Chapter 4
Piezoelectric Mechanical Energy Harvesters and Related Materials

4.1 Examples of Energy-Harvesting Systems

Energy harvesting (or 'energy scavenging') is a subject that continues to receive both industrial and academic interest since it provides a route to create autonomous and self-powered low-power electronic devices, example applications include wireless sensor networks. An excellent commercial example is the recent commercial system developed which converts the vibration of rolling stock into electrical power for the wireless communication of sensors that predict the failure of rail wheel bearings [1]. The ability to deliver sustainable power to a wireless system network by energy harvesting is attractive since it removes the cost of DC batteries and it also reduces the time and cost that is necessary to replace and maintain the batteries. The labour costs that are necessary to install complex wired systems are also avoided. This is particularly relevant to the installation of sensors that are deployed in areas that are either inhospitable or difficult to reach; example includes safety-monitoring devices [1], structure-embedded micro-sensors and medical implants. There are also environmental benefits associated with limiting the use and subsequent disposal of batteries.

Energy-harvesting devices therefore provide a 'battery-less' solution by scavenging energy from ambient sources of energy such as mechanical vibrations, heat, light, water etc., and converting it into a useable form, often electrical power [2]. While energy-harvesting technologies have been continuously improving in the last years, there are also parallel improvements in microprocessor technology leading to an increase in power efficiency and reduced power consumption. Local electrical energy storage solutions are also improving: we mention, for example, the development of super-capacitors [3] and even 'structural power' [4]. It is the successful convergence of harvesting, storage and electronics that will ultimately lead to successful energy-harvesting products and systems.

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As a result of its topical nature, there are already a number of excellent reviews in the area of energy harvesting, which often concentrate on modern nano-scale materials and devices ('nano-generators') [5–13] or surveys of the various potential devices and systems [14–19]. In this chapter we discuss examples of energy harvesters and piezoelectric materials that can be used as active elements within such systems.

4.1.1 *Energy-Harvesting Materials and Systems: General Characteristics*

Piezoelectric materials are attractive for a number of applications concerned with energy conversion and harvesting. This includes the potential to convert mechanical vibrations into electrical energy via the direct piezoelectric effect, the conversion of thermal fluctuations into electrical energy via the pyroelectric effect and the prospect of using the internal electric fields present in ferroelectrics or strained piezoelectric materials to influence electron-hole recombination in solar-cell devices or chemical reactions, such as water-splitting. The aforementioned materials belong to so-called active dielectrics, and their physical properties are often exploited in external electric, mechanical or thermal fields. Figure 4.1 shows the relationships between the active dielectrics (see the left part of the diagram) and links between the active and passive dielectrics. Among the active dielectrics, ferroelectrics are of particular interest because of the combination of pyroelectric and piezoelectric properties and because of an influence of additional factors (e.g. relaxor, semiconductor or ferroelastic characteristics of some ferroelectrics) on these properties. It is probable that the left part of the diagram shown in Fig. 4.1 may be modified in the future due to a more detailed classification of ferroelectrics and related materials. As follows from Fig. 4.1, all pyroelectrics are piezoelectric and all ferroelectrics are piezoelectric and pyroelectric. Since the aforementioned properties are, in many cases, present in the same material, it provides the intriguing prospect of a material that can harvest energy from multiple sources including, for instance, vibration, sound waves, thermal fluctuations, and light.

Mechanical harvesting, which is the focus of the present monograph, converts energy from movement or vibration into electrical energy. There are a wide variety of sources of mechanical energy including vibrations from industrial machinery and transport [1], fluid flow such as air movements [20, 21], direct human action from walking [22], or in-body motion such as chest and heart movement to power pacemakers [23] and orthopaedic implants [22]. Many of these sources are also used for large-scale power generation, e.g. wind, but energy-harvesting technologies are predominately focussed on small-scale power generation (as a rule, from 10^{-6} W to 10^{-3} W) at the point of use, typically to power small electronic devices where mains or battery power does not provide a viable or convenient solution. In general there are

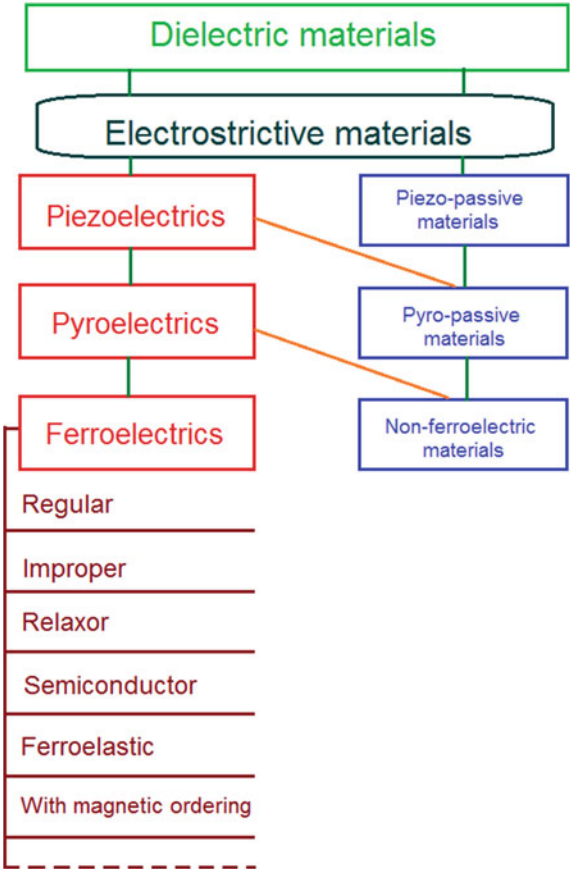

Fig. 4.1 Relationships between dielectric materials

two main ways of extracting energy from a mechanical source. These main ways are described in this chapter as '*inertial*' and '*kinematic*' [24].

Inertial energy harvesting relies on the resistance to acceleration of a mass. This generates a force in a mass-spring system when the source moves. These systems are commonly used for vibration harvesting systems that are connected to the source at a single point [24]. When the source moves, a vibration is set up in the mass-spring system and electrical energy can be extracted. The amplitude of the vibration is not simply related to the source amplitude since the vibration amplitude of a system, if operating at resonance, can be significantly larger than the amplitude of the source movement.

Kinematic energy harvesting couples the energy harvester directly to the relative movement of different parts of the source. Examples of kinematic energy harvesters include harvesting energy from the bending of a tyre wall to power a tyre pressure sensor [24], or the motion of human limbs to power low power electronics [25]. These energy-harvesting mechanisms do not rely on inertia or resonance as in

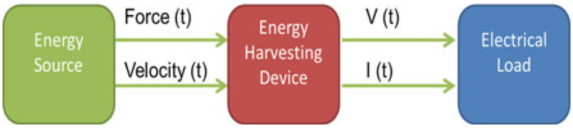

Fig. 4.2 Schematic diagram of an energy-harvesting system. $V(t)$ and $I(t)$ are dependent on voltage V and current I at time t (reproduced from paper by Bowen et al. [24], with permission from The Royal Society of Chemistry)

inertial energy harvesting. Since the strain in the harvester is coupled to flexure or extension of the source, they are connected at more than one point.

An electro-mechanical energy harvester extracts energy from the motion of a source using one of the mechanisms described above and converts it to electrical energy that is delivered to an electrical load. An example of the schematic diagram is shown in Fig. 4.2.

To fully understand the operation of an energy harvester, it is useful to know:

(i) the characteristics of the energy source,
(ii) how energy is transferred from the source to the energy harvester,
(iii) the nature of the electromechanical conversion in the energy-harvesting transducer (e.g. piezoelectric), and
(iv) how energy is transferred from the energy harvester to the electrical load.

Losses can be incurred in the system shown in Fig. 4.2, not just within the energy-harvesting transducer [26], but at all stages in this process. For vibration harvesting, the simplest vibration source is a single frequency sinusoid which is characterised by its frequency and amplitude. The amplitude is commonly defined by the acceleration in energy harvesting applications, but it could also be defined by the velocity or the displacement since they are simply related through the frequency of vibration [24] in accordance with formulae

$$a(t) = -a_0 \sin(2\pi ft), v(t) = v_0 \cos(2\pi ft) \text{ and } l(t) = l_0 \sin(2\pi ft),$$

where a, v and l are acceleration, velocity and distance, respectively, a_0, $v_0 = a_0/(2\pi f)$ and $l_0 = a_0/(2\pi f)^2$ are their amplitudes, f is the frequency, and t is time. In real applications, most vibration sources are rarely simple sinusoids, but there are a number of sources, e.g. machinery operating at AC mains frequency, which have a strong frequency component at a frequency accessible to energy-harvesting devices. Typical vibration sources with an identifiable frequency peak have been characterised [27] by their amplitude at their fundamental mode; for example, producing an acceleration of 3 $m \cdot s^{-2}$ at 13 Hz for a car instrument panel or an acceleration of 12 $m \cdot s^{-2}$ at 200 Hz for a car engine compartment. However, many vibration sources cannot be characterised in this way. For this reason, the energy-harvester performance in complex and broadband vibrational environments must largely be evaluated empirically.

There are a number of transduction technologies for using motion to generate electrical power. Electromagnetic generators are a well-established means of converting mechanical to electrical energy and have been deployed for vibration energy harvesting [1]. These technologies use established manufacturing and engineering methods and are effective both in terms of cost and performance at sizes from a few cubic centimetres upwards. However, performance and ease of manufacture falls rapidly at smaller length scales, so this technology is generally unsuitable for small-scale energy-harvesting applications (e.g. thin sections with areas approximately 1 cm^2 or less). Piezoelectric energy-harvesting materials, the focus of the present monograph, provide a route for solid-state conversion between electrical and mechanical energy, and the materials can be manufactured at small scales and integrated into micro-scale devices and electronic circuits. Power density for piezoelectric transduction exceeds that for electromagnetic generators below around 0.5 $W \cdot cm^{-3}$ [28].

To produce electrical energy, the piezoelectric material must be able to generate both charge and voltage. Many piezoelectric materials of technological importance for energy-harvesting applications possess a well-defined polar axis, and the energy-harvesting performance depends on the direction of the applied strain (or stress) relative to this polar axis. In a poled FC or ferroelectric polymer, the polar axis is the poling direction, whilst for non-ferroelectric crystalline materials such as zinc oxide (ZnO), gallium nitride (GaN) or aluminium nitride (AlN), this is defined by the orientation of the crystallographic axes. In these cases, the polar axis is referred to as the '*3*' direction. By symmetry all directions in the plane at right angles to the polar axis are equivalent and are referred to as the '1' direction; this is typical for most ceramic piezoelectrics. A strain (or stress) can be applied either in the direction of the polar axis, or at right angles to it, resulting in two configurations commonly used for piezoelectric generators, termed '*33*' and '*31*' modes as shown schematically in Fig. 4.3. Other configurations are possible (such as shear, '*15*' mode), and the situ-

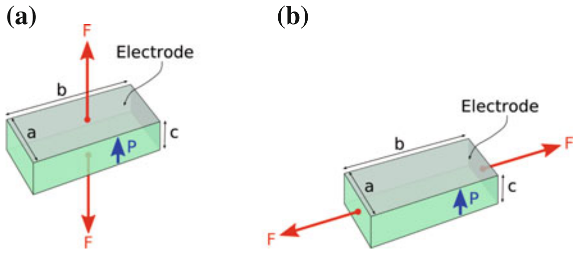

Fig. 4.3 33 (**a**) and 31 (**b**) piezoelectric stress-driven generator configurations. ***F*** is the applied force, ***P*** is polarisation direction, *a*, *b* and *c* are linear sizes of piezoelectric elements. Maximum energy per cycle is $d_{33}g_{33}F^2c/(ab)$ for the 33 generator or $d_{31}g_{31}F^2/a$ for the 31 generator (reproduced from paper by Bowen et al. [24], with permission from The Royal Society of Chemistry)

ation is more complex for materials with lower symmetry, but the '*33*' and '*31*' configurations apply to most practical piezoelectric energy harvesters.

The performance of an energy-harvesting material is directly related to the piezoelectric coefficients and electromechanical properties of the material (see Chaps. 2 and 3), however the applied stress or strain is also an important factor. Efficient coupling between the mechanical source and the piezoelectric material is therefore an important factor in determining the energy-harvesting performance. The energy output also depends on the ability of the piezoelectric material to sustain and withstand the applied force or to repeatedly undergo a recoverable strain without degradation or fatigue of the mechanical or electrical properties. This is particularly important for kinematic energy harvesters, for example a material attached to a deforming tyre wall and subjected to large strains. In many cases it is these limits in the strength and elasticity of the materials that may be the dominant factors in the energy-harvesting performance rather than simply the piezoelectric coefficients.

Piezoelectric inertial vibration harvesters exploit the same piezoelectric properties, but the strain in the piezoelectric material is created by the inertia of a suspended mass undergoing acceleration, rather than being directly deformed by the source. There are many ways of achieving this coupling, but the most common approach is to use a simple piezoelectric cantilever configuration, as shown in Fig. 4.4.

The piezoelectric cantilever is clamped at one end (termed the cantilever 'root') to the vibration source. A mass is fixed to the other end, and when the source accelerates, the inertia of the tip mass induces bending in the piezoelectric cantilever. The magnitude of the tip mass can be used to tune the resonant frequency of the harvester. Bending of the piezoelectric element in Fig. 4.4 leads to the creation of equal and opposite strains on the inside and outside of the bend (the upper and lower surfaces of the cantilever). For a piezoelectric this will lead to the cancellation of electrical charge, so that no net current is generated. To be effective as a generator, it is necessary to move the piezoelectric layer away from the neutral axis and this is often achieved either by fixing the piezoelectric material to a

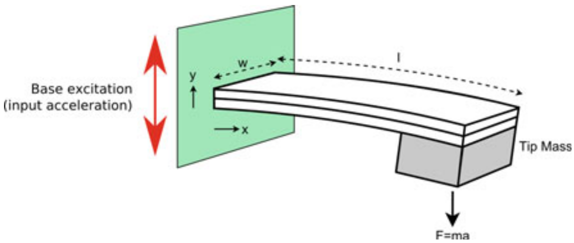

Fig. 4.4 Schematic diagram of the piezoelectric cantilever vibration harvester. The external force ***F*** is applied (reproduced from paper by Bowen et al. [24], with permission from The Royal Society of Chemistry)

non-piezoelectric elastic layer (a 'unimorph'), or by joining two piezoelectric layers that are poled in opposite directions (a 'bimorph') [24].

4.1.2 Resonant and Non-resonant Performance

As described in Sect. 4.1.1, the inertial harvesting devices are usually operated in a frequency range at or close to resonance, where the amplitude of the tip oscillation is limited by the losses from the mechanical system resulting from the energy harvested along with internal and external losses due to friction, internal electrical losses and air damping. As a result, the most effective energy harvester does not necessarily employ material with the highest piezoelectric coefficients. Poled PZT FC is a widely used piezoelectric material and is obtainable in a range of compositions from "hard" ferroelectric materials which have low losses but small piezoelectric coupling, through to "soft" ferroelectric materials with much higher piezoelectric coupling, but also much higher losses. Table 1.2 shows the electromechanical properties of these FC materials along with a range of other well-known FCs for comparison. It has been shown that the hard materials, which have smaller piezoelectric coefficients than soft materials, can produce larger power output [29]. However, the best FC material is not immediately obvious, and its performance depends on the magnitude of the electrical power harvested compared to other sources of loss, i.e., the efficiency, and non-harvested losses dominate for many systems. This demonstrates the importance of efficiency, not only in controlling the loading of the source, but also in optimising power output and material selection.

Piezoelectric energy harvesters do not operate under the same thermodynamic constraints as thermal converters and, in theory, the efficiency of conversion could reach 100 % [30]. In practice the losses are usually significantly larger than the energy converted, and typical efficiencies in the order of 20 % [31]. In some cases the mechanical source is not an infinite supply, and the harvesting of energy damps the vibration producing it. In these cases, one can only hope to extract at most the power available from the source and this is best done with a high efficiency, low loss harvester.

There are a range of loss mechanisms which can include air friction and the influence of the clamping arrangement. Internal losses due to ferroelastic hysteresis and inelastic behaviour at joints and interfaces can also contribute. Electrical losses can occur internally before any energy is transferred to the load and are due to capacitive loading of regions of the piezoelectric element that are not being strained significantly; charge flows from the high strain regions to the low strain regions resulting in loss. The tip of the cantilever is only subjected to a small strain, therefore concentrating the piezoelectric material towards the root provides the most effective use of material. It has been shown that for a rectangular cantilever, a piezoelectric coverage of exactly 2/3 of the beam area produced the maximum power output [26]. Positioning the piezoelectric material under the clamp can also significantly increase losses. It should therefore be avoided, although thinning of the structure at the root can reduce stiffness and cause the maximum strain to be developed away from the piezoelectric region and thus reducing overall effectiveness. Optimisation methodologies can be used to maximise harvester performance and will be discussed later in this chapter (see Sect. 4.3).

4.1.3 Linear and Non-linear Performance

One of the limitations of a resonant-based harvesting device is that the power output decreases rapidly away from the resonance frequency [32]. This means that they are only effective in a situation where there is a large component of vibration amplitude at or near to the resonant frequency; in many cases the vibration source consists of multiple or time-varying frequencies. To overcome this limitation a number of strategies have been pursued to increase the bandwidth of energy harvesting devices [33, 34]; this include the use of tuneable resonators, multi-frequency arrays, and non-linear oscillators. Non-linearity is often introduced by engineering two stable states in the device (bistability). Above a specific amplitude the system can switch between the two states in a highly non-linear, non-resonant and chaotic manner. This lack of a well-defined resonant frequency means that the device is effective across a wider frequency range. A recent study of the use of a non-linear piezoelectric harvester to power a heart pacemaker [35] showed that the device was effective from 7 beats per minute to 700 beats per minute. The pacemaker harvester used opposing permanent magnets to create the bistability. Recent reviews on bistable harvesting [36, 37] have classified the potential methods to induce bistability, such as employing magnetic attraction or repulsion on cantilever structures and imparting mechanical bistability into a piezoelectric structure, for example, by engineering asymmetric composite laminates supporting the piezoelectric [38], as shown in Fig. 4.5.

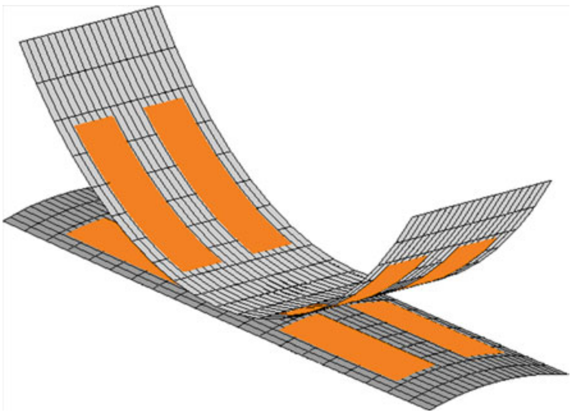

Fig. 4.5 Two stable states of a bistable $[0^P/0/90/90^P]_T$ laminate. *Orange* regions are locations of piezoelectric material (reproduced from paper by Betts et al. [38], with permission from the American Institute of Physics)

An important advantage of piezoelectric materials for energy harvesting is their scalability to a small device size. Integrating the piezoelectric element with silicon electronics using MEMS (Micro-Electro-Mechanical System) fabrication methods offers the promise of low cost high volume self-powered electronic devices and much work has gone into developing devices and processes to make this possible [28]. High-performance piezoelectric materials such as PZT-type FCs can present problems with regard to process compatibility, but significant progress has been made in integrating CMOS (i.e., complementary metal–oxide–semiconductor) compatible materials such as AlN. Although the piezoelectric coefficients d_{ij} of AlN are lower than those of PZT (see data in Table 4.1), Elfrink et al. [53] demonstrated that the piezoelectric coupling compared more favourably due to its low dielectric constant, high squared figure of merit $(Q_{33})^2 = d_{33}g_{33}$, and it is also a lead-free alternative to PZT-based FCs [54]. Microgen recently announced commercial scale production of AlN-based piezoelectric MEMS energy harvesters [55]. Effective micro-scale development requires measurement techniques for measuring the piezoelectric performance at the scale of interest, so recent work has developed MEMS metrology devices to measure the piezoelectric performance at the micro-scale, potentially in situ or in production [56].

In addition to efforts to develop small-scale piezoelectric harvesters, there is also strong research interest in developing nanostructured materials to provide novel energy-harvesting devices and routes to production [5, 9]. ZnO is a piezoelectric material that can be grown as nano-rods on a large scale and significant improvements in the energy-harvesting performance have been reported in work [6, 12, 57, 58]. Power densities in the region of 0.2 $W\cdot cm^{-3}$ have been reported [59] based on measurements of peak short-circuit current and open-circuit voltage for an impulsive mechanical excitation. Recent work on measurement techniques for nano-generators has shown that, in common with the inertial vibration harvesters described above, the output power is dependent on the electrical load, and that the power delivered to the load, averaged over multiple loading cycles, will be smaller than the instantaneous peak power [60] and dependent on the source of excitation. The ability to produce a material that is both functional and manufactured through low cost and energy efficient processes is valuable when considering the development of a new energy-harvesting system. When compared with a number of piezoelectric materials such as poled PZT FC, there are clear environmental benefits. However, since ZnO is non-ferroelectric, its piezoelectric coefficients (d_{33}, d_{31} and d_{15}), as those of AlN and GaN, are relatively small in comparison to d_{ij} of the PZT-type FC (see Tables 4.1, 2.1 and 1.2). Computational investigations of size effects in ZnO nanowires have shown that piezoelectric properties may be enhanced as the diameter of the nano-rods is reduced below around 1.5 nm [61], although current growth methods produce nano-rods with diameters in the range 10–100 nm [44]. Experiments have also shown a possible increase in the piezoelectric effect in GaN nanowires compared to bulk material [40] while nano-scale ferroelectrics have been recently reviewed by Varghese et al. [62].

The operation of piezoelectric materials to enhance energy conversion from a variety of natural sources relies on the development of the piezoelectric potential

Table 4.1 Comparison of room-temperature electromechanical properties of some piezoelectric materials

	GaN	AlN	ZnO	$BaTiO_3$ FC	PZT-4 ('hard' FC)	PZT-5H ('soft' FC)	Domain-engineered PMN–0.33PT SC	$LiNbO_3$ SC	Poled PVDF
d_{33}, pC/N	3.7 [39] 13.2 (NW) [40]	5 [39]	12.4 [43] 14.3–26.7 (nanobelt) [44]	149 [45]	289 [45]	593 [45]	2820 [48]	6 [49]	–33 [51]
d_{31}, pC/N	–1.9 [39] –9.4 (NW) [40]	–2 [39]	–5.0 [43]	–58 [45]	–123 [45]	–274 [45]	–1330 [48]	–1.0 [49]	21 [51]
d_{15}, pC/N	3.1 [41]	3.6 [41]	–8.3 [43]	242 [45]	495 [45]	741 [45]	146 [48]	69 [50]	–27 [51]
k_{33}	–	0.23 [42]	0.48 [43]	0.49 [46]	0.7 [47]	0.75 [47]	0.94 [48]	0.23 [50]	0.19 [52]

Notes

1. Experimental data on electromechanical properties of numerous FCs and relaxor-ferroelectric SCs are given in Tables 1.1, 1.2, 2.4, and 2.5
2. Data for GaN nanowires are marked '(NW)'

through the development of a strain in the material. Since piezoelectrics, and indeed ferroelectrics, can be treated as semiconductors that can sustain a crystal dipole, there is an intimate relationship between the semiconductor properties of the material and any device behaviour resulting from a strain. This relationship has long been understood for piezoelectric materials with early reports correctly identifying barrier height changes in III–V semiconductor structures [63] and strain induced piezoelectric effects in GaN optoelectronic devices [64]. These reports have led to a variety of devices being produced that exploit these relationships for a range of piezoelectric materials. The development of such devices has rapidly come to maturity, and there are now a large number of applications where the piezoelectric, or ferroelectric nature, of a device is harnessed to generate energy under a controlled environment [60]. There is also now growing evidence that ferroelectric materials, such as $BaTiO_3$, $LiNbO_3$ and PZT are true semiconductors, and we marked the semiconductor feature of ferroelectrics in the diagram (see Fig. 4.1, left part). For example, undoped PZT FC is a wide-band gap semiconductor with a band gap of between 2.6 eV and 3.5 eV [65]. The PZT FC material also exhibits p-type electric conductivity due to the presence of low-valence impurities substituting for higher-valence Pb ions. This causes A-site (Pb ion) vacancies to act as electron acceptors, leading to the production of holes in a FC sample [66]. The behaviour is modified due to the non-centrosymmetric crystal structure, and this can be used to enhance a number of interesting device and materials performance parameters, such as photo-voltaic performance or photochemical yield.

4.2 Physical Characteristics of Piezoelectric Materials for Energy Harvesting

4.2.1 High-Temperature Harvesting

A considerable amount of research has concentrated on vibration harvesting at ambient temperatures since one motivation is to power low-power electronic devices and wireless systems. However there are a number of applications, such as power, transport or oil/gas/space exploration, where there is a need to operate at higher temperatures. As an example, temperatures up to 600 °C are widely encountered in engines of different types and industrial processes.

In terms of the piezoelectric material for high-temperature , many ferroelectric materials are characterised by a Curie temperature $T_C < 600$ °C. For example, PZT-based ferroelectrics have a Curie temperatures $T_C < 400$ °C and gradual reduction in power with temperature up to 150 °C has been reported for soft PZT harvesters [67]. Comyn et al. [68] have recently processed $BiFeO_3$-based polycrystalline ceramics with T_C up to 650 °C and $Bi_4Ti_3O_{12}$, another ferroelectric, has been shown to be stable up to 500 °C and has been considered as a potential material for use at the ambient temperature of Venus (460 °C) [69].

In addition to ferroelectrics, wide-band gap semiconductor and piezoelectric and piezoelectric materials with wurtzite structures are of interest. GaN is a potential piezoelectric material that exhibits the semiconductor and piezoelectric properties that is advantageous for the realisation of high-temperature harvesting. While the piezoelectric coefficients d_{ij} are not as high as in ferroelectrics (compare GaN with the PZTs in Table 4.1), GaN nanowires have demonstrated high piezoelectric coefficients [40], and piezoelectric sensors based on GaN have been reported [70]. In Table 4.1 we show piezoelectric data for GaN nanowires and bulk SC samples. Due to their wide band gap, these materials are expected to operate in a broad temperature range and retain low electric conductivity, and being semiconductors have the potential to integrate with device electronics associated with the energy harvester. In terms of device electronics, the relatively narrow band gap of silicon results in device functionality being degraded at temperatures in the region of about 350–400 °C since the intrinsic densities of electrons and holes become significant compared with doping densities. The use of wideband gap materials, such as GaN or SiC, is one possible solution for energy harvesting in hostile environments [71].

Another potential high-temperature material is AlN. Like GaN, AlN has a wurtzite crystal structure, does not exhibit a phase transition on heating and has a melting point of 2000 °C [72]. As is known from work [73], *c*-axis orientated thin films of AlN have been used in high-temperature piezoelectric transducers. Piezoelectric activity in AlN is observed even at temperatures as high as 1150 °C, and the material also has low electric conductivity owing to its large band gap. AlN can be used at low oxygen partial pressures, an advantage if the transducer must operate under reducing conditions to prevent oxidation of packaging.

Ferroelectric $LiNbO_3$ is another option for high-temperature piezoelectric operation and has been considered for high-temperature actuation and sensing in harsh environments for applications such as ultrasonic drills, corers, and rock abrasion tools [74]. Under shear conditions $LiNbO_3$ SC shows relatively large piezoelectric activity (see d_{15} in Table 4.1) and electromechanical coupling factors, a pre-requisite for efficient energy conversion, and a very high Curie temperature (T_C = 1142–1210 °C) [75, 76]. By using high-purity $LiNbO_3$ SCs, transducers operating at temperatures up to 1000 °C have been reported with no significant oxygen loss or resistance change over 600 °C [63], but there is less work on energy harvesting using this material [77]. Bedekar et al. [78] have shown that $YCa_4O(BO_3)_3$ and $La_3Ga_5SiO_{14}$ exhibit stable piezoelectric and dielectric properties up to 1000 °C. $GdCa_4O(BO_3)_3$ piezoelectric SCs have also been considered for ultra-high temperature (>1000 °C) applications [79]. Zhang et al. [80] have provided an excellent overview on piezoelectric sensor materials for high-temperature applications. While there is evidence of research on using piezoelectric materials for high-temperature transducers, such as sensors, there is less work specifically on harvesting and the associated circuits and storage challenges under extreme conditions.

4.2.2 Compliant Piezoelectrics

Many of the piezoelectric materials described in Sects. 4.1 and 4.2 (e.g. PZT, GaN, ZnO, and $LiNbO_3$) are inorganic and inherently hard, high stiffness and brittle with the potential to fracture at low tensile strains [81]. Polymeric materials that exhibit piezoelectric behaviour are of independent interest for energy harvesting due to their flexibility, toughness, low density, biocompatibility, and low-cost characteristics. Example applications include wearable or implanted devices [82] where the polymer material is subjected to bending or stretching by limb motion or lung and cavity expansion during respiration [11]. The most common piezoelectric polymer is PVDF whose piezoelectric behaviour originates from orientated molecular dipoles, which are formed by a combination of mechanical deformation and electrical poling of ferroelectric β-phase PVDF [81]. The material has a failure strain of 2 % or higher [11]; however the piezoelectric coefficients d_{ij} and ECFs k_{ij} are relatively low in comparison to the parameters of the aforementioned inorganic piezoelectrics (see Table 4.1). Example applications include harvesting footsteps (using foils) [83], respiration (using microbelts) [84], rainfall and wind [85]. As with the inorganic materials, methods to manufacture PVDF at the nano-scale have been developed by employing electro-spinning using a needle [11] or disc [81] to form nano-fibre webs. The formation of β-phase PVDF for optimum piezoelectric properties can be promoted since the electro-spinning process can be undertaken under high electric field and mechanical stress.

Ferroelectret polymers have been explored for vibration harvesting to a lesser extent. In this case their piezoelectric properties originate from internally charged voids [86, 87]. Their potential advantage over PVDF are the higher piezoelectric coefficients (e.g. $d_{33} > 200$ pC/N) and greater elastic compliance [88] (e.g. $s_{11} \approx 1100\ \mathrm{pPa}^{-1}$ [89]); although they have low electromechanical coupling factors (e.g. $k_{33} < 0.1$ [90]), and the output voltage was observed to degrade at lower temperatures compared to PVDF [86]. Other attempts to create flexible piezoelectric structures is the use of fine-scale 'wavy' PZT ribbons on flexible rubber substrates to allow stretching and flexing modes for harvesting biomechanical energy [91, 92]. In this way the high piezoelectric activity of the PZT FC material can be exploited, especially when enhanced by operating in a buckling mode. Such piezoelectric 'nano-ribbons' have also been used to form a biocompatible interface with cells to act as sensors, with the potential to act a harvester of biomechanical sources [93]. We add that bio-piezoelectric devices have also been considered based on genetically modified bacterial viruses (M13 phages) with an aligned protein coat structure to form the necessary electrical dipole [94].

In summary, whilst piezoelectric transducers have been studied for many years both as sensors and actuators, it is only recently that significant attention has been devoted to their use as an energy source. Whilst the fundamental principles of piezoelectric coupling of electrical and mechanical energies are unchanged, there are many complexities associated with their application to energy production that have only recently been addressed. As the technology develops, new opportunities will arise for new materials, techniques and innovations. As the technology moves towards production scale-up and wider market penetration, this knowledge will need to be transferred to industrial standards for device performance and reliability.

4.3 Optimisation for Piezo-Based Harvesting

Energy-harvesting devices and systems are complex multi-physics systems that require advanced methodologies to maximise their performance. Section 4.3 examines the approaches that optimise these complex systems via mathematical programming or population-based optimisation techniques such as the genetic algorithm. The majority of the literature to date has considered the conversion of mechanical vibrations into electrical energy conversion using piezoelectric materials [95, 96]. Due to simplicity and the existence of the well-understood models, cantilever beams, as described in Sect. 4.1, continue to be the system of choice for optimisation studies, although in recent years, researchers have begun to optimise two-dimensional plates. Design optimisation for harvesting elements comprises of a coupled system of three elements. The first element is the dynamic response of the harvesting structure, which is a mature field. The second element is the electrical circuit that is necessary to condition the voltage and charge that is generated, this is an area where there has been active development [97–101]. The final element is the coupled electro-mechanics of the system, which represents the key step in energy harvesting and poses a challenging multi-physics problem to the optimisation community. Some of the published research has considered optimisation of material properties, e.g. optimisation of the microscopic crystallite configuration to maximise the electromechanical coupling in specific ferroelectric materials [102]. However, the majority of research has taken a structural optimisation approach to piezoelectric energy-harvesting systems at the device level. This section examines these research efforts and the methods employed.

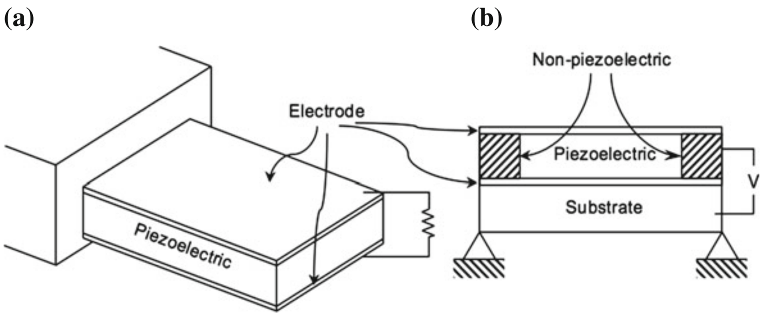

Fig. 4.6 Common piezoelectric energy-harvesting configurations: cantilevered beam (**a**) and cross-section of a plate (**b**) (reproduced from paper by Bowen et al. [24], with permission from The Royal Society of Chemistry)

The most common configurations for optimisation studies are cantilevered beam and plates, examples of which are shown in Fig. 4.6. Studies have shown that the lay-out, position and configuration of the piezoelectric material can have a significant influence on the energy-harvesting performance of a device [103–105]. Dietl and Garcia [104] used a combination of the constrained pattern search algorithm and gradient search method to optimise the width of a bimorph cantilever beam with a tip mass to maximise the voltage generation over time. The first two modes of vibration were included for the optimisation study and it was found that the optimum configuration of the beam tapered down from the root and then widened again near tip. Other researchers also found higher and more uniform strain areas could be achieved by developing a trapezoidal tapered beam along the beam span [105] and through-thickness [106], thereby leading to an increase in both the specific output power per unit volume. In addition, Goldschmidtboeing and Woias [107] obtained an optimum harvester configuration for a unimorph cantilever beam device of plan-form geometry; this was a triangular geometry for a single excitation mode. Here they defined the optimum performance to be the device efficiency, which was characterised by the output power and the maximum tolerable amplitude, taking into account the stress homogeneity. Interestingly, they found the plan-form shape to have little impact on the overall efficiency but is highly sensitive to stress which, in turn, influences the tolerable vibration amplitude. This supports the observation of Wang [108] in that under a static load the plan-form structure has little influence on the efficiency of the electrical energy conversion, but a trapezoidal cross-section enhances the output voltage.

In contrast to the effort on the optimisation of linear energy harvesters presented in this section, Betts et al. [38] optimised a non-linear bistable piezo-composite energy harvester, described in Sect. 4.1.3, using sequential quadratic programming. The design space was highly nonlinear and multimodal however, it was possible to consistently find all local and global optima by employing multiple random starting solutions [38]. As with the above studies, the dimensional parameters of the rectangular plate geometry were optimised to maximise the energy output characterised by the maximum strain. Due to the nonlinear nature of the bistable structure, the strain is large and the power output can be as much as an order of magnitude greater than a linear harvester with an added benefit of harvesting appreciable energy over a broad spectrum of excitation frequencies [109].

The investigations of the shape of the structure for energy-harvesting device have so far been limited in that the majority of the literature either constructs a simplified analytical model or a reduced order model and then conducts the optimisation analytically or study a small set of geometries. Using linear elasticity, much of the understanding of the optimum energy-harvesting performance relates to the precise position of the piezoelectric material; this is usually in high strain areas of the device and in these cases the lowest bending mode is most beneficial. As such work only considers quadrilateral and triangular geometries, the design space is inherently limited and the understanding of the optimum design and potential of energy harvesting are also limited. Park et al. [110] opened up the design space by applying shape optimisation to the beam planform. Since there was

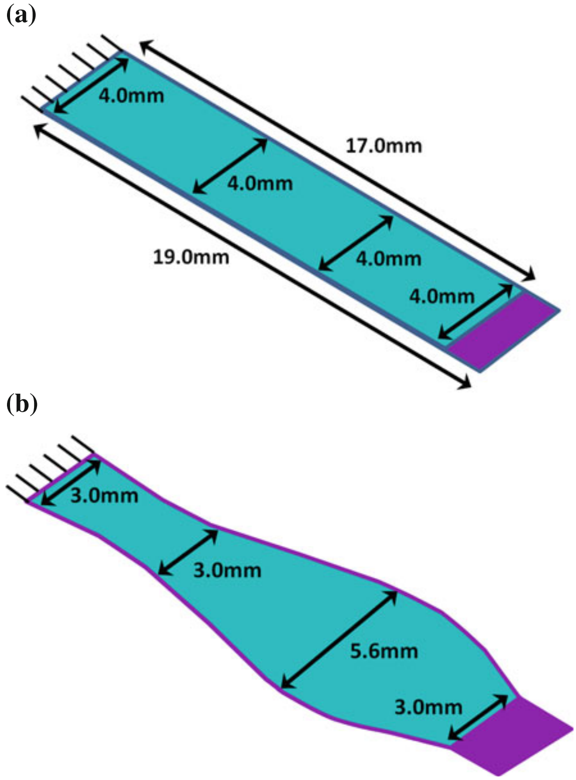

Fig. 4.7 **a** Initial and **b** optimum bimorph beam shape for piezoelectric cantilever beam for maximum power by rotary motion. The bimorph is in parallel connection clamped at upper left hand side end of the beam. *Blue* is the piezoelectric and purple is the substrate where the tip region is deflected. Length dimensions are fixed. Adapted from work by Park et al. [110] (reproduced from paper by Bowen et al. [24], with permission from The Royal Society of Chemistry)

limited design space in their application domain, they specify a maximum length of the cantilever beam and they allow an arbitrary width variation to maximise the output power of the energy harvester, as shown in Fig. 4.7. The optimum solution (Fig. 4.7b) was demonstrated to achieve 37 % improvement compared with the rectangular plan-form of the same volume (Fig. 4.7a).

Researchers consistently agree that consideration of the electromechanical coupling of the harvester is important [111]. Work on addressing this complex multi-physics problem employs stochastic optimisation, which does not require an analytical model or gradient sensitivities. Gonsalez et al. combined a genetic algorithm (GA) [112], which is a heuristic search algorithm based on natural selection to evolve a population of potential solutions with a reduced order model to maximise the power output of a piezoelectric-substrate beam combination. This approach enabled optimisation of the piezoelectric and substrate thickness, mechanical loss factor and electrical impedance [112]. Benkhelifa et al. used a well-established genetic algorithm for multiple objectives, MOGA-II, to maximise the harvested power and voltage output whilst minimising the size of a bimorph piezoelectric beam when it was subjected to a single excitation frequency [113]. Bourisli and Al-Ajmi optimised a unimorph cantilever beam to maximise the conversion of mechanical energy to electrical energy for the first three vibration modes of the device using a genetic algorithm [114]. Bourisli and Al-Ajmi [114] examined the optimum piezoelectric coverage pattern for different substrate materials, namely brass, steel and aluminium. The study revealed that the optimum designs are not influenced by the choice of the substrate materials, and the optimum location of the piezoelectric material coincided with the regions of maximum strain for each vibration mode. We also note the optimisation study of Hadas et al. [115], who applied a Self-Organisation Migrating Algorithm (SOMA) which mimics the behaviour of wild animal groups; although their application domain was electromagnetic vibration energy harvesting. For their numerical studies of multi-objective optimisation, SOMA was considered superior to GA although they are both able to find the optimum solutions. Gurav et al. studied the maximisation of the power output of small-scale MEMS-based energy harvesters [116]. In order to address the manufacturing challenges and control of the material properties and microstructure, uncertainty-based design optimisation was applied to determine an optimum combination of geometric variables.

Understanding that the shape has a significant effect on an energy harvester, the approaches so far consider only a small number of geometrical variables and have explored a relatively small design space, i.e. mainly studying well-defined geometries such as rectangles and trapezoids. In addition, the complex multi-physics dynamics of energy harvesting is not well understood and an ‘intuitive’ design may not be an optimum. In order to explore a greater design space to include unintuitive designs, researchers have developed topology optimisation for linear energy harvesters. Topology optimisation is a class of structural optimisation that provides the most creative solution independent of the preconceived or initial design. In the last decades, topology optimisation is gaining popularity in many different domains of physics [117]. Two categories of approaches have emerged over the past three decades. The traditional elemental approach is to formulate the design problem as a material distribution problem where each small unit or element of material is considered to be a design variable which can take either 1 (material) or 0 (void). The design space therefore becomes the distribution of material and voids, which represents the topology or the general layout solution [118]. The most popular methodology in this category of approaches is termed ‘Solid Isotropic Material with Penalisation’ (SIMP). The alternative approach is commonly referred to as the *Level Set Method* which represents the structural boundaries as a set of implicit signed distance functions and the boundaries are moved to minimise the objective function, thus producing the topologically optimum solution [119, 120].

Topology optimisation has been applied to piezoelectric energy-harvesting systems. The more common approach is an extension of SIMP where the key approach is to relax the binary design variables to a continuous variable between 0 and 1 ($0 < x \leq 1$) then penalise the infeasible solutions using a power law, where $x \in \{0, 1\}$. Extending this to the problem of piezoelectrics, the power law is applied to elastic stiffness, piezoelectric and dielectric parameters [121]. Researchers found

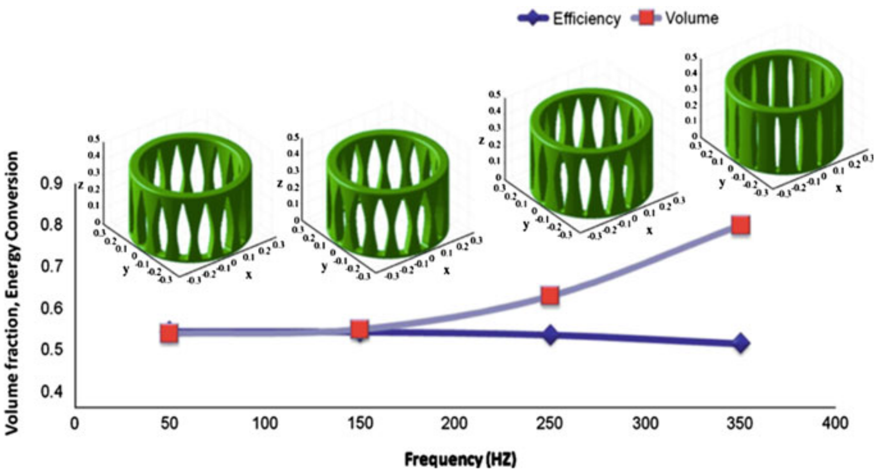

Fig. 4.8 Optimum topology for piezoelectric energy harvester operating in the '33' mode, using the level set method (reprinted from paper by Chen et al. [124], with permission from Elsevier)

that the choice of the three exponents can lead to different solutions or even non-convergence, thus they need to be carefully selected [122, 123]. The alternative level set method avoids the challenges associated with using the power law [124], and both the '31' and '33' operation modes, shown in Fig. 4.3, have been considered using this approach.

Chen et al. [124] applied the level set method to optimise a cylindrical energy harvester using two materials that operated in the '33' mode, see Fig. 4.8. Optimisation for multiple materials was achieved by a '*Reconciled Level Set'* method [125]. Sun and Kim [126] also optimised two materials in a magneto-electro-elastic laminate composite. In their study the thickness of each material was optimised using a micro-mechanics based model under the influence of a static load. They found that the SIMP-type material interpolation model was unable to converge to a solution with distinct phase states for this complex multi-physics problem. By far the more common configurations considered in the topology optimisation literature remain to be simple flat cantilevered beams and plates as in Fig. 4.6 [121–123, 127–129], albeit there are variations, e.g. with or without substrates, with or without tip mass. Rupp et al. [127] optimised the electrical circuit parameters simultaneously with the general layout. Their numerical studies showed that the simultaneous optimisation of both structural topology and circuit did not fundamentally change the topological designs, but did influence the optimal resistance of the circuit.

For energy-harvesting devices designed for quasi-static applications or at an excitation frequency much lower than the resonance frequency, the optimisation objective tends to be to maximise the ECF k_{ij} [126, 128–130] since it characterises an efficiency of conversion between mechanical and electrical energies in a

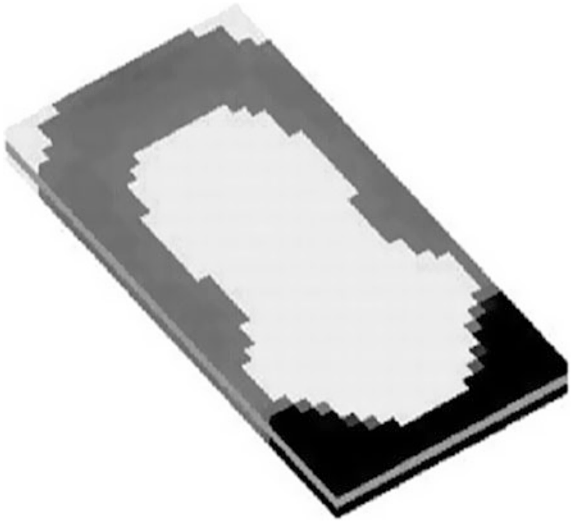

Fig. 4.9 Optimum cantilever beam topology of piezoelectric material under excitation frequencies 10–400 Hz. The beam is configured as in Fig. 4.7a, clamped on upper left side. *Black* represents the material is 1 and white is void, 0. Grey is an intermediate density between 0 and 1 (reprinted from paper by Lin et al. [131], with permission from Springer)

piezoelectric medium. In Chap. 2 we analysed examples of ECFs of numerous piezoelectric materials at various oscillation modes.

In a case of dynamic applications, the harvested power for the given vibration environment is maximised [127, 130–132]. Wein et al. [132] added a stress constraint to their optimisation to control the peak stress in a piezoelectric and substrate composite system using linear elasticity so that the device can sustain an applied force or to repeatedly undergo a recoverable strain. It is interesting to note that Chen et al. [124] optimised a dynamic system but used a mean steady-state energy conversion efficiency similar to the ECF.

Most dynamic optimisation studies considered a single frequency environment and the structural layout was optimised to 'tune' its resonant modes to the excitation frequency. Lin et al. [131] optimised a cantilevered beam energy harvester for broadband random vibration (Fig. 4.9). Comparing solutions for objective functions and for a broadband environment, one can state that their topological designs are fundamentally different. Thus, more research is needed in dynamics and particularly for broadband and random ambient vibration conditions. We also note that there exists very little research beyond the cantilever beam and plate configurations and optimisation of more recently developed harvesters such as piezoelectric nano-generators would be a fruitful avenue for future research and discussions.

4.4 Conclusion

Energy harvesting remains a topic of intense interest, and this chapter provides a timely overview of the variety of energy-harvesting mechanisms employed by piezoelectric and related materials due to their electromechanical coupling.

Piezoelectric materials are solid-state dielectric materials that provide effective conversion between electrical and mechanical energy and can be manufactured at small scales and integrated into micro-scale devices or even electronic circuits. There are a number of potential materials and device configurations and properties and loss mechanism need also be considered, along with the potential scale of the system (from 10^{-2} to 10^{-9} m). One of the main limitations of resonant-based devices is that their power output decreases rapidly away from the resonant frequency and non-linearity can be introduced to enable more 'broadband' harvesting. As vibration harvesting matures it is likely that they will need to be deployed in more hostile environments. Promising candidate materials for such applications include high Curie temperature ferroelectrics and wideband gap semiconductor materials, although the associated circuits and storage challenges under extreme conditions must also be met. In applications, where a high strain is required, more compliant systems based on polymers or composite systems are being considered.

The electromechanical coupling in piezoelectric-based devices and the complex dynamic response harvester devices mean that optimisation of the harvesting device remains a complex task. In many cases simplified analytical models or reduced order models are used to optimise analytically or study a small set of geometries. A variety of approaches are however available to maximise performance in terms of efficiency or total power; this can include methods to optimise an 'initial' design or topology optimisation which has the potential to develop a creative solution independent of the preconceived or initial design. To date most optimisation studies have concentrated on mechanical energy harvesting, although there is potential to apply these approaches to other systems, such as pyroelectric harvesting or even combined harvesting systems.

In summary, piezoelectrics, pyroelectrics and ferroelectrics (Fig. 4.1) represent main groups of active dielectrics and can be regarded as important materials for energy-harvesting applications not any due to their efficiency, ease of use, scale, integration with electronics but also because of their versatility and the variety of modes that they can be deployed.

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