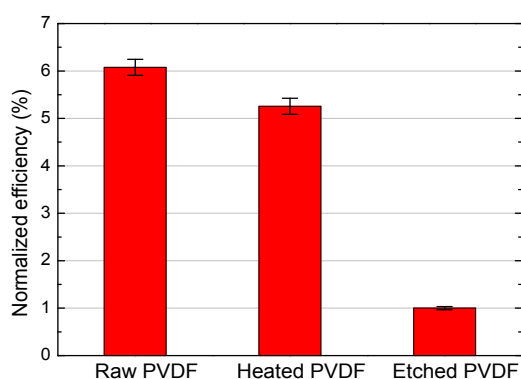


Figure 4: Normalized piezoelectric efficiency of: raw PVDF films, heated PVDF films and track-etched PVDF films.

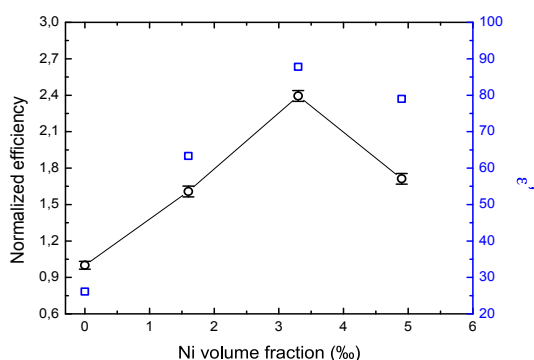


Figure 5: left Y axis: normalized piezoelectric efficiency against volume fraction of Ni NWs - right Y axis: measured permittivity at 0.01 Hz against volume fraction of Ni NWs.

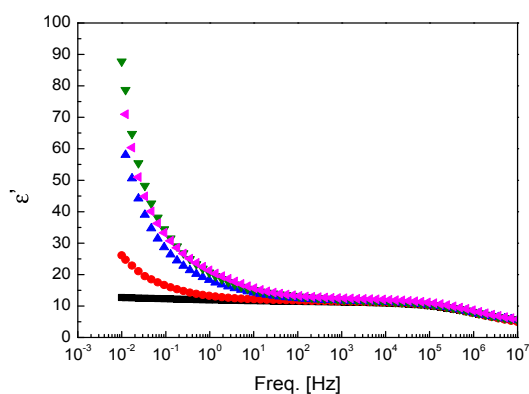


Figure 6: Dielectric permittivity ϵ' versus frequency of: (■) raw poled PVDF film, (●) etched PVDF film, Ni NWs/PVDF composite with (▲) 1.6%, (▼) 3.3% and (▼) 4.9% Ni volume fraction.

A plot of the frequency dependence of M'' allows to study the relaxation phenomena. The relaxation peaks for the etched PVDF and nanostructured PVDF/Ni NWs composite are displayed at low frequency and room temperature in Figure 7. The untreated polarized PVDF does not show any relaxation. The first relaxation peak, observed at frequency ≈ 0.1 Hz, is associated with the etched PVDF. Exactly as for inclusions or fillers, the difference of permittivity between air

(embedded in nanopores) and the PVDF generates an interfacial polarization.

In the case of nanostructured PVDF/Ni NWs composite, since the nanopores are not completely filled by the Ni, we can suppose a combined relaxation effect. Broader and bimodal curves were observed. Moreover, the second peak, attributed to the presence the Ni NWs (≈ 10 Hz) is more evident for 4.9% volume fraction of Ni.

Beyond the volume fraction of 3.3%, a reduction of the dielectric permittivity at low frequency of the nanocomposite PVDF/Ni NWs (Figure 7) was observed. It has a direct consequence in the piezoelectric efficiency for samples with a 4.9% Ni volume fraction (Figure 5). It shows that the piezo-potential delivered by nanostructured PVDF/Ni NWs composites is strongly dependent on the static dielectric permittivity.

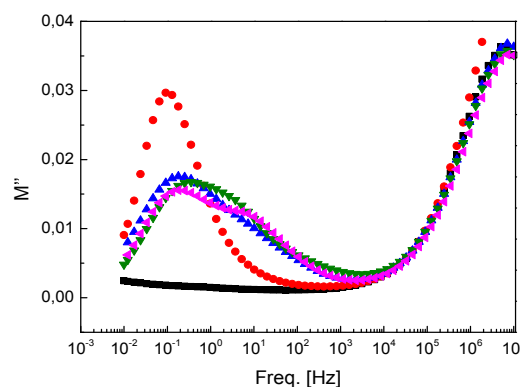


Figure 7: Electric modulus M'' versus frequency of: (■) raw polarized PVDF film, (●) etched PVDF film, Ni NWs/PVDF composite with (▲) 1.6%, (▼) 3.3% and (▼) 4.9% Ni volume fraction.

The quantity of charge stored on electrode surface under applied stress cycles depends on the capacitance of the nanostructured PVDF/Ni NWs composite and hence on the permittivity. Although both etched PVDF and nanostructured PVDF/Ni NWs composite present an interfacial polarization, only conductive Ni NWs contribute to extend the electrode surface. Since the nucleation of Ni NWs during electro deposition starts from the bottom gold layer, the NWs form a sort of ramification of the bottom electrode inside the piezoelectric polymer. Therefore, a larger electrode surface allows to collect additional electrical charges with a consequent increase of piezoelectric efficiency.

Conclusion

A 1D-nanostructured system based on piezoelectric PVDF/Ni NWs composite was investigated as a serious candidate to fabricate novel ultra-compact and efficient flexible piezoelectric generators. Motivated by the moderate influence of irradiation on the piezoelectric response of polarized PVDF [11], we have proposed a new way to nanostructure PVDF thin films using the track-etching technique. A nanocomposite made of polarized poly(vinylidene fluoride) (PVDF) embedded Ni NWs was fabricated and investigated in view of harvesting energy application. Different steps were involved in the fabrication process. Swift heavy ion irradiation (SHI) first generated, in PVDF film, cylindrical local damaged zones, so-called latent tracks. By subsequent chemical etching, the latent tracks were revealed. Finally, the resulting nanoporous PVDF membrane was used as a template to grow Ni NWs by electrodeposition.

A homemade pressure cell was designed to test the piezoelectric efficiency of the PVDF/Ni NWs composites. The presence of Ni NWs array has resulted in a non-negligible increase of the piezoelectric efficiency respect to the etched PVDF membrane. Dielectric measurements were performed to investigate deeper the role of the Ni NWs and their contribution to the piezoelectric response. The increase of permittivity at low frequency range suggested the existence of an interfacial polarization between PVDF/nanopores and PVDF/Ni NWs. Due to the high aspect ratio of the Ni NWs, the electrode surface was extended via Ni NWs inside the piezoelectric PVDF bulk. The larger electrode surface may thus explain the increase of registered piezoelectric efficiency. For even further improvements, one possible recommendation may be to change the nature of NWs. In particular, semi-conductor NWs having piezoelectric properties exhibit today a serious potential to improve the scavenging of mechanical energy and to convert it into electrical one. Alternative solution to Ni NWs may be found using notably ZnO NWs respectively in the piezoelectric and thermoelectric context. It is worth mentioning that the latter perspective is very challenging as the ZnO should grow with the right crystallization orientation to exhibit interesting piezoelectric properties.

Acknowledgements

This work was conducted in the frame of the TREND-X research program of Ecole Polytechnique, supported by Fondation de l'Ecole Polytechnique. The authors want also to point out that SHI irradiation experiments were performed at Grand Accelérateur National d'Ions Lourds (GANIL) Caen, France, and supported by the french Network EMIR. The selection committee of GANIL would find herein gratitude of involved researchers.

References

- Jean-Mistral C, Basrouf S, Chaillout JJ (2010) Comparison of electroactive polymers for energy scavenging applications. *Smart Mater Struct* 19: 085012.
- Liu Y, Tian G, Wang Y, Lin J, Zhang Q, et al. (2009) Active piezoelectric energy harvesting: general principle and experimental demonstration. *J Intell Mater Syst Struct* 20: 575-585.
- Vatanserver D, Hadimani RL, Shah T, Siores E (2011) An investigation of energy harvesting from renewable sources with PVDF and PZT. *Smart Mater Struct* 20: 6.
- Nakajima T, Okaya K, Ohta K, Furukawa T, Okamura S (2011) Performance of piezoelectric power generation of multilayered poly (vinylidene fluoride) under high mechanical strain. *Jpn J Appl Phys* 50.
- Lu MP, Song J, Lu MY, Chen MT, Gao Y, et al. (2009) Piezoelectric nanogenerator using p-type ZnO nanowire arrays. *Nano Lett* 9: 1223-1227.
- Lee HY, Choi B (2013) A multilayer PVDF composite cantilever in the Helmholtz resonator for energy harvesting from sound pressure. *Smart Mater Struct* 22.
- Cha S, Kim SM, Kim H, Ku J, Sohn JI, et al. (2011) Porous PVDF as effective sonic wave driven nanogenerators. *Nano Lett* 11: 5142-5147.
- Ferry M, Ngono-Ravache Y, Aymes-Chodur C, Clochard MC, Coqueret X, et al. (2016) Ionizing radiation effects in polymers. *Mater Sci Eng*.
- Zhang QM, Bharti V, Zhao X (1998) Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly (vinylidene fluoride-trifluoroethylene) copolymer. *Science* 280: 2101-2104.
- Giegerich U, Wust J, Jungnickel BJ (2000) *IEEE Transactions on Di-electrics and Electrical Insulation* 7: 353-359
- Melilli G, Lairez D, Gorse D, Garcia-Caurel E, Peinado A, et al. (2018) Conservation of the piezoelectric response of PVDF films under irradiation. *Radiat Phys Chem* 142: 54-59.
- Pham DC, Biziere N, Melilli G, Pajon R, Lacour D, et al. (2014) Strain-induced inverse magnetostriction measured on a single contacted Ni nanowire in a polymer matrix. *Mater Res Express* 1: 045017.
- Yaman M, Khudiyev T, Ozgur E, Kanik M, Aktas O, et al. (2011) Arrays of indefinitely long uniform nanowires and nanotubes. *Nat Mater* 10: 494-501.
- Kumar B, Kim SW (2012) Energy harvesting based on semiconducting piezoelectric ZnO nanostructures. *Nano Energy* 1: 342-355.
- Jung WS, Do YH, Kang MG, Kang CY (2013) Energy harvester using PZT nanotubes fabricated by template-assisted method. *Current Applied Physics* 13.
- Siddiqui S, Kim DI, Nguyen MT, Muhammad S, Yoon WS, et al. (2015) High-performance flexible lead-free nanocomposite piezoelectric nanogenerator for biomechanical energy harvesting and storage. *Nano Energy* 15: 177-185.
- Viter R, Iatsunskiy I, Fedorenko V, Tumenas S, Balevicius Z, et al. (2016) Enhancement of electronic and optical properties of ZnO/Al₂O₃ nanolaminate coated electrospun nanofibers. *The Journal of Physical Chemistry C* 120: 5124-5132.
- Whitby JA, Ostlund F, Horvath P, Gabureac M, Riesterer JL, et al. (2012) High spatial resolution time-of-flight secondary ion mass spectrometry for the masses: a novel orthogonal ToF FIB-SIMS instrument with in situ AFM. *Adv Mater. Sci Eng* 2012.
- Cuscito O, Clochard MC, Esnouf S, Betz N, Lairez D (2007) Nanoporous β -PVDF membranes with selectively functionalized pores. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 265: 309-313.
- Dang ZM, Yuan JK, Zha JW, Zhou T, Li ST, et al. (2012) Fundamentals, processes and applications of high-permittivity polymer-matrix composites. *Prog Mater Sci* 57: 660-723.
- Fang J, Wang X, Lin T (2011) Electrical power generator from randomly oriented electrospun poly (vinylidene fluoride) nanofibre membranes. *J Mater Chem* 21: 11088-11091.
- Psarras GC, Manolakaki E, Tsangaris GM (2002) Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles. *Composites Part A* 33: 375-384.
- da Silva AB, Arjmand M, Sundararaj U, Bretas RES (2014) Novel composites of copper nanowire/PVDF with superior dielectric properties. *Polymer* 55: 226-234.
- Tsangaris GM, Psarras GC, Kouloumbi N (1998) Electric modulus and interfacial polarization in composite polymeric systems. *J. Mater. Sci.* 33: 2027-2037.