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Chapter 2

Flexible and Wearable Piezoelectric Nanogenerators

Debarun Sengupta and Ajay Giri Prakash Kottapalli

In this age of advanced smartphones and wearable devices, the need for unlimited power has become a basic necessity. Most of the gadgets rely on some sort of power source in the form of batteries or power adapters. For example, smartwatches have become very common these days and have a huge potential for implementation of energy harvesters. In the near future, it will be highly desirable to have self-powered smart wearable devices which meet their energy needs by scavenging mechanical energy produced by physical activities. In order to solve the problem of fast battery depletion in modern smart devices, a significant amount of research has been carried out in the field of energy harvesters especially using thin film technologies and polymer nanofibers. Nanogenerators using polymers with piezoelectric properties like PVDF have attracted a special attention due to their low production cost and high conversion efficiency. Polymer-based nanofiber energy harvesters are not only relevant for wearable devices and smartphones but also for biomedical energy scavenging applications primarily due to their biocompatibility. This chapter particularly deals

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with the current scenario of different types of flexible piezoelectric energy harvesters. A comprehensive review of the recent and ongoing research work in the field of nanofiber-based energy harvesters is also presented in this chapter.

2.1 Introduction

In 1880, two scientists, Pierre and Jacques Curie, observed the piezoelectric effect for the first time. They found that when certain crystals (quartz, Rochelle salt, and tourmaline) were subjected to deformation in a particular direction, charges appeared on their opposite faces which were proportional to the amount of deformation. The main problem with naturally occurring piezoelectric materials were their low piezoelectric coefficients. In the 1950s, the discovery of lead zirconate titanate (PZT) and barium titanate (BaTiO_3) exhibiting very high piezoelectric properties brought the much-needed breakthrough [1, 2]. Till now, PZT has been the most widely used piezoelectric material.

2.1.1 Mechanism of Piezoelectric Effect

Materials demonstrating piezoelectric effect have a constituent crystalline structure with no symmetry center regarding the negative or positive ions of the crystal lattice. Hence, there exists polar axis inside the crystal [3]. This can be demonstrated with the help of an α -quartz crystal in Fig. 2.1.

When the crystal is deformed along the X_1 -axis, a net polarization is generated along the axis. The displacement of positive and negative ions of the crystal lattice relative to each other leads to the appearance of charges on the faces perpendicular to the X_1 -axis which is manifested in the form of the resultant polarization (Fig. 2.2).

Fig. 2.1 Schematic diagram showing the structure of α -quartz. (Figure reproduced from [1] with permission of ©Springer)

Fig. 2.2 (a) Direct longitudinal piezoelectric effect. (b) Direct transversal piezoelectric effect. (Figure reproduced from [1] with permission of ©Springer)

2.1.2 Piezoelectric Materials

As discussed earlier, the piezoelectric property is found in materials lacking inversion symmetry. Most commonly used piezoelectric materials used today can be subdivided into the following categories:

- *Lead-based piezoelectric materials:* Among all the piezoelectric materials, lead-based piezoelectric materials are most versatile and widely used. Some common lead-based piezoelectric materials are lead titanate (PbTiO_3 – though not used commercially, lead titanate can be modified or used to form solid solution yielding excellent piezoelectric properties) and lead zirconate titanate ($\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ or PZT is a solid solution of PbTiO_3 and PbZrO_3 where these two compounds are soluble in all proportions) [2]. PZT is the most widely used piezoelectric material.
- *Lead-free piezoelectric materials:* Though PZT-based piezoelectric materials are most common and widely used due to their excellent piezoelectric properties, awareness of negative effects of lead on human health and overall environment has led to the exploration of alternative environment-friendly lead-free piezoelectric materials. The lead-free system can be subdivided into two categories, namely, perovskites like BaTiO_3 (BT), BNT, KNbO_3 , NaTaO_3 , etc. and non-perovskites like tungsten-bronze-type ferroelectrics, bismuth layer-structured ferroelectrics (BLSF), etc. [3].
- *Piezoelectric polymers:* This category of piezoelectric materials has gained increasing research attention recently mainly because of their mechanical property like flexibility and biocompatibility. Piezoelectric polymers can be divided into three subcategories [4]: (a) bulk piezoelectric polymers like polyvinylidene fluoride

(PVDF), polyamides, parylene-C, liquid crystal polymers, polyimide, and polyvinylidene chloride (PVDC); (b) polymer piezoelectric composites or polymer materials having inorganic piezoelectric materials embedded; and (c) voided charge polymers or polymers having internal gas voids. When the surfaces surrounding the voids get charged, these materials behave like piezoelectric materials.

In the field of MEMS/NEMS sensors, principles of piezoelectric [5–12] and piezoresistive [13–19] sensing have mostly been exploited to form sensing elements of the sensors. Piezoelectric polymers have been of great interest recently. In the past few years, piezoelectric polymers have found extensive applications in the field of biomimetic devices [20–22] and MEMS/NEMS applications [23–27]. As the core focus of this chapter is flexible self-powered sensors, the next section will deal with the piezoelectric polymers in more details.

2.2 Piezoelectric Polymers

As discussed in the previous section, the main reason behind the popularity of polymer-based piezoelectric materials is their flexibility and biocompatibility. Polymer-based piezoelectric materials have generated enough interest in the past two decades to be used as an alternative to conventional piezoceramics. Their low piezoelectric coefficients are compensated by biocompatibility and excellent mechanical flexibility. It is also important to note that a standard piezoelectric polymer like PVDF has much higher piezoelectric stress constant (g_{31}) in comparison to piezoceramic like PZT. This implies better sensing capabilities [6]. Table 2.1 shows the comparison between PZT and PVDF representing piezoceramic and polymer-based piezoelectric materials, respectively.

Polymer-based piezoelectric materials can be divided into three broad categories: (a) bulk piezopolymers, (b) voided charged polymers, and (c) polymer piezocomposites [4]. The following schematic diagram (Fig. 2.3) shows the subcategories of piezoelectric polymers.

The individual categories are discussed briefly in the next three subsections. Though all the individual categories are discussed, the core focus of this chapter is the bulk piezopolymers as they are mostly used in flexible sensors and energy harvesters which is the main focus of this chapter.

Table 2.1 Comparing standard piezoceramic (PZT) with piezoelectric polymer (PVDF) [28]

	d_{31} , pm/V	g_{31} , (mV.m)/N	k_{31}	Salient features
Polyvinylidene fluoride (PVDF)	28	240	0.12	Excellent flexibility, biocompatibility, and lightweight
Lead zirconate titanate (PZT)	175	11	0.34	Toxic, brittle, heavy

Fig. 2.3 Schematic diagram showing various categories under which the polymer-based piezoelectric materials can be categorized. (Figure reproduced from [4] with permission of ©IOPSCIENCE)

2.2.1 Bulk Piezopolymers

The piezoelectric effect is seen in bulk piezoelectric polymers due to their orientation and molecular structure. Bulk polymers can be further divided into two sub-categories: semicrystalline and amorphous polymers [28]. The following four critical requirements are to be satisfied by any polymer to exhibit piezoelectric properties [28]:

1. Permanent molecular dipoles should exist in the material.
2. It should be possible to align the molecular dipoles.
3. Once achieved, the alignment should be sustained.
4. When subjected to large stress, the material should be able to undergo large strain.

The polymers having a semicrystalline structure like polyvinylidene fluoride (PVDF) [7], parylene-C [8], liquid crystal polymers, and polyamides [6] are known for exhibiting piezoelectric properties. Their principle of operation is similar to that of conventional piezoelectric inorganic materials. The bulk of such materials contain randomly oriented microscopic crystals. By the process of poling, these

crystallites are reoriented along a preferred orientation thus achieving a piezoelectric response out of the bulk [5].

Some noncrystalline polymers like polyvinylidene chloride (PVDC) [6] and polyimide [9] having molecular dipoles in their structure are also known to exhibit piezoelectric property. For these polymers, the poling is performed at a temperature which is few degrees more than the glass transition temperature which aligns the molecular dipoles along the applied electric field [5].

Among all the bulk piezopolymers, PVDF is the most commonly used polymer primarily due to its large piezoelectric coefficient of 20–28 pC N⁻¹ in comparison to other piezopolymers [5, 6]. Table 2.2 summarizes the properties of the most common bulk piezopolymers, namely, PVDF, PVDF-TrFE, parylene-C, and polyimide. Figure 2.4 shows the molecular structure of these bulk piezopolymers.

Table 2.2 Summarizing the properties of bulk piezopolymers [4]

		PVDF [28, 29]	PVDF-TrFE [11, 28, 29]	Parylene-C [30, 31]	PI (β-CN) APB/ ODPA [28, 32]
Density	(kg m ⁻³)	1800	1900	1290	1420
Young's modulus Y	(GPa)	2.5–3.2	1.1–3	2.8	2–3
Dielectric constant ϵ_r		12	12	3.15	4
Dielectric loss tan δ_e		0.018	0.018		0.001
Mechanical loss tan δ_m		0.05	0.05	0.06	0.06
d_{31}	(pC N ⁻¹)	6–20	6–12		
d_{33}	(pC N ⁻¹)	13–28	24–38	2.0	5.3–16.5
k_{31}		0.12	0.07		
k_{33}		0.27	0.37	0.02	0.048–0.15
Maximum use temp.	°C	90	100		220

Fig. 2.4 Diagram showing the molecular structure of bulk piezoelectric polymers: (a) PVDF, (b) PVDF-TrFE, (c) parylene-C, and (d) PI (β-CN) APB/ODPA. (Figure reproduced from [4] with permission of ©IOPSCIENCE)

2.2.2 *Polymer Piezoelectric Composites*

A piezo-composite is a material in which inorganic piezoelectric materials are embedded inside a polymer material. In this type of materials, the polymer is non-electroactive [4]. Mixing polymers with piezoelectric polymers helps in combining the excellent mechanical flexibility offered by the polymer with the large piezoelectric coefficient and dielectric constant of the ceramic.

Newnham et al. discussed microstructural arrangement of component phases in composites (also known as connectivity) which was later amended by Pilgrim et al. [33, 34]. There are 16 possible connectivity patterns for composite consisting of two phases. They vary from [0-0] (which means neither of the phases is self-connected) to [3] (each phase is self-connected in three dimensions) [35]. Companies like Smart Materials commercially manufacture [1–3] composites where the ceramic rods are arranged or scattered randomly in polymer bulk films [36]. For MEMS applications, the most commonly used configuration is rods or particles embedded in bulk polymer films [4].

2.2.3 *Voided Charged Polymers*

Voided polymer electret was first used in 1962 when G.M. Sessler and J.E. West from Bell Telephone Laboratories invented a condenser microphone with a solid dielectric between its two electrodes [37]. It was considered as “space charged electrets.” It was not until the 1980s that researchers started investigating the pyro- and piezoelectricity of such films [38].

Voided charged polymers have gas voids embedded inside of the polymer film. These materials behave like piezoelectric materials when the polymer surfaces surrounding the gas voids get charged. The poling process of voided charge polymers is similar to that of the conventional electrical poling process followed in case of bulk piezoelectric polymers (Fig. 2.5). The process starts with a polymer film with embedded air voids which is subjected to electrical poling. Upon the application of a certain electric field, the gas molecules inside the voids get ionized. The ionized molecules accelerate in the direction of the applied electric field and get implanted in the wall of the voids [38]. These voids act like artificial dipoles which respond to an externally applied electric field or mechanical force imitating a conventional piezoelectric material.

Some common voided charged polymers found in the literature [4]:

- *Void formation and expansion-based VCPs*: Cellular polypropylene, fluorinated and post-treated cellular polypropylene, COC-based cellular electrets, and cellular polyethylene-naphthalate (PEN)
- *Multilayer VCPs*: PTFE/FEP multilayer VCP, FEP multilayer, cellular PDMS, and micromachined integrated cellular parylene

Fig. 2.5 Schematic diagram showing piezoelectricity in voided charge polymers: (a) polymer with embedded air voids before charging, (b) poling process to form the dipoles, (c) equivalent model to explain the piezoelectric response of the voided charged polymer. (Figure reproduced from [4] with permission of ©IOPSCIENCE)

2.3 Piezoelectric Energy Harvesters

Due to a surge in the demand for wearable and portable devices with long-lasting battery lives, the field of energy harvesting has seen a massive growth over the past two decades. Though there has been a lot of progress in the field of conventional power sources used in portable devices in the form of introduction of lithium ion and lithium polymer batteries with high energy packing density, there still remains a huge scope for improvement in the present scenario. Both academia and industry are now trying to develop efficient energy harvesters to supplement the conventional power sources in order to increase the battery life of wearable and portable devices. Also, there are environments and applications where periodic charging and replacement of batteries might not be possible. The pacemaker is one such device where changing the battery is difficult and poses a serious risk to the host. With the advancement of technology, wireless implants are also becoming popular where the power sources have to be long lasting which raises a serious question on their practicability.

Considering all these scenarios, it is safe to assume that energy harvesters will be the future of portable and wearable devices. Simply put, energy harvesters are devices which convert the ambient energy surrounding it into electrical energy which can be used for powering various devices. There are different types of macro-scale energy harvesters known to us like thermal power, hydroelectric power, solar power, biogas, etc. In the context of microsystems and biomedical applications, piezoelectric energy harvesting is the most preferred method for energy scavenging [39].

The main focus of this section is to discuss various types of piezoelectric energy harvesters developed so far. For this purpose, we have segregated the energy

harvesters into two subcategories: piezoelectric thin film/bulk energy harvesters and piezoelectric nanofiber energy harvesters. In the following subsections, each of them is discussed separately.

2.3.1 Piezoelectric Thin Film/Bulk Energy Harvesters

Piezoelectric thin film/bulk energy harvesters for wearable/implantable systems have been widely researched in the past two decades. Gonzalez et al. carried out an extensive study on the energy harvesting potential from the human body [40]. They divided human activities into two subcategories, namely, continuous and discontinuous activities. Activities like blood flow and chest expansion during breathing were grouped under the continuous category, whereas upper limb movements and walking were grouped under the discontinuous category. They calculated that continuous activities like blood flow generate 0.93 watts, and chest expansion can generate up to 0.83 watts of power. However, it is important to note that harnessing all of the 0.93 watt power generated during blood flow will hinder the normal functioning of the heart. In contrast, discontinuous activities like finger movement during typing (generates 19 mW), upper limb motion during regular activities (generates 3 W), and walking (generates 67 W) generate significantly more power. Another study carried out by Niu et al. found that up to 2.2 W, 2.1 W, 39.2 W, 49.5 W, and 69.8 W of power could be generated from the shoulder, elbow, hip, knee, and ankle motion, respectively [41]. After all the evaluations, the authors concluded that placing of piezoelectric energy scavenger inside a shoe sole qualified as the best candidate for harvesting energy from human body motion.

The fundamental characteristic of human motion is low-frequency large amplitude movements which pose some serious challenges in the design of miniature resonant generators [42]. Hence, for human-centric applications, mechanical to electrical transduction is usually achieved by direct straining of the piezoelectric element.

Previously, research has been carried out at MIT media laboratory to study the amount of energy dissipated while walking. It was found that for an average human being weighing 68 Kg with average gait, 67 watts of power was generated at the heel [43]. Here, it is important to note that extracting this amount of power will interfere with a person's gait. Nonetheless, the aforementioned study showed the potential of parasitic energy harvesting in shoes.

Two piezoelectric energy harvesters were developed at MIT media laboratory which were used for demonstrating the feasibility of harnessing useful power from the shoes (Fig. 2.6) of a moving person [44]. The first system harnessed the energy generated during the bending of the sole. The system consists of a "stave" which is bimorph structure where the 2 mm-thick central flexible plastic core is sandwiched between eight-layer stacks of electrode-laminated PVDF with thickness of 28 μm (Fig. 2.7). This "stave" was placed inside the sole of a sports sneaker where the bending of the sole caused strain in the PVDF stacks hence producing charge (d_{31} mode). This setup delivered an average power of 1.3 mW to a 250 k Ω load at a footfall rate of 0.9 Hz.

Fig. 2.6 Diagram showing the placement of the two discussed insole energy scavengers. (Figure reproduced from [45] with permission ©IEEEXplore)

Fig. 2.7 Schematic diagram showing the design of PVDF “stave”. (Figure reproduced from [44] with permission ©IEEEXplore)

The second system which is referred to as dimorph consists of spring steel bonded to a flexible piezoceramic patch. This method harvests the energy dissipated under the heel by flattening curved, prestressed spring metal strips laminated with a semiflexible form of PZT [45]. This dimorph structure consisted of two piezoelectric transducers (Thunder TH-6R) made by Face International Corporation [46]. The structure is designed such that there is a difference of thermal expansion coefficients in the materials which leads to a curved structure (Fig. 2.8). This curved structure leads to a com-

Fig. 2.8 Schematic diagram showing the design of PZT dimorph. (Figure reproduced from [42] with permission ©IOPSCIENCE)

pressive stress in the PZT layer which allows it to bend much more than conventional PZT structures. The transducer is deformed with each taken step when the heel hits the ground and returns to its original shape when the heel is lifted. This setup delivered an average power of 8.4 mW to a 500 k Ω load at a footfall rate of 0.9 Hz. Due to these research efforts, today insole energy harvesting is becoming mainstream.

Sohn et al. carried out a detailed study where they conducted theoretical modeling and finite element method (FEM) simulations to evaluate the practicality of using commercially available piezoelectric films for harnessing energy from fluctuating pressure source such as human blood pressure [47]. They modeled and compared several circular and square PVDF films. It was concluded that the maximum power (0.61 μ W) was generated by a circular PVDF film of radius 5.62 mm with a thickness of 9 μ m when subjected to a uniformly distributed pressure (5333 N m $^{-2}$) equivalent to human blood pressure. The result was experimentally validated using a setup consisting of a 28 μ m-thick circular PVDF film placed inside an aluminum jig having inlet and outlet ports for pumping in and pumping out liquid (Fig. 2.9a, b). A pneumatic compressor was used to supply the uniform pressure of 5333 N m $^{-2}$ emulating human blood pressure. A digital oscilloscope was used for measuring the voltage generated by the PVDF film. When subjected to a sinusoidal (1 Hz) pressure of 5333 N m $^{-2}$, the film produced 0.33 μ W of power.

Platt et al. demonstrated the application of piezoelectric ceramics in energy harvesting from total knee replacement (TKR) units [48]. An extensive study was carried out to model the energy harvester in total knee replacement unit where factors such as efficiency, longevity, energy conversion, load matching, form factors, and energy storage were taken into consideration. The model was experimentally validated with a prototype total knee replacement unit (Fig. 2.10) using a force profile of 2600 N which emulates the axial force generated in human knees while walking. A raw power of 4 mW was generated. The maximum regulated power generated from the setup was 0.85 mW.

Cantilever geometries with piezoelectric materials attached on the top and bottom are most suitable for vibrational energy harvesting due to their low resonant frequencies which can be further reduced by attaching proof masses at the tips [42]. They are designed to operate in the d_{31} mode where the piezoelectric materials are strained when the cantilevers are bent.

Fig. 2.9 (a) Schematic diagram showing the experimental setup, (b) diagram showing the jig. (Figure reproduced from [47] with permission ©Sage journals)

Fig. 2.10 (a) Individual components of the self-powered TKR unit, (b) test setup for the total knee replacement unit. (Figure reproduced from [48] with permission ©IEEEExplore)

Roundy and Wright developed and evaluated a vibration-based piezoelectric energy harvester for wireless network applications [49]. Their basic design consists of a bimorph structure with a proof mass attached at the free end (Fig. 2.11).

Their argument for choosing a bimorph cantilever structure was mainly due to two reasons:

1. The cantilever configuration leads to the highest value of average strain for a particular input force. The average strain directly impacts the power output.
2. For a particular size, the cantilever configuration results in the lowest resonant frequency.

A detailed mathematical analysis was carried out by the authors [49]. First, a prototype generator was fabricated which consisted of a central steel shim sandwiched between two PZT-5A layers. An alloy mass (made of tin and bismuth) was attached to the end of the bimorph cantilever. The prototype was tested by subjecting it to a 2.5 ms^{-2} vibration at a frequency of 120 Hz. The power generated was

Fig. 2.11 Schematic diagram showing the design of the bimorph cantilever energy harvester. (Figure reproduced from [49] with permission ©IOPSCIENCE)

Fig. 2.12 Plot comparing the simulated values with experimental data for power delivered as a function of load resistance. (Figure redrawn from [49])

plotted as a function of load resistance (Fig. 2.12). The agreement between the simulated results and measured data was deemed sufficient by the authors for using the basic design as a stepping stone for further optimizations. Two designs having an overall volume constraint of 1 cm^3 were developed using PZT-5H (with brass as the center shim). For a detailed description of the optimized designs, the readers are referred to [49].

Jeon et al. developed a MEMS-based energy harvester and named it as “piezo-electric micro power generator (PMPG)” [50]. The harvester developed by the team was based on thin film PZT as the piezoelectric layer operating in d_{33} mode. The device consisted of a flat cantilever structure with a proof mass attached to its tip. In order to make the device operate in the desired d_{33} mode, the top Pt/Ti electrode was patterned into an interdigitated layout on top of the spin-coated sol-gel PZT thin

film. For detailed fabrication process, the readers can refer to the work by the authors presented in [50]. The PMPG was excited at its resonant frequency (13.9 kHz) which generated a dc voltage of 3 V across a resistive load (10.1 M Ω). Vibrating at the same resonant frequency, the energy harvester delivered a maximum of 1 μ W continuous power to a 5.2 M Ω load at a dc voltage of 2.4 V developed across the load. The energy density of the device was reported as 0.74 mW h/cm², which is comparable to that of Li-ion batteries. The voltage generated by the device (operating in d_{33} mode) was found to be 20 times higher than the voltage generated by an equivalent cantilever design operating in d_{31} mode [50].

Lee et al. developed a novel fabrication technique involving aerosol deposition method to fabricate two different PZT thin film-based MEMS energy harvesters operating in d_{31} and d_{33} modes [51]. For the details regarding the aerosol deposition technique, the readers could refer to the authors' works in articles [51–53]. The energy harvester operating in d_{31} mode generated a maximum open-circuit voltage of 2.675 V_{p-p} with a maximum power output of 2.765 μ W at 1.792 V_{p-p} when excited at its resonant frequency (255.9 Hz). Whereas, the energy harvester operating in d_{33} mode generated a maximum open-circuit voltage of 4.127 V_{p-p} with a maximum power output of 1.288 μ W at 2.292 V_{p-p} when excited at its resonant frequency (214 Hz). A comparison was also made by exciting both the devices at an acceleration value of 2 g (see Table 2.3).

Aktakka et al. presented the fabrication and testing of a bulk piezoelectric ceramic-based CMOS-compatible energy harvester [54]. The main advantages of this bulk PZT-based technology over other piezoelectric thin film technologies are fabrication flexibility and enhanced device performance due to bulk piezoelectric properties. They were able to obtain 5 μ m to 100 μ m-thick films without any chemical patterning. The fabricated energy harvester generated a power output of 0.15 μ W when excited with 0.1 g acceleration at 263 Hz. The same harvester generated 10.2 μ W power when excited with 2 g acceleration at 252 Hz.

Though electroactive polymers like PVDF are very flexible and easy to process, their low piezoelectric d_{31} and d_{33} coefficients limit their usability in energy harvesting applications. To overcome this problem, inorganic fillers like barium titanate, PZT, lead titanate, etc. can be added to PVDF matrices. In their work, Rahman et al. reported the energy harvesting capabilities of PVDF graphene nanocomposite-based films [55]. Nanocomposites of PVDF and graphene oxide (PVDF-GO) and PVDF and reduced graphene oxide (PVDF-RGO) made by in situ thermal reductions of graphene oxide were analyzed in terms of ferroelectric properties and energy harvesting capabilities. The three different energy harvesters were made by attaching the PVDF, PVDF-GO, and PVDF-RGO to a 400 μ m-thick cantilever beam of length

Table 2.3 Comparison of the two devices excited at 2 g acceleration [51]

Operation mode	Resonant frequency	Optimal load	Power output	Output voltage (open circuit)	Output voltage (with load)
d_{31}	255.9 Hz	150 k Ω	2.099 μ W	2.415 V	1.587 V
d_{33}	214.0 Hz	510 k Ω	1.288 μ W	4.127 V	2.292 V

Fig. 2.13 Plot comparing the peak-to-peak voltages generated by the PVDF, PVDF-GO, and PVDF-RGO films. (Figure reproduced from [55] with permission ©IOPSCIENCE)

25 mm and width 10 mm made of FR-4 material. The peak-to-peak voltages generated by the three devices were compared (Fig. 2.13) by exciting the devices with an acceleration level of 1 g at 41 Hz. The PVDF-RGO-based cantilever showed the best peak-to-peak performance of 1.3 volts. The PVDF-RGO film-based energy harvester generated a power of 36 nW when connected to a 704 k Ω resistive load.

Won et al. developed a piezoelectric poly(vinylidene fluoride trifluoroethylene) (P(VDF-TrFE))-based flexible power generator fabricated using cellulose paper as the substrate [56]. The final structure of the energy harvester consisted of Pt (150 nm)/P(VDF-TrFE) (1 μ m)/Pt (200 nm)/cellulose paper (200 μ m). To demonstrate the practical application of the energy harvester, the flexible energy harvester was placed on the back of a hand and was secured using a latex glove (Fig. 2.14a). The output of the harvester was measured while gripping and releasing the hand periodically at two different frequencies (0.25 Hz and 2 Hz). The harvester generated 0.4 V and 0.6 V at 0.25 Hz and 2 Hz, respectively (Fig. 2.14b, c). The authors also reported having generated a maximum open-circuit voltage of 1.5 V and short-circuit current of 0.38 μ A implying a power density of 2.85 mW/cm³ while bending the device by 0.7 cm at a frequency of 1 Hz.

2.3.2 Piezoelectric Nanofiber Energy Harvesters

Other than the thin film/bulk-based piezoelectric nanogenerators/energy harvesters, there is another class of energy harvesters made out of electrospun piezoelectric nanofibers. Electrospun nanofibers have been of important research interest for the last three decades. A significant amount of progress has been made in fabrication technologies and applications related to electrospinning. The main features of

Fig. 2.14 (a) Images of cyclic gripping and releasing of the hand while placing the flexible energy harvester on the back of the hand under the glove. (b) Voltage generated at 0.25 Hz periodic hand movement. (c) Voltage generated at 2 Hz periodic hand movement. (Reprinted from [56], with the permission of AIP Publishing)

nanofibers which make them attractive for a wide range of applications are their large surface area to volume ratio, superior mechanical properties like tensile strength and stiffness, and excellent flexibility [57]. Due to their superior mechanical performance and ease of fabrication, many research groups all over the world have engaged in electrospinning piezoelectric materials for fabricating piezoelectric nanofibers for self-powered sensors and energy harvesters for the last two decades. The two most attractive features of electrospinning which makes it popular for fabricating piezoelectric nanofibers are mechanical stretching and in situ poling associated with the electrospinning process. Due to the intense stretching of the released polymer jet during electrospinning process in the presence of a high electric field, the nanofibers are poled in situ thus circumventing the electrode poling process as seen in case of piezoelectric thin films/bulks. The process of electrospinning is well researched and has been discussed by a lot of review articles in the past [57–61]. Of all the piezoelectric nanofibers, polyvinylidene fluoride-based nanofibers have been widely used for energy scavenging applications [62]. Nanofibers can be fabricated by either of the two most popular electrospinning processes:

- *Near-field electrospinning (NFES)*: This method is suitable for fabricating and depositing a single continuous nanofiber in a controlled way [63].

- *Far-field electrospinning (FFES)*: This is the more conventional method which is suitable for producing a large mat of dense nanofibers [57].

The main difference between the NFES and FFES lies in the needle tip to collector distance. While NFES allows the needle tip collector gap as low as 1 mm, the corresponding gap for the FFES is usually more than 10 mm [5]. This section discusses some of the piezoelectric nanofiber-based energy harvesters fabricated by the process of electrospinning.

PZT-based energy harvesters exhibit better power output and maximum voltage in comparison to other piezoelectric materials for a given volume of the material. However, like all other ceramic materials, the main problem with PZT thin film/bulk-based structures is their extreme fragility. Thin films which are very sensitive to vibrations of high frequency face even higher risk of failure due to breakage [64]. Earlier, Chen et al. have successfully demonstrated the capability of PZT nanofibers to solve the problems associated with the thin films/microfibers by exhibiting high mechanical flexibility and mechanical strength while demonstrating a high value of piezoelectric voltage constant (g_{33} , 0.079 Vm/N) [65]. In another work, the same research group demonstrated a PZT nanofiber-based energy harvester [64]. Laterally aligned PZT nanofibers were placed on interdigitated electrodes made of fine platinum wire arrays of 50 μm diameter assembled on a silicon substrate (Fig. 2.15). The diameters of the nanofibers were reported to be 60 nm, and the gap between two adjacent electrodes was kept at 500 μm . The nanofibers were poled separately by applying an electric field of 4 V/ μm across the electrodes at an elevated temperature of 140 $^{\circ}\text{C}$ for 24 h. A maximum output voltage of 1.63 V was achieved during the tests. The nanogenerator was able to generate a maximum power of 0.03 μW when connected to a 6 M Ω resistive load.

Fig. 2.15 (a) Schematic diagram of the layout of the energy harvester showing the PZT nanofibers placed on interdigitated electrodes. (b) SEM images of electrospun PZT nanofiber mat. (c) SEM image showing the cross-sectional view of the PZT nanofibers embedded in PDMS matrix. (d) Schematic diagram showing cross-sectional view of the final energy harvester structure with PDMS encapsulation. (e) Schematic diagram explaining the charge generation mechanism of the energy harvester. (Reprinted (adapted) with permission from [64]. Copyright (2010) American Chemical Society)

The two main problems associated with the use of PZT nanofibers for energy scavenging applications are:

- The requirement of high temperature ($\sim 650^\circ\text{C}$) annealing to achieve pure perovskite phase [64].
- For electrospinning, PZT has to be mixed with a suitable solvent which lowers the PZT content in the electrospun nanofibers which in turn leads to the lowering of piezoelectric coefficient thus lowering the overall energy scavenging capability of such nanofibers [62].

In comparison, polyvinylidene fluoride-based piezoelectric nanofibers offer a unique combination of mechanical flexibility, biocompatibility, and lightweight coupled with an easy fabrication process (which does not require high-temperature annealing or poling) making them an ideal candidate for fabricating piezoelectric nanofiber-based energy harvesters for wearable devices and human implant applications.

Chang et al. made use of the direct-write technique by means of near-field electrospinning to place PVDF nanofibers on substrates (Fig. 2.16) in a controlled fashion [66]. As discussed earlier, the nanofibers are mechanically stretched and poled

Fig. 2.16 (a) Schematic diagram illustrating the NFES to place PVDF nanofiber on a substrate. (b) SEM image showing the top view of the nanogenerator consisting of a single PVDF nanofiber placed on two separate electrodes deposited on a plastic substrate. (c) Voltage generated by the nanogenerator under a cyclic (frequency of 2 Hz) strain. (d) Current generated by the nanogenerator under a cyclic (frequency of 2 Hz) strain. (Reprinted (adapted) with permission from [66]. Copyright (2010) American Chemical Society)

in situ during the electrospinning process which leads to the alignment of the dipoles in the nanofiber crystals thus leading to transformation of nonpolar α -phase to the polar β -phase (interested readers may refer to some of the works where detailed studies have been carried out to find out the effect of various parameters on phase transformation in PVDF thin films and nanofibers [5, 67]). Nanofiber diameters of 500 nm to 6.5 μm were reported. The length of the nanofibers depended on the separation (100–600 μm) between the metallic electrodes. A voltage output in the range 5–30 mV and a current output of 0.5–3 nA was reported after testing of 50 nanogenerators. A highest conversion efficiency of 21.8% and an average conversion efficiency of 12.5% were observed for 45 tested nanogenerator samples. The authors also reported having enhanced the output voltage and current of the nanogenerators by connecting them serially and parallelly, respectively.

Hansen et al., for the first time, demonstrated the integration of PVDF-based nanogenerator with biofuel cell for in vivo energy harvesting applications [23]. A modified far-field electrospinning process was adopted for electrospinning the PVDF nanofibers on a kapton film (Fig. 2.17a). The split electrode approach helps in aligning the nanofibers [68]. The nanofibers were secured with silver paste. As the fabrication method was far-field electrospinning process, the nanofibers had to be poled separately with an electric field of 2 MV/cm for 15 min using an in-plane electrode poling process. The nanogenerator was encapsulated with PDMS (Fig. 2.17b). The PVDF nanogenerator was integrated with a biofuel cell (Fig. 2.17c). The nanogenerator generated a maximum voltage of 20 mV and a maximum current output of 0.3 nA with a fixed strain rate of 1.67%/s (Fig. 2.18).

As seen in the previous section on piezoelectric thin film/bulk energy harvesters, copolymers of PVDF have also been used to fabricate nanofiber-based energy harvesters. Mandal et al. reported electrospun poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) nanofiber-based pressure-type nanogenerator [69]. A far-field electrospinning process with rotating mandrel collector was used for the electrospinning of the PVDF-TrFE nanofibers. A maximum voltage of 400 mV was reported to have been generated by the fabricated nanogenerator consisting of 43 μm -thick nanofiber web under periodic pressure tests with 0.2 MPa pressure at 5.3 Hz frequency. Nanofiber webs were also serially connected to either double the total voltage output or cancel out thus reducing the total voltage output of the nanofiber webs depending on their polarity (Fig. 2.19b).

Fig. 2.17 Schematic diagram of (a) the modified FFES using split electrode method. (b) The nanogenerator with PDMS encapsulation. (c) PVDF nanogenerator and biofuel cell integration. (Reprinted (adapted) with permission from [23]. Copyright (2010) American Chemical Society)

Fig. 2.18 Plot showing: (a) The open-circuit voltage. (b) The short-circuit current of the nanogenerator under different strain conditions. (Reprinted (adapted) with permission from [23]. Copyright (2010) American Chemical Society)

Fig. 2.19 Plot showing: (a) The output of the nanofiber web-based generator before and after annealing at 130 °C. (b) The output of serially connected nanogenerators where the output depends on polarity of individual nanofiber webs. (Figure reproduced from [69] with permission ©Wiley-VCH)

Liu et al. reported a hollow cylindrical near-field electrospinning (HCNFES) process to fabricate nonwoven well-aligned PVDF nanofibers having diameters in the range 200 nm to 1.16 μm (for different applied electrospinning voltages) [70]. The so-called hollow cylindrical near-field electrospinning (HCNFES) process consisted of a rotating glass tube collector with copper foil placed inside the internal wall grounded with an electrical brush. Figure 2.20 shows the details of the electrospinning setup. The nonwoven nanofiber fabric was transferred to a polyethylene terephthalate (PET) substrate with copper foil electrodes and secured using silver paste to make a PVDF nanofiber-based energy harvester (Fig. 2.21a). The assembly of substrate and the nanofiber fabric was covered with a thin polymer layer. The assembly was subjected to a 7 Hz periodic stretching and releasing with a strain of 0.05% using the setup shown in Fig. 2.21b. The nanogenerator produced a maximum power of 577.6 pW cm^{-2} , an average peak voltage output of -76 mV (across a 10 M Ω resistive load), and -39 nA peak current.

Fig. 2.20 Schematic diagram describing the HCNFES process. Due to in situ electric poling and intense stretching of polymer jet, the phase transformation (nonpolar α -phase to polar β -phase) of PVDF takes place. (Figure redrawn from [70])

2.3.3 Piezoelectric Nanowire Energy Harvesters

In the past few years, a significant amount of research has been carried out to develop energy harvesters employing piezoelectric nanowires. The features of nanowires which make them attractive for energy scavenging applications are their exceptional sensitivity to small random mechanical disturbance/stimulation, high mechanical robustness, enhanced flexibility, and lightweight [71, 72]. In this section, a brief overview of piezoelectric nanowire-based energy harvesters developed by various research groups across the world is presented.

Among all the one-dimensional nanomaterials, zinc oxide is preferred because of the following reasons [73]:

- ZnO is most suitable for electromechanically coupled sensor applications because of its unique combination of piezoelectric and semiconductor properties.
- Zinc oxide is relatively bio-safe and can be used for biomedical applications (with little toxicity).
- ZnO is known to exhibit most diverse configurations.

Fig. 2.21 (a) The fabricated nanogenerator. (Figure reproduced from [70] with permission ©IOPScience) (b) Experimental setup for testing the nanogenerator. (Figure redrawn from [70])

Wang and Song carried out a pioneering work in the field of nanoscale energy harvesters when they converted mechanical energy to electrical energy using an array of piezoelectric zinc oxide nanowires [73]. An array of relatively short ($0.2\ \mu\text{m}$ to $0.5\ \mu\text{m}$) aligned ZnO nanowires were grown on c plane-oriented $\alpha\text{-Al}_2\text{O}_3$ by vapor-liquid-solid (VLS) process (Fig. 2.22a, b). The outputs of the nanowires were measured using an atomic force microscope (AFM) with a platinum-coated silicon tip having a 70° cone angle (Fig. 2.22c). The output voltage generated by the nanowires across a $500\ \text{M}\Omega$ resistive load was observed when the AFM tip deflected the nanowires while scanning. The measurements were reported to have been carried out in AFM contact mode with a normal force of $5\ \text{nN}$ maintained between the AFM tip and sample surface. Though a practical application was not demonstrated in this work, the authors theoretically estimated the feasibility of such nanowire

Fig. 2.22 (a) SEM images showing aligned zinc oxide nanowire array on α - Al_2O_3 substrate. (b) TEM images showing structure of individual zinc oxide nanowire with/without gold nanoparticle on top. Inset: showing electron diffraction pattern from a ZnO nanowire. (c) AFM experimental setup for testing the voltage output from individual nanowires. (Figure reproduced from [73] with permission ©SCIENCE)

nanogenerator for powering nanodevices. The power density of the nanowire array was estimated as $10 \text{ pW}/\mu\text{m}^2$ assuming that the density of nanowires per unit surface area is $20/\mu\text{m}^2$ and a nanowire typically has a resonant frequency of 10 MHz thus generating a power output of 0.5 pW each. It was thus concluded that the power generated by a $10 \mu\text{m} \times 10 \mu\text{m}$ nanowire array would be sufficient for powering a nanotube/nanowire-based device.

Wang et al. expanded on their previous work [73] to drive all the individual zinc oxide nanowires simultaneously using ultrasonic wave by means of a zigzag metal electrode in order to have a practical nanowire-based energy harvester capable of generating a continuous current [74]. The zinc oxide nanowires grown on GaN substrate were covered with a zigzag silicon electrode coated with platinum which increased the conductivity of the electrode and created a Schottky contact at the interface (Fig. 2.23). The density of the nanowires per unit surface area was reported to be $10/\mu\text{m}^2$. The height and diameter of the individual nanowires were reported as $\sim 1 \mu\text{m}$ and $\sim 40 \text{ nm}$, respectively. The packaged device was driven by an ultrasonic wave of 41 kHz frequency, and the output current and voltage were measured. The voltage and current output of the nanogenerator were monitored by turning on and off the ultrasonic wave. When the ultrasonic wave was turned on, the output exhibited a $\sim 0.15 \text{ nA}$ jump from baseline current. A similar result was observed for the

Fig. 2.23 (a) Schematic diagram of the nanogenerator with Si electrode coated with Pt. (b) Aligned ZnO nanowires on gallium nitride (GaN) substrate. (c) Zigzag Si electrode fabricated by standard etching process. (d) SEM image showing cross-sectional view of the nanogenerator. (Figure reproduced from [74] with permission ©SCIENCE)+

voltage output with ~ -0.7 mV drop. For details regarding the mechanisms behind the negative voltage drop, the readers are referred to the original work [74].

Driving a nanogenerator with AFM tips or ultrasonic waves has limitations in practical applications involving energy scavenging from human bodily movements like heartbeat, footsteps, etc. The same research group which previously developed the ultrasonic wave driven d.c. nanogenerator came up with a novel nanogenerator made up of piezoelectric zinc oxide nanowires grown radially around Kevlar 129 fibers [75].

The basic nanogenerator consists of two entangled Kevlar 129 fibers with single crystalline zinc oxide nanowires (with a typical length ~ 3.5 μm and diameter ~ 50 – 200 nm) grown radially all around using hydrothermal approach (Fig. 2.24). The gap between the individual nanofibers grown on the textile fiber surface is of the order of few hundred nanometers. The continuous zinc oxide layer on the surface of the Kevlar fiber acted as the common electrode connecting the bottom of all ZnO nanowires for electrical contact. One of the two fibers is coated with 300 nm layer of gold, and the other is left in the as-grown state. Figure 2.25a shows the schematic diagram of the double fiber nanogenerator system. The gold-coated fiber was attached to an external rotor by means of a string to stimulate relative brushing motion between the two Kevlar fibers. Here, it is worth observing that the gold-coated zinc oxide nanowires on one of the two Kevlar fibers emulate an array of scanning metal tips which in principle is similar to the zigzag silicon electrode seen in the previous case of ultrasonic wave-driven energy harvester. Figure 2.25c, d shows the schematic illustrations explaining the charge generation principle of the nanogenerator. The total output current from the system is the sum of the individual currents generated by the individual zinc oxide nanowires. The rotor was made to rotate at 80 r.p.m. to stimulate stretching and releasing of the gold-coated fiber (thus

Fig. 2.24 (a) Scanning electron microscopy image showing a zinc nanowire-coated Kevlar 129 fiber. (b) Magnified scanning electron microscopy image showing zinc nanowires on Kevlar fiber. (c) Illustration showing cross-section of zinc nanowire-coated TEOS-enhanced Kevlar fiber. (Figure reproduced from [75] with permission ©Nature Publishing Group)

Fig. 2.25 (a) Schematic diagram explaining the working of a basic two-fiber nanogenerator. (b) Optical image of two entangled Kevlar fiber (one of which is coated with gold). (c), (d) Schematic diagram showing the teeth-to-teeth contact between the gold-coated nanowires and the as-grown nanowires leading to charge generation. (Figure reproduced from [75] with permission ©Nature Publishing Group)

leading to a constant scrubbing between two fibers), and open-circuit voltage and short-circuit current were continuously monitored. Here, the authors reported to have used a “switching polarity” method for the measurements where the current and voltmeter are both forward and reverse connected (w.r.t. polarity) to the nanogenerator to weed out any system artifact.

For forward-connected current meter, a ~ 5 pA current signal was observed for each pull release cycle (blue line in Fig. 2.26a). For reverse connection, a current output of ~ -5 pA was observed (pink line in Fig. 3.26a). The same “switching polarity” method was used for measuring the open-circuit voltage, and a voltage amplitude of ~ 1 – 3 mV was observed (Fig. 2.26b). The authors also reported having investigated approaches for increasing the overall power generation capacity of the

Fig. 2.26 Plots showing: (a) Output short-circuit current of the two Kevlar fiber nanogenerator setup. (b) Output open-circuit voltage of the two Kevlar fiber nanogenerator setup. (Figure reproduced from [75] with permission ©Nature Publishing Group)

nanogenerator. A test consisting of three pairs of nanowire-coated Kevlar fibers emulating a real yarn was carried out with the same conditions as that of the basic experiment consisting of a single pair of Kevlar fibers. The current output was increased to ~ 0.2 nA.

2.4 Conclusions and Future Work

The last two decades have seen an immense rise in the popularity of portable and wearable smart devices. With the growing popularity of portable devices, the need for long-lasting power sources has become an absolute necessity. Reliable batteries coupled with efficient energy harvesters will pave the way for long-lasting portable devices and self-powered sensors. In this chapter, a systematic review has been carried out covering some of the most pioneering and influential works related to the field of bulk, thin film, and nanofiber energy harvesting devices and sensors. A brief history of piezoelectricity and its mechanism was provided followed by materials and technologies. Recent advancements in piezoelectric nanofiber energy harvesters and nanowire energy harvesters were also briefly reviewed.

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