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Review

Mechanical energy harvesting: From piezoelectric effect to ferroelectric/ferroelastic switching

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ABSTRACT

Mechanical energy harvesters show great potential as clean and sustainable energy sources to replace or supplement currently used chemical batteries. Conventional piezoelectric energy harvesting is constrained by low power density, which cannot generate sufficient electrical power for some electronics, particularly in space-sensitive applications. This review systematically examines the existing literature on piezoelectric energy harvesting, with an emphasis on the improvement of energy density by using different energy harvesting strategies. Then, attempts to use the non-linear electromechanical properties of ferroelectric/ferroelastic switching for energy harvesting are reviewed. Critical aspects of mechanical energy harvesting are covered: principles of energy conversion, operational modes, structure design, material properties, energy output, and applications. Comparing the piezoelectric effect to ferroelectric/ferroelastic switching, orders of magnitude increase in power density can be achieved by controlling polarization and residual stress. This review indicates that ferroelectric/ferroelastic switching could be a promising alternative to piezoelectrics for mechanical energy harvesting and identifies opportunities and future directions for practical applications.

1. Introduction

Currently, four main trends exist in electronics, namely miniaturization, multi-functionality, portability and low-power consumption [1,2]. However, these trends are accompanied by challenges associated with powering electronic devices. Wired electronic systems lack the flexibility required in mobile applications [3–5]. However, batteries have limited service life, energy density, and storage capacity, while their environmental impact is of growing concern [6,7]. Energy harvesting provides a potential solution for wearable electronics, embedded microsystems, biomedical sensors/actuators, and Internet of Things [8–13]. For instance, it is desirable that power sources for implanted devices can operate without requiring regular replacement [14,15]. Similarly, sensors that are located remotely or must operate for long periods without maintenance can benefit from energy harvesting [16,17]. Therefore, energy harvesting technologies that convert ambient energies into useful electrical energy, are attractive as ways to provide sustainable power.

The main energy sources suitable for energy harvesting are solar, electromagnetic, thermal, and mechanical. Corresponding energy conversion mechanisms are photovoltaic, electromagnetic coupling, pyroelectric or thermoelectric, and electromagnetic induction, triboelectric, or piezoelectric effects. All of these are, to some extent, already found in everyday life, see Fig. 1.

Among all the ambient energy sources, mechanical/kinetic energy is particularly widely distributed; this source also has the advantages of cleanliness, stability, and relative insensitivity to the environment. A further advantage is the compactness of mechanical energy harvesters, due to the relatively high energy density of the source [18,19]. Vibration, which can be created by the motion of machines, living organisms and fluid flows, is widely available in different environments [20,21]. Generally, research has focused on three main mechanisms of mechanical-to-electrical conversion: piezoelectric [17,22–25], electromagnetic [26–30] and electrostatic / triboelectric [31–38]. Meanwhile, combining two or three mechanisms into energy harvesting systems to enhance the energy output performance is commonly reported in recent publications [39–43]. Zhao et al. [39,44] proposed a novel concept of mechanical intelligent energy harvesting combining both triboelectric and electromagnetic effects, which can identify external excitation and regulate the harvester by mechanical structure or mechanism rather than electrical components. The method of mechanical intelligent energy harvesting has enhanced the output power and reliability of the harvester significantly.

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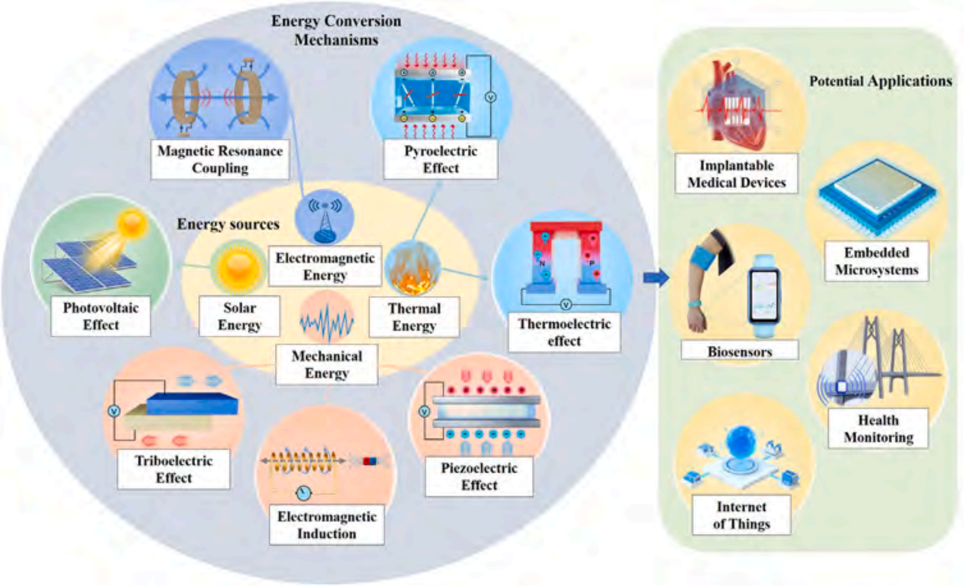

Fig. 1. Energy sources, energy conversion mechanism and applications.

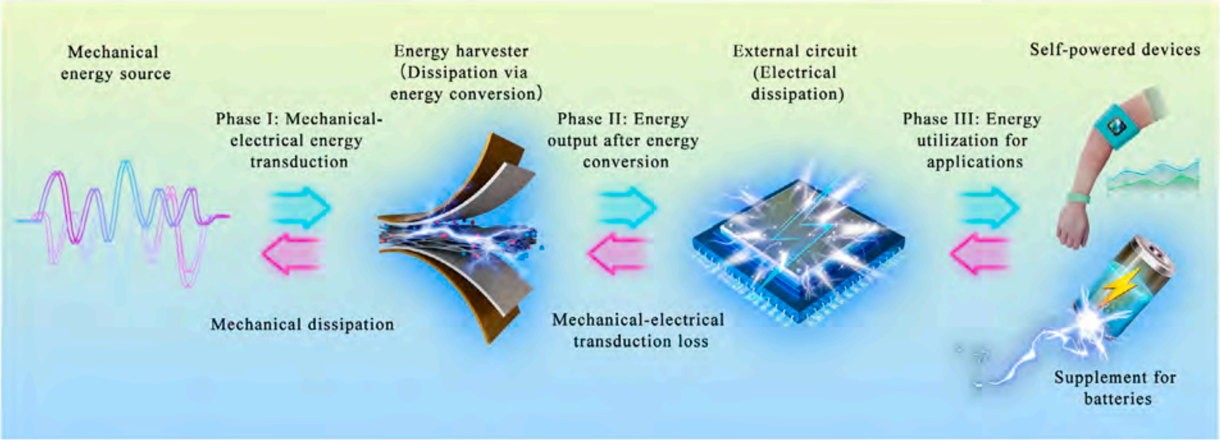

Fig. 2. Energy flows in a typical mechanical energy harvester.

Fig. 2 illustrates the energy flow in a typical mechanical energy harvester, showing how energy is absorbed, converted, and utilized throughout the harvesting cycle. Initially, the harvester responds to motion, absorbing kinetic energy. Some of this mechanical energy is typically dissipated as heat. The energy harvester next converts mechanical energy into electrical energy through one of the conversion mechanisms listed above. This conversion is always imperfect leading to further dissipation. Next, electrical energy is converted and conditioned for use by an external circuit. Again, a degree of dissipation is expected, especially where voltage and frequency conversions are required. Finally, the harvested energy can be stored in batteries or used immediately as a power source. Any excess energy in either case can potentially be returned to the energy source, or may be lost to the environment. Most vibrational energy harvesters utilize a simple damped spring–mass system, designed to maximize energy absorption at a resonant frequency. However, energy harvester performance can be enhanced by applying external forces or excitations that cause non-linearity or modify the resonance. Various mechanical adjustments, such as frequency up-conversion, excitation type conversion, and force/motion amplification, can achieve this effect [45–51]. The mechanisms of mechanical energy harvesting each have their advantages and disadvantages:

- Electromagnetic generators scale well to allow large-scale electricity generation facilities. Their capability to maintain a consistent and stable output of electrical power over extended periods helps to ensure a reliable energy supply. Moreover, these generators can achieve high efficiency in converting mechanical energy into electrical energy, thereby minimizing conversion losses. However, they are typically bulky and heavy due to the need for ferrous magnetic components and windings, limiting their use in applications where space and weight constraints are critical, such as portable electronics and wearable devices. Additionally, the generators consist of complex components, including coils, magnets, and moving parts, which increases manufacturing complexity, maintenance demands, and the risk of mechanical failure [52–54].
- Electrostatic/triboelectric generators are capable of producing high-voltage electrical outputs. They offer the advantage of being compact and lightweight, making them ideal for portable or space-limited applications. They adapt readily to variations in mechanical input making them particularly suitable in dynamic or changing environments. However, electrostatic generators typically have lower power density than electromagnetic generators, limiting their use in power-intensive applications. Additionally, there is often a requirement for down-conversion of voltages. The

devices also exhibit sensitivity to environmental factors such as humidity, temperature, and air pressure, which may affect their performance and reliability [55–57].

- Piezoelectric energy harvesters are solid state devices, resulting in reduced maintenance requirements and extended operational lifespans. The devices can generate a range of output voltages but are typically limited to low currents. They are adaptable for small scales, such as micro-electromechanical systems but also useful in larger energy harvesting systems. However, the performance of piezoelectric energy harvesters is significantly influenced by the properties of the piezoelectric materials employed, which may degrade over time or in harsh environmental conditions. Furthermore, the efficiency of energy conversion is highly dependent on the frequency of the mechanical vibrations [58,59].

Piezoelectric energy harvesting thus demonstrates several advantages that make it suitable for wide-ranging applications. Over the past decade, numerous types of piezoelectric energy harvesters have been proposed and implemented to enhance efficiency [60–72]. Existing review articles cover various aspects of the topic [6,39,58,59,73–76], such as materials [77–84], structures [85–90], energy sources [91–96] and applications [16,97–103]. A key issue is that piezoelectric systems suffer from relatively low power density when subjected to ambient vibrations with working frequency below about 1 kHz. This is because the cycle energy density is low, so high power is only achieved at high frequency. Furthermore, the resonant frequency of the active component is often in the 10 kHz–100 kHz range, so low frequency excitation does not excite significant response amplitude. Using the full non-linear capabilities of piezoelectric materials, such as ferroelectric/ferroelastic switching, could significantly boost energy density. Thus ferroelectric-based energy harvesting technologies have attracted attention for their high cycle energy density and suitability in low-frequency environments, which are proposed as a promising alternative to piezoelectric systems for mechanical energy harvesting. Both theoretical exploration and experimental research in this field are ongoing. However, to date, few studies have thoroughly evaluated ferroelectric energy harvesters. It is thus timely to summarize existing technology and assess the potential for ferroelectric/ferroelastic energy harvesting.

This work explores developments in mechanical energy harvesting, highlighting a development from traditional reliance on the linear piezoelectric effect towards non-linear piezoelectricity or ferroelectric/ferroelastic switching. Ferroelectric energy harvesters based on domain switching or phase changes are reviewed, alongside a summary of developments in piezoelectric energy harvesters. Additionally, the cycle energy densities of various energy harvesting technologies are compared. The structure of the review is as follows: Section 2 introduces piezoelectric energy harvesting, focusing on enhancements through the development of materials and structural forms. Section 3 systematically demonstrates the working principle of energy harvesters using ferroelectric/ferroelastic switching, contrasting their power density with that of piezoelectric energy harvesting mechanisms. Finally, Section 4 provides conclusions and outlines perspectives for future development.

2. Piezoelectric energy harvesting with material and structure improvements

Piezoelectric energy harvesters (PEHs) typically house the working material in a structure that responds to vibration or movement. Imposed motion then causes deformation of the working material and thus produces a displacement of electric charge. The structure of a PEH can be designed in various forms to meet specific needs. Potential structures can include beams, cantilevers, membranes, and other configurations. In each case the role of the structure is to convert kinetic energy to deformational energy in the piezoelectric material. Thin conductive electrodes at the surface of the working material then collect charge; often, a protective cover shields the device. The generated electricity can be used directly or further converted via conditioning circuits. This simple but effective design concept facilitates the conversion of mechanical energy into electrical energy, to power diverse electronic devices and sensors.

Piezoelectric materials are polar crystalline materials, typically polarized by the application of a strong electric field using surface electrodes. Once polarized, these materials become piezoelectric with a polar axis defined by the poling process, in which the crystals have a non-centrosymmetric structure. The PEHs utilize the piezoelectric effect as the foundational mechanism, which is described as the asymmetric shift of charges or ions of piezoelectric when exposed to mechanical loading. When stress is applied to the materials, the central ion is moved or squeezed aligned with the loading direction, thereby changing the spontaneous electrical dipole of the crystals. This displacement generates a surface charge on the material, resulting in a voltage difference across it. This is called the direct piezoelectric effect. Conversely, if an electric field is applied to the material, it will undergo mechanical deformation, which is the converse piezoelectric effect. The constitutive equations of piezoelectric effect are as follows [104,105].

$$D_i = d_{ijk}\sigma_{jk} + \epsilon_{ik}E_k \tag{1}$$

$$e_{ij} = s_{ijkl}\sigma_{kl} + d_{kij}E_k \tag{2}$$

Where σ_{jk} is stress, E_k is electric field, D_i is electric displacement, e_{ij} is strain, s_{ijkl} is elastic compliance, d_{kij} is piezoelectric coefficient and ϵ_{ik} is the dielectric permittivity.

The piezoelectric effect is characterized by a third-rank tensor of piezoelectric coefficients, which describes the relationship between mechanical stress and electric polarization in the material. The principal coefficients measure piezoelectric response to stresses applied in different directions: the longitudinal coefficient (d_{33}) characterizes response to direct stress aligned with the polar direction. The transverse coefficient (d_{31}) characterizes response to direct stress perpendicular to the polar direction. A shear coefficient (d_{15}) characterizes response to shear stress, see Fig. 3. The symmetries of strain, stress and the material itself, reduce the number of independent piezoelectric coefficients, typically to just these three [106]. Thus an understanding of the d_{33}, d_{31}, and d_{15} coefficients is sufficient to design configurations of PEHs that can be optimized for various applications.

Corresponding to the piezoelectric coefficients, there are three main operational modes for PEHs, as shown in Fig. 3: d_{31} mode, d_{33} mode, and d_{15} mode [107–109]. PEH designs often comprise a beam as a structural member with the piezoelectric element in the form of a layer adhered to the beam's surface. In this case, bending of the beam produces in-plane stresses in the piezoelectric, and the natural mode of operation is the d_{31} mode of Fig. 3(a). However, the d_{33} coefficient is typically about twice the magnitude of d_{31}, suggesting that d_{33} mode can enhance energy output [108,110]. To operate a bending beam PEH in d_{33} mode, interdigital electrodes (IDEs) are required so that in-plane poling and charge displacement may be achieved. Optimizing IDE design in d_{33} mode can achieve superior energy output and voltage compared to d_{31} mode, but the resulting higher voltage levels risk electrical breakdown. Consequently, the simpler d_{31} mode is often preferred. The piezoelectric coefficient d_{15} is normally greater in magnitude than either d_{33} or d_{31}. One approach for a PEH operating in d_{15} mode involves attaching a piezoelectric wafer to the surface of a cantilever, in the region near the cantilever root. When the cantilever bends, shear stress in the wafer drives the energy harvesting cycle. However, this design imposes relatively high stresses in the bond line between the cantilever and the wafer [109,111].

Efforts have been made to improve the energy conversion performance of piezoelectric transducers by modifying device geometry and optimizing material properties [73,76,84,112–124]. To improve the

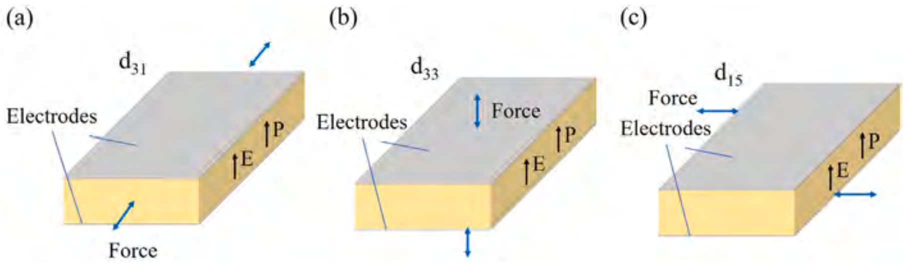

Fig. 3. Operating modes in piezoelectric materials: (a) d_{31} (b) d_{33} (c) d_{15}.

performance of PEHs, significant efforts have been dedicated to optimizing the structural configuration. Reduction of resonant frequency by adjusting structural parameters can enable improved matching to ambient vibration frequencies [48]. Conversely, other studies aim to enhance adaptability by expanding the bandwidth of vibration frequencies [70,125–128]. Enhancements in the materials used for energy harvesters are also seen as a viable approach to boost performance and broaden the range of applications. Various types of piezoceramics, such as Lead zirconate titanate (PZT), $LiNbO_3$, $BaTiO_3$, $PbTiO_3$, and $LiTaO_3$, are commonly considered for piezoelectric energy harvesting. Other materials including the polymer polyvinylidene fluoride (PVDF), ZnO and high performance single crystals such as lead zinc niobate-lead titanate (PZN-PT) and lead magnesium niobate-lead titanate (PMN-PT) have been introduced in PEH designs [74,76,82,94]. The following subsections review typical structural and material developments.

2.1. Improvements of structure design

It is widely recognized that when the resonant frequency of a structure is close to the ambient vibration frequency, the amplitude of the resonant vibration can reach a maximum value. This results in greater mechanical displacement, which consequently generates more electrical energy [129,130]. However, energy harvesters are often ineffective at capturing the low-frequency vibration energy typically found in the environment, which is commonly at frequencies around 1–20 Hz. In the last decade, numerous configurations have been explored to reduce the resonant frequency and widen bandwidth.

2.1.1. Reduction of resonance frequency

Effective strategies for the reduction of the resonance frequency focus on reduced stiffness, and increased proof mass. Additionally, integrating damping mechanisms such as tuned mass dampers or viscoelastic materials can modify the structure's resonant frequency. These combined approaches allow for better alignment with ambient vibration frequencies, enhancing the overall performance. However, a constraint on all of the designs is that the strain in the piezoelectric element must be limited so as to avoid fatigue or fracture.

The basic concept of a PEH in the form of a cantilever with attached piezoelectric layers is shown in Fig. 4(a) [135]. The PEH is a bimorph beam if it has two piezoelectric layers on opposite sides of the beam, while a unimorph beam has just one active layer [5,86]. Based on these ideas, Fang et al. improved the design by adjusting the cantilever's length-to-thickness ratio to over 100, achieving a resonance frequency less than 1 kHz [136]. Following this line of innovation, Anand et al. proposed a multi-perforated cantilever structure that demonstrated low resonant frequency [137]. Yu et al. increased the inertial mass using a seesaw-like PEH capable of achieving a low second-order resonant frequency [131] (Fig. 4(b)).

Zigzag-shaped cantilevers and related structures with high length to thickness ratio typically achieve reduced stiffness and low resonance frequency. Karami et al. [133] introduced an innovative zigzag structure as shown in Fig. 4(c). The zigzag-like structure was further developed into a two-dimensional energy harvester by Sharpes et al. [138], using concentrated stress to increase the amount of energy produced. By altering the beam's shape in two dimensions, they effectively reduced torsional effects while minimally impacting the resonance frequency. Shi et al. [139] used two zigzag piezoelectric springs and a rolling metal ball in their design. The movement of the ball causes the springs to deform, allowing them to capture energy from slight external vibrations. By manipulating factors such as the spring length and the ball mass, natural frequency can be adjusted to meet environmental conditions. Additionally, ring or spiral-shaped cantilever designs can achieve low resonant frequency [140]. Yang et al. [141] further developed this concept by introducing a piezoelectric energy harvester with an arc-shaped design that encourages even stress distribution. However, in space-sensitive applications, performance is limited by mechanical constraints within the zigzag structure at low frequencies. To address this issue, Karami et al. [132] introduced a spiral beam arrangement, see Fig. 4(d). In this arrangement, both bending and torsion are significant, but harvesting energy from the torsional vibration is particularly challenging, requiring additional electrodes. Along these lines, Zhao et al. [142] created a spiral energy harvester with multiple modes and capable of harvesting energy at multiple frequencies simultaneously.

Drawing inspiration from traditional cantilever structures as well as modified spiral and zigzag configurations, several innovative techniques such as preloading, the use of multiple degrees of freedom (DOF) and exploitation of auxetic substrates have emerged as methods to enhance performance. Leland et al. [129] made a breakthrough by introducing preload, enabling dynamic control of the resonance frequency, see Fig. 4(e). This approach offers a practical solution for adapting energy harvesting systems to different vibration sources [146,147]. Building on this, Rezaeisaray et al. developed a PEH with multiple DOF [134], see Fig. 4(f). Their design includes a proof mass supported by four piezoelectric components, allowing the device to demonstrate the first three vibration modes at low frequencies, below 200 Hz. This multi-DOF design increases deflection, thereby significantly enhancing the energy harvesting capability. Further advancements have been made by Ebrahimian et al. [144], who introduced an auxetic substrate to their PEH which gives the advantage that the unidirectional stress normally associated with beam bending, becomes biaxial, thereby enhancing the response of the energy harvester.

Table 1 provides a comprehensive overview of efforts to reduce the resonant frequency in piezoelectric energy harvesting. An essential indicator in this field is the cycle energy density, which measures the energy generated per unit volume of active material during each working cycle. The table shows a general trend of decreasing resonance frequencies through optimized structural designs. However, these improvements have not led to a significant increase in cycle energy density suggesting that alternative approaches are needed to achieve increased energy density.

Despite these innovative designs, recent progress in further reducing the resonance frequency of cantilever-based piezoelectric energy harvesters has been limited. Current research has shifted focus to broadening the effective bandwidth [45,148–151], investigating dynamic damping [148,152], and selecting materials to improve performance [153–156]. This shift reflects the need to enhance the

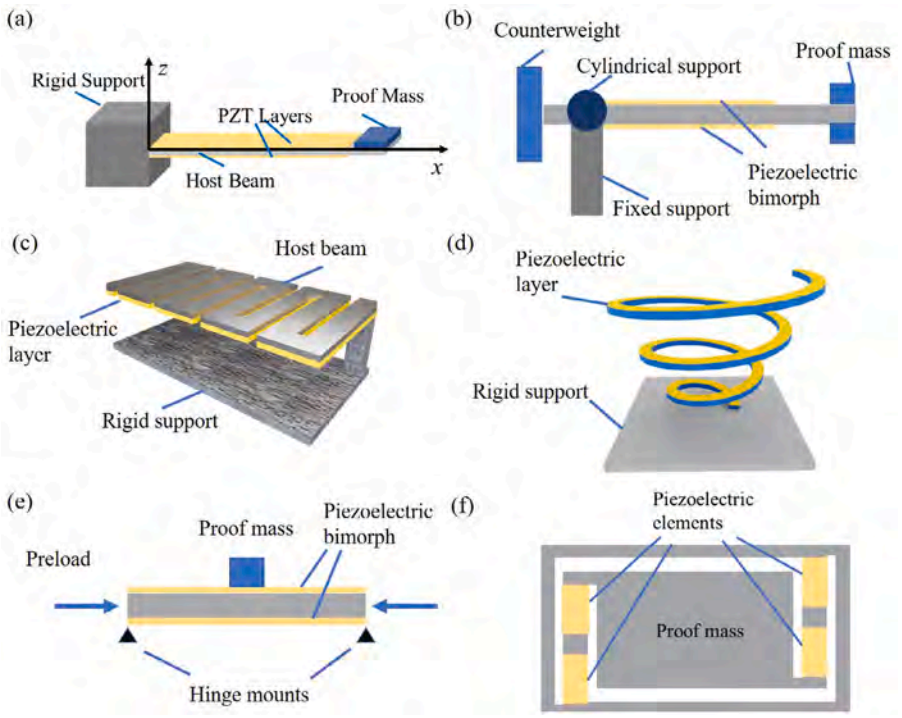

Fig. 4. (a) Basic prototype concept of a cantilever piezoelectric energy harvester. (b) Seesaw-like energy harvester [131]. (c) Zigzag energy harvesting structure [132]. (d) Spiral beam [133]. (e) Energy harvester with preloads [129]. (f) Energy harvester with multiple degrees of freedom [134].

Table 1
Summary of improvements in structure design to reduce resonance frequency of piezoelectric energy harvesting.

Year	Resonant frequency (Hz)	Shape/ strategy	Active material	Active material volume (cm^3)	Power output (μW)	Cycle energy density (μJcm^{-3})	Ref.
2006	608	Cantilever	PZT	1.97×10^{-6}	2.16	1810	[136]
2006	200–250	Preload	PZT	77×10^{-3}	300–400	20	[129]
2010	8.18–142	Zigzag	–[a]	15.5×10^{3}	–	–	[133]
2011	64	Ring	AIN	–	–	472	[140]
2012	27.4	S shape	PZT	1.664×10^{-5}	1.117×10^{-3}	2.44	[143]
2015	97	Multi DOF	AINF	–	0.136	–	[134]
2015	68.1	Zigzag	PZT	0.197	81.3	6	[138]
2016	16	Spiral	PZT	–	330	3.13	[142]
2017	37	Curved	PZT	0.2512	2530	270	[141]
2021	52.3	Auxetic clamped–clamped	PZT	60×10^{-3}	1500	478	[144]
2021	0.5–5	Zigzag with piezoelectric spring	PZT	756	5680	2.5	[139]
2022	19.18	Seesaw-like	PZT	0.18	4030	1167	[131]
2023	98.59	multi-perforated cantilever	ZnO	4.3×10^{-3}	7.15	1670	[137]
2024	37	zigzag	PLLA	2.4×10^{-4}	8×10^{-6}	0.89×10^{-3}	[145]

[a] Not available.

adaptability and overall efficiency of energy harvesters for diverse applications.

In practical applications, large strains in energy harvesters arise due to the cyclic nature of mechanical vibrations, which subject the materials to continuous high mechanical loading. High-amplitude vibrations cause substantial deformation, while resonance effects amplify oscillations, further increasing strain. Additionally, the use of brittle or rigid materials and compact designs often concentrates strain in small areas, accelerating fatigue or fracture over repeated cycles. To address these challenges, multiple smaller or segmented piezoelectric units can be distributed across the structure instead of a single monolithic layer [157,158], effectively reducing stress concentration. Incorporating compliant layers or stoppers can also help by limiting excessive displacement [159,160], thereby protecting the piezoelectric material. Using multi-layered piezoelectric components further enhances durability by distributing strain across thin layers, achieving the same output voltage with less strain per layer. By adopting these strategies, engineers can better align design with the durability requirements of real-world applications.

2.1.2. Broadening effective bandwidth

A challenge in piezoelectric energy harvesting is the narrow operational frequency range of resonant structures, which restricts efficient energy capture from ambient vibrations. To expand the potential uses of piezoelectric energy harvesters, it is essential to widen the usable frequency range around resonance, allowing the PEH to function effectively under diverse vibration conditions. Over the past decade, significant advances have been made on this problem, as summarized in Table 2.

Table 2
Summary of improvements in structure design to broaden the effective bandwidth of piezoelectric energy harvesting.

Year	Frequency bandwidth (Hz)	Shape/ strategy	Active material	Active material volume (cm^3)	Max power output (μW)	Max cycle energy density (μJcm^{-3})	Ref.
2008	113–281	Cantilever array	PZT	40.5×10^{-3}	–	–	[161]
2008	226–234	Cantilever array	PZT	18×10^{-6}	3.15	764	[130]
2009	16.4/49.3	L-shaped	PZT-5A	0.394	4900/2920	758/150	[162]
2011	1080–1620	Doubly clamped beam	PZT	21×10^{-6}	45	1648	[163]
2013	65–170	PPCBs	PZT	0.04	–	–	[164]
2014	15–22	multi-stage force amplification	PZT	0.24	19 000	3770	[165]
2014	2.5–4.8	Cantilever with a amplitude limiter	ZnO NWs	0.915	–	–	[166]
2018	61.99–69.88	Cantilever proof mass tuning	PZT	0.129	0.107	12	[167]
2019	2–8	X-structure	–[a]	–	60	–	[168]
2019	21–35	Moving center of gravity and cylinders rotational and vibration motion	PVDF	11.4×10^{-3}	13.18	52.6	[169]
2020	26.5–32.5	frequency-tuning synchronized electrical charge extraction technique	PMN-PT	0.45	93	7126	[23]
2020	20–200	L-shaped	PZT	2.59	1.79	12.4	[170]
2021	10–40	Auxetic nonlinear	PZT-5A	0.12	122	33.8	[171]
2022	28.9–38.6	Multi-frequency response piecewise-linear	PZT	0.36	290	27.8	[172]
2024	12.3–27.5	6 DOF stepped beam	PZT	0.2	374	116.9	[173]

[a] Not available.

One approach to broadening bandwidth is the introduction of geometric non-linearity. For example, Hajati et al. [163] addressed the problem by using the nonlinear stiffness of a doubly clamped beam structure in which stretching strain affects resonance. Their PEH achieved amplitude-stiffened Duffing mode resonance, with bandwidth outperforming conventional devices. Yang et al. [165] used both geometric nonlinearity and multiple closely placed resonances due to asymmetry to broaden bandwidth. Later, Brenes et al. [23] introduced a frequency-tuned synchronized charge extraction method. The resulting broad-spectrum PEH is optimized for low frequencies and has an automatic procedure for monitoring the peak power point and dynamically tuning the device. Chen et al. [171] combined the performance advantage of an auxetic substrate with nonlinearity due to a doubly clamped beam arrangement to gain enhanced efficiency and bandwidth.

An alternative way to achieve non-linear response is the introduction of stoppers, which modify the beam length depending on vibration amplitude. This can achieve a significant improvement in energy harvesting. Song et al. [166] laid the foundation for this development by proposing a stopper model, as shown in Fig. 5(a). This model allows for adjustments to the resonant frequency by changing the distance between the stopper and the cantilever. Building on Song's model, Liu et al. [175] explored several configurations, including stoppers on one or both sides of the cantilever. Halim et al. [176] introduced both rigid and soft stoppers, providing greater flexibility in adjusting vibrational characteristics. Their work integrated insights from both Song and Liu, making stopper-based frequency control methods more versatile and applicable. Wang et al. [177] advanced this research by introducing a stopper-plate configuration that accounted for various nonlinear effects. They considered nonlinear dynamics such as the Duffing-spring effect, impact effect, preload effect, and air elastic effect, providing a comprehensive approach to controlling the bandwidth of vibrational energy harvesters. Wang's work synthesized these nonlinear considerations, offering a more holistic understanding of frequency control mechanisms. To improve environmental robustness and performance, Zhang et al. [172] developed a piecewise-linear PEH capable of multiple frequency responses. Their model incorporated three cantilever beams that interact in active and colliding states, displaying nonlinear characteristics. This work combined linear multi-frequency resonance methods with nonlinear frequency broadening techniques. Qi et al. [178] applied the methodology to a two-degree-of-freedom self-coupled structure, further broadening the operational bandwidth.

Introducing multiple DOFs has proved an effective way to enhance bandwidth in traditional energy harvesters. Erturk et al. [162] developed an L-shaped PEH, as shown in Fig. 5(b). The design allows the first two resonant frequencies to be adjusted either closer together or further apart by modifying the mass and beam parameters, thus controlling bandwidth. Expanding on Erturk et al.'s foundation, Li et al. [170] addressed the issue of torsional effects during energy harvesting cycles, providing deeper insights into the mechanical interactions within the system. Meanwhile, Chen et al. [164] achieved a breakthrough in bandwidth expansion using a one-dimensional phononic piezoelectric cantilever beam (PPCB), as illustrated in Fig. 5(c). They created a band gap between different sections of the beam, which limits the propagation of vibrational waves in specific directions. This design enables different parts of the structure to harvest energy at distinct driving frequencies, significantly broadening the operational bandwidth.

Another way to achieve multiple DOFs is to use a cantilever array [130,161,179–181]. Here, multiple distinct cantilevers with different resonances are employed. This method not only increases the effective bandwidth but can also improve the output power. For instance, in 2008, Liu et al. [130] used three cantilevers to harness ambient vibration energy, achieving a total output power that exceeds the sum of the individual cantilever powers, due to phase differences, see Fig. 5(d). Moon et al. [167] further refined the method by adjusting a proof mass composed of two different materials to broaden the effective bandwidth. A further innovation involves integrating a cavity into the cantilever design, which can improve energy output by expanding the operational frequency range to include both second-order and first-order resonant frequencies. This approach has been demonstrated by multiple researchers [182–188], indicating its effectiveness in broadening bandwidth and enhancing energy harvesting capabilities. Effective bandwidth can also be broadened by automatic tuning of the resonant frequency. Chandwani et al. [169] made significant progress by introducing a dual-band PEH capable of operating in distinct frequency bands. This device adjusts the resonance frequency

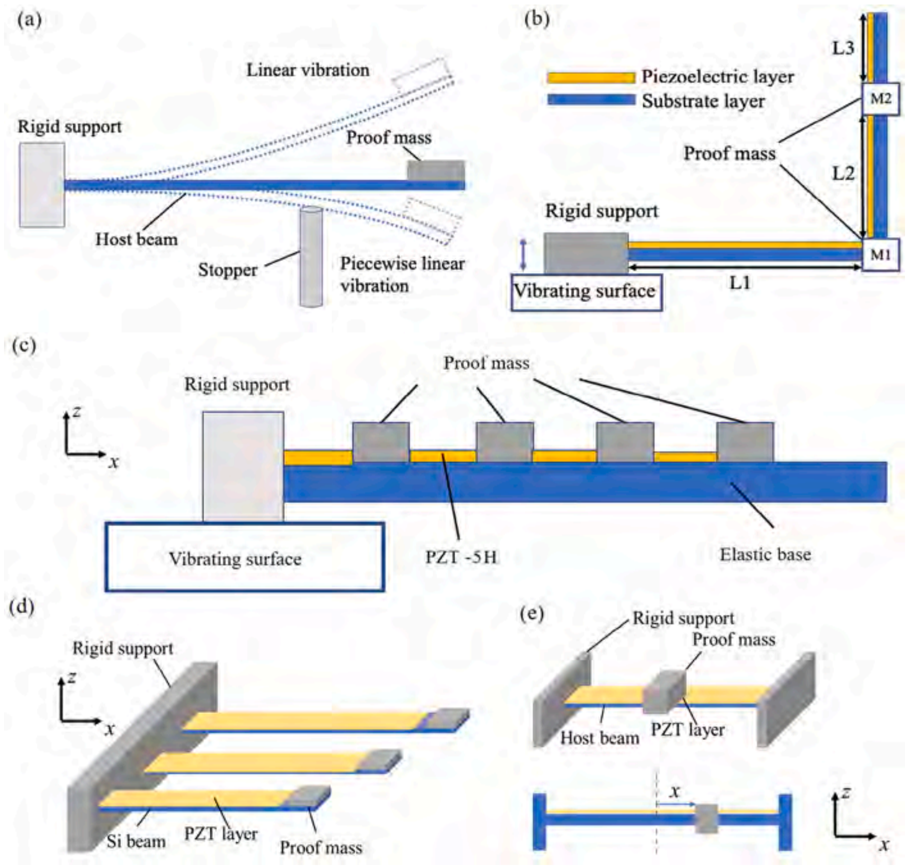

Fig. 5. (a) Cantilever vibration with a stopper [166]. (b) L-shaped multi-directional piezoelectric energy harvester [162]. (c) A one-dimensional PPCB [164]. (d) Cantilever arrays for broadband excitation [130]. (e) Automated resonance tuning with a moving mass [174].

of beams by moving the proof mass. Building on this, Shin et al. [174] developed an automatic resonance tuning method by incorporating a moving mass into a clamped–clamped beam structure, see Fig. 5(e).

In summary, significant advances in piezoelectric energy harvesting with expanded bandwidth have come from the introduction of geometric nonlinearity, contact nonlinearity, multiple DOFs and controllable structures. Table 2 presents these main designs and their associated characteristics, highlighting significant bandwidth expansion compared to earlier simple cantilever designs, especially in the low-frequency range. Despite these advances, challenges remain in optimizing design parameters, practical integration, dynamic environmental adaptation, and ensuring robustness and versatility. Addressing these issues requires further innovative structural designs, material advances, and practical engineering solutions.

2.1.3. *Enhancing energy output*

Breakthroughs in enhancing the energy output of PEHs have occurred through the use of non-linear dynamics, stress distribution optimization in the active materials, and the integration of metamaterial designs. These advances have led to increased efficiency and energy output.

Introducing nonlinear dynamic characteristics through the application of magnetic forces has emerged as a highly effective method in improving the electrical output of energy harvesting. Daqaq et al. [189] provided an extensive summary of developments in this field up to 2014, with more recent reviews also available [46,190]. By incorporating permanent magnets, a ferromagnetic cantilever can experience magnetic forces that induce non-linear effects, see Fig. 6(a). This can increase the cantilever's displacement, especially when the driving frequency and resonant frequency are close. Furthermore, this method can increase energy output, as shown in numerous works using diverse configurations that capitalize on magnetic force [191–199]. However, further research is needed to optimize and standardize these techniques across various configurations and applications. Additionally, exploring novel materials and designs could lead to even greater improvements in energy harvesting efficiency by using this strategy.

New and creative designs are being explored to make PEHs more powerful by optimizing the stress/strain distribution of the active materials. The most basic PEH design, using a simple cantilever, exhibits substantial variation in strain over the active material, with the consequence that the active material is not used efficiently. The innovative designs fall into several categories, including cymbal-type design, shell structures, parallel linkages, trapezoidal geometries and four-point bending. Li et al. [200] developed a cymbal-type energy harvester in which the elastic element is shaped like a cymbal, see Fig. 6(b). This element can split the vertical load into two types of stress: one that pulls perpendicular to its direction, and another that compresses along its direction. The effect is to improve structural stability and boost power. Similar designs were explored by Wang et al. [201], Yesner et al. [202], and Tufekcioglu et al. [203]. By contrast, shell structures, sometimes called 'rainbow' designs, can generate greater strain than traditional flat plates. Kathpalia et al. [204], Esmaeeliet al. [205], and Yoonet al. [206] developed this concept, see Fig. 6(c). Meanwhile, Wang et al. [207] introduced a circular PEH that mimics a beam with fixed ends and pre-loads, showing increased output voltage and power density compared to individual PEHs. Circular membrane-based systems with various load patterns have been investigated [208–211]. Another approach is using piezoelectric material in parallel linkages, see Fig. 6(d), as explored by Asano et al. [212]. This configuration evenly spreads the input force over multiple links, and minimizes the maximum stress on the piezoelectric elements. A trapezoidal beam shape has also gained attention because it distributes strain more

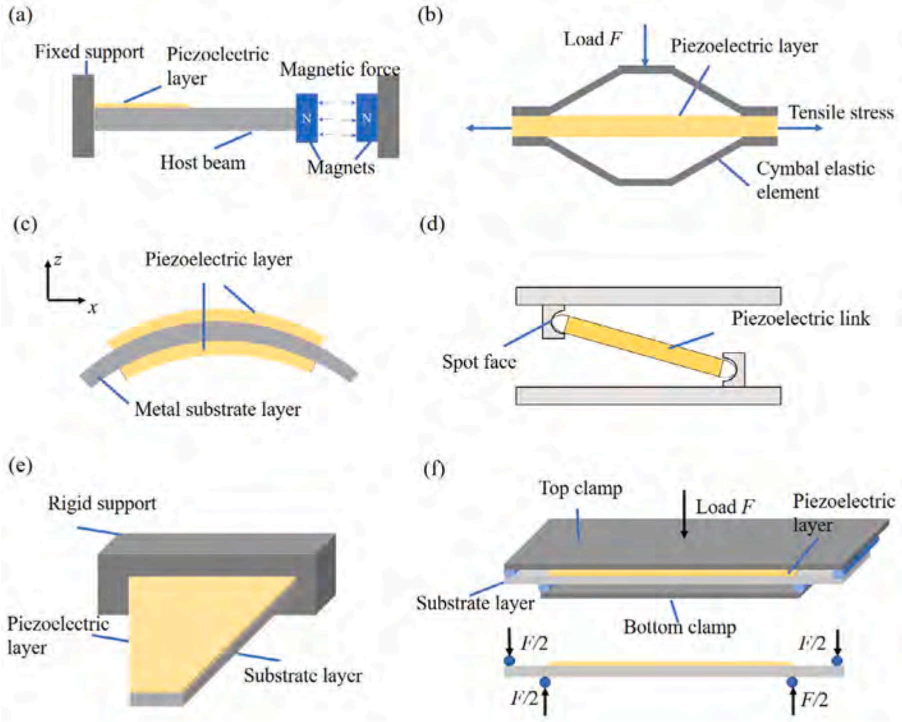

Fig. 6. (a) Basic concept of the non-linear effects caused by magnetic force [189]. (b) Cymbal type energy harvester [200]. (c) Rainbow design [202]. (d) Basic unit of the parallel piezoelectric link [212]. (e) A trapezoidal energy harvester for improved uniformity [213]. (f) A four-point bending piezoelectric energy harvester [218].

evenly than a uniform cantilever, see Fig. 6(e). Roundy et al. [213] and Khazaee et al. [214] have shown that this shape can double the power density of traditional PEHs. Du et al. [215] introduce an apple-shaped bluff body design, developed from a conventional square prism using topology optimization. The rounded contours of the apple-shaped body enhance fluid separation at the edges, which reduces the low-pressure wake, lowers aerodynamic drag, and amplifies vibration amplitude. These improvements collectively boost energy conversion efficiency from fluids. A similar concept of elliptical cylinder interference based on bluff body design can also be found in [216]. By adjusting the length of one cantilever and thereby changing the relative impact position, Wang et al. [217] proposed a two-cantilever piezoelectric energy harvesting system with different amplitudes, improving the energy output compared with system of two same cantilevers. Finally, a four-point bend configuration, Fig. 6(f), of PEH can generate uniform bending moment and hence more uniform stress in the active material; this consequently offers improved energy density [218].

Metamaterials have emerged as a promising avenue for enhancing performance in PEHs. Mechanical metamaterials, typically operating in the low-frequency range, offer novel material properties for the substrate or structure of the PEH, thereby providing opportunities for improved functionality. A typical example is the use of auxeticity (or negative Poisson's ratio) to convert uniaxial strain in a bending beam to biaxial strain [219–221], resulting in enhanced d_{31} mode performance. Other metamaterial configurations include lattice, chiral, and origami metamaterials. These materials are engineered to exhibit unique mechanical properties that advantageously modify deformation or the propagation of mechanical waves. By contrast, acoustic metamaterials primarily function in the high-frequency range to interact with acoustic waves. These include metasurfaces and meta-atoms that exploit local resonance and Bragg scattering to manipulate the propagation of acoustic waves, as indicated in Fig. 7. Acoustic metamaterials can thus control the transmission, reflection, and absorption of sound waves, thereby enabling optimized energy absorption at the PEH. A simple example is the use of a metasurface to collect and focus acoustic energy onto a PEH. Considerable strides have been achieved in energy harvesting with integrated metamaterials, as highlighted by Lee et al. [222]. Leveraging advances in 3D printing and electrospinning technology, these metamaterials capitalize on triboelectric, piezoelectric, and electromagnetic effects to efficiently convert mechanical energy into viable electrical energy [223–225].

There are numerous examples of the use of metamaterials to manipulate or redirect mechanical waves for use in PEHs. [243–248]. In lattice materials, when the incident acoustic wavelength matches the lattice scale, propagating waves undergo scattering due to interference between waves and unit cell. This can create a bandgap or stop band, preventing the propagation of specific frequencies and allowing the concentration of acoustic energy on a piezoelectric element [249–251]. Furthermore, integrating piezoelectric materials into a metamaterial structure can enable the extraction of low-frequency acoustic energy as shown by Wang et al. [252], Jin et al. [253], and Eghbali et al. [254]. For instance, local resonance can be accomplished by integrating a beam-based piezoelectric transducer into a cavity sealed by two mass-attached membranes, leading to maximum sound pressure amplification and a significant improvement in energy harvesting performance [252]. Apart from using meta-atoms, using an acoustic metasurface structure to concentrate incoming acoustic energy at a particular spatial location can significantly improve energy harvesting efficiency. For instance, a labyrinthine acoustic metasurface is capable of directing incoming acoustic waves to a specific region where a piezoelectric element is placed [249–251]. Experimental results have shown increased output voltage and power when combined with a labyrinthine metasurface [249,250].

These designs provide innovative methods for enhancing output energy. However, vibrations with random directions present an obstacle to their practical use, especially with single direction PEHs. To tackle this, researchers are adjusting the designs to capture energy from randomly directed vibrations [113,255–259]. This design enables improved performance output while effectively capturing energy from multiple directions. There is also a pressing need for research into the

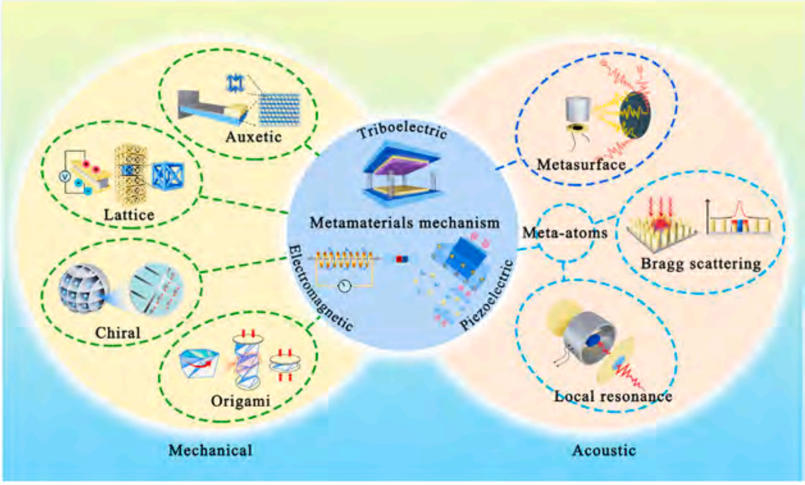

Fig. 7. Metamaterials for energy harvesting: mechanism and categorization.

Table 3
Summary of piezoelectric ceramics/single crystals for energy harvesting.

Shape/ strategy	Year	Active material	d_{31} (pCN^{-1})	d_{33} (pCN^{-1})	Operation frequency (Hz)	Active material volume (cm^3)	Power output (μW)	Cycle energy density (μJcm^{-3})	Ref.
Cymbal	2018	PNN-PZT	–[a]	1753	780	53.2×10^{-3}	14 000	340	[226]
Bending	2023	KNN-5NN	−215	590	1	0.882	–	5.61	[227]
Pressing	2015	NKN-BNT	–	204	1	78.5×10^{-3}	19.3×10^{-3}	0.246×10^{-3}	[228]
Pressing	2015	BNT-BT	–	164	–	–	18×10^{-3}	–	[229]
Pressing	2018	BZT-BCT	–	464	–	–	–	158	[230]
Pressing	2018	KNN–BNZ –AS–Fe	–	500	2	–	–	–	[231]
Pressing	2020	BS-PT with Bi excess	–	452	1	–	–	480	[232]
Pressing	2022	Sm^3+ doped PMN-PT	–	1406	100	–	–	–	[233]
Pressing	2023	PSN-PZT	–	857	10	0.565	17 500	3090	[234]
Cantilever	2008	PMN-PZT	−2252	–	1744	0.106	1410	7.6	[235]
Cantilever	2009	PMN-PT	–	400	1300	1.63×10^{-3}	300	140	[236]
Cantilever	2009	PMN-PZT	–	–	630	31.3×10^{-3}	280	0.5	[237]
Cantilever	2012	PMN-PT	−650	–	102	0.125	3700	300	[238]
Cantilever	2016	PZN-PT	–	–	37.5	28.8×10^{-3}	430	398	[107]
Cantilever	2016	PMN-PT	−920	–	38	28.8×10^{-3}	257	235	[107]
Cantilever	2016	PZT-5H	−275	–	39.5	28.8×10^{-3}	110	96.7	[107]
Cantilever	2017	PZN-PZT+MnO_2	–	314	90	–	98	324	[239]
Cantilever	2017	Mn-KNN	–	122	90	0.5	16	3.6	[240]
Cantilever	2018	BZT-BCT	−130	–	92	5.51	68	13	[241]
Cantilever	2021	M3.0C1.0PZT-PZNN	−230	–	140	0.399	30 000	537	[242]

[a] Not available.

durability and resilience of the materials employed, especially in varying environmental conditions. Additionally, the successful integration of energy harvesting systems into real-world applications requires both cost-effectiveness and suitability for manufacture. Future efforts are likely to focus on tackling these challenges so as to fully achieve the potential of PEHs.

2.2. Improvements in materials

Piezoelectric materials are constantly developing; recent developments in single crystals, ceramics, polymers, and composites, are all relevant to PEH transducer performance. Piezoelectric ceramics, while achieving high piezoelectric coefficients and dielectric constants, are typically brittle, limiting their capability to endure strain. Single crystals, though potentially offering higher piezoelectric coefficients, are more expensive, with reduced toughness, and increased damping, hence increased energy loss in dissipation. By contrast, piezoelectric polymers are more flexible but generally have lower piezoelectric coefficients. Therefore, combining single crystals or ceramics with polymers in piezoelectric composites presents an attractive route towards flexible and efficient PEHs with high power output. Furthermore, due to concerns about lead toxicity, there is a significant shift toward lead-free piezoelectric materials. This section provides an in-depth evaluation of materials for PEHs, including those using single crystals, ceramics, polymers, nanowires (NWs), porous piezoelectrics, and composites, highlighting their improved properties and potential applications. Each material presents its own mix of advantages and disadvantages, making material selection specific to each application and its energy-harvesting needs.

2.2.1. Piezoelectric ceramics and single crystals

Piezoelectric ceramics and single crystals, such as PZT and PMN-PT, are widely used in energy harvesting due to their cost-effectiveness and high piezoelectric coefficients, as noted by Shin et al. [260]. Table 3 summarizes recent developments in PEHs using both ceramics and single-crystals. Single crystals can achieve greater piezoelectric coefficients than PZT ceramics, giving a technical advantage for energy-harvesting. According to Table 3, several single crystals also exhibit greater cycle energy density than electroceramics.

Research efforts to develop piezoelectric ceramics have focused on enhancing their coupling coefficients. Typically, the piezoelectric coefficients (d_{31} and d_{33}) for these ceramics are around −50 pC/N

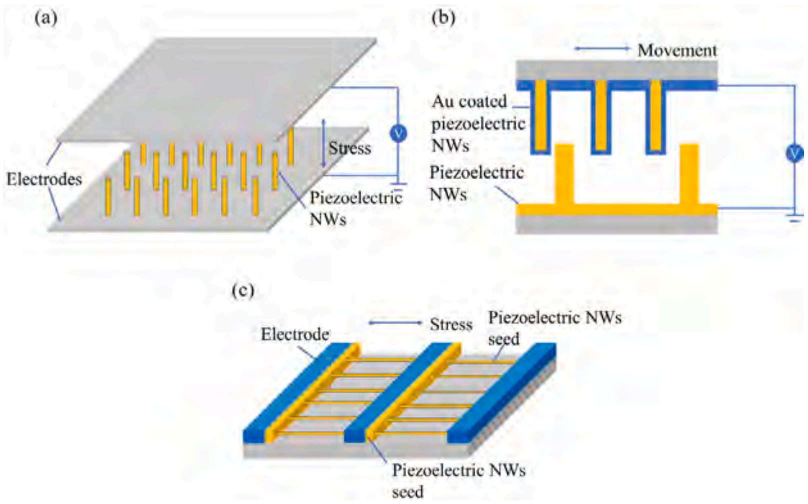

Fig. 8. The operational concepts of the piezoelectric nanowire-based energy harvesters. (a) The design and mechanism of the vertically-aligned nanowire arrays [264]. (b) The vertically-aligned NWs are driven by a transverse oscillatory forces [265]. (c) The design and mechanism of laterally-aligned NW networks for energy harvesting [266].

and +100 pC/N, respectively. Gao et al. [226] developed a piezoelectric ceramic alloy nickel-niobium-lead zirconate titanate (PNN-PZT), with coupling coefficient comparable to high-performance piezoelectric single crystals. Additionally, Yue et al. [239] developed a Mn-doped PZN-PZT, which achieved a d_{33} coefficient exceeding 300 pC/N. Significant advances in lead-free piezoelectric materials are detailed in studies by Banerjee et al. and Yan et al. [261,262], including BNT-BT, KNN-5NN, NKN-BNT, BZT-BCT and others. While lead-free electroceramics have shown notable improvements in piezoelectric coefficients for energy harvesting, their performance still does not match that of the best lead-based ceramics.

A low-frequency, high-performance cantilever energy harvester employing the single-crystal piezoelectric material PMN-PT was investigated by Xu et al. [238]. Studies by Erturk et al., Mathers et al., and Moon et al. [235–237] provide further evidence of the advantages of single crystal PMN-PT and PMN-PZT. To illustrate the differences between single crystals and ceramics, Yang et al. [107] compared the technical properties of cantilever energy harvesters made with ceramic PZT, and single crystal PZN-PT or PMN-PT. Energy harvesters based on PZN-PT and PMN-PT demonstrated higher output power density and voltage than PZT. Similarly, Shahab et al. [263] assessed single crystals against ceramics within the structure of a bimorph cantilever energy harvester. Their findings suggest that PMN-PT is advantageous in situations characterized by off-resonance vibrations with a limited frequency range. However, materials with higher quality factors (hence lower loss), such as hard ceramics and single crystals, can yield higher energy output at the resonance.

The research found that hard piezoelectric ceramics or hard piezoelectric single crystals can offer greater performance due to the higher electromechanical coupling factor weighted by the mechanical quality factor when exposed to broadband random excitation covering the fundamental resonance of the harvester.

2.2.2. Piezoelectric nanowires

An innovative strategy to enhance the efficiency of piezoelectric energy harvesters uses arrays of aligned piezoelectric nanowires, a concept first introduced by Wang et al. [267] using ZnO. The three typical operational concepts for energy harvesters based on piezoelectric NWs are shown in Fig. 8. Nafari et al. [268,269] further developed this concept using ultra-long lead titanate NWs with a high Curie temperature, capable of operating in environments above 300 °C. This method is effective regardless of variations in loading frequency or excitation patterns. Each nanowire is a single crystal; atomic force microscopy enables observation of their deflection and piezoelectric properties. Due to their significant potential, there has been considerable progress in using nanowires made from materials such as PZT, $BaTiO_3$, PMN-PT, PVDF-TrFE, and BZT-BCT for energy harvesting, as shown in Table 4. These materials show high sensitivity to mechanical loads and, with suitable design, can achieve the low resonant frequencies [270,271] desirable for vibration energy harvesting. However, the development of innovative nanowires is crucial for improving efficiency and power output. While this approach can achieve a higher cycle energy density than monolithic electroceramics or single crystals, as shown in Table 3, it has not yet been proven more effective than the piezoelectric composites listed in Table 5. Nanowire-based energy harvesters have great potential for practical applications due to their high specific surface area, flexibility, sensitive response to mechanical stimulus, and superior directional strength. They are especially effective in small-scale devices, wearable fabrics, and electronics. Additionally, they are capable of adapting to challenging environmental conditions and scaling down to nanoscale dimensions without losing functionality, enhancing their potential for diverse applications.

2.2.3. Piezoelectric polymers and composites

Among piezoelectric polymers, PVDF stands out for its high piezoelectric coefficient. It also offers low density, affordability, and exceptional flexibility. However, its piezoelectric coefficient, though high for a polymer, is still less than one-tenth that typical of PZT. One method to enhance the piezoelectric performance of PVDF is by increasing its β phase content, which boosts its piezoelectric coefficient making it potentially suitable for applications in flexible and wearable electronics. Researchers have made significant efforts to raise the β phase content of PVDF to levels between 62% and 88.5% using various techniques. As a result, the versatility of PVDF has been shown, with cycle energy densities ranging from 0.7 to 3.1 mJ/cm^3 [286–293]. However, compared to ceramic materials with greater piezoelectric coefficients, PVDF produces limited electrical output. Consequently, PVDF-based energy harvesters may be inadequate for applications requiring high power output or efficiency.

Piezoelectric composites combine the desirable features of single crystals with those of polymers, resulting in high piezoelectric coefficients together with remarkable flexibility and durability. Due to these attractive properties, there is a significant research focus on incorporating composites into energy-harvesting devices to improve their performance. Table 5 presents an overview of several common piezoelectric composites used in energy harvesting applications, demonstrating that their cycle energy densities could surpass those listed in Table 3.

Table 4
Summary of piezoelectric NWs for energy harvesting.

Shape/ strategy	Year	Active material	Length of NWs (μm)	Operation frequency (Hz)	Active material volume (cm^3)	Power output (μW)	Cycle energy density (μJcm^{-3})	Ref.
Brushing	2008	ZnO NWs	3.5	1	–[a]	–	2900 – 11 400	[265]
Stretching	2009	ZnO NW	200 – 300	67×10^{-3}	3.5×10^{-6}	2.51×10^{-6}	11	[266]
Sound	2013	ZnO NWs	2.5	100	–	–	0.9	[272]
Vibration	2014	$BaTiO_3$ NWs	1	190	–	–	33×10^{-3}	[271]
Vibration	2014	$BaTiO_3$ NWs	40	155	4×10^{-3}	0.123×10^{-3}	0.2	[270]
Bending	2010	ZnO NWs	5	2	–	–	1350	[273]
Bending	2012	ZnO NWs	1.3	175	2.6×10^{-3}	–	52.2	[274]
Bending	2014	Li/ZnO NWs	–	0.5	1.7	90 000	5290	[275]
Bending	2017	PMN-PT NW	10	0.25	–	–	0.701×10^{-3}	[276]
Bending	2017	$BaTiO_3$ NWs	450	2.5	0.135	3	8.8	[277]
Bending	2021	GaN/Al2O3 core–shell NWs	6.5	3	0.78×10^{-3}	0.25	110	[277]
Pressing	2010	PZT NWs	5	50×10^{-3}	3×10^{-5}	–	56×10^{-3}	[278]
Pressing	2014	PVDF-TrFE NWs	–	5	2×10^{-3}	16.5×10^{-3}	8.25	[279]
Pressing	2017	PMN-PT nanobelts	100	50	–	600	–	[280]
Pressing	2018	PZT NWs	6	10	–	0.79/1.48	3950/7400	[281]
Pressing	2021	ZnO NWs	0.7	5	0.84×10^{-3}	64×10^{-3}	15.23	[282]
Pressing	2024	ZnO NWs	1.8	–	–	8.5×10^{-6}	–	[283]
Cantilever	2014	PZT NWs	–	43	–	–	55.8	[284]
Cantilever	2016	BZT-BCT NWs	–	37	–	–	60.8	[285]
Cantilever	2017	PZT NWs	45	187	–	0.67	2.65	[268]

[a] Not available.

Table 5
Summary of piezoelectric composites for energy harvesting.

Shape/ strategy	Year	Active material	d_{31} (pCN^{-1})	d_{33} (pCN^{-1})	Operation frequency (Hz)	Active material volume (cm^3)	Power output (μW)	Cycle energy density (μJcm^{-3})	Ref.
Bending	2011	$NaNbO_3$ NWs/PDMS	–[a]	–	0.33	–	–	2000	[294]
Bending	2012	$BaTiO_3$-Carbon/PDMS	–	–	2.5	0.3	–	–	[295]
Bending	2013	PVDF/MWCNTs	–	–	0.8	–	81.8×10^{-3}	–	[296]
Bending	2015	$BaTiO_3$/PVDF-TrFE	–	960	2.7	3×10^{-3}	–	1670	[297]
Bending	2018	MgO/P(VDF-TrFE)	–	−65	1	0.98×10^{-3}	–	–	[298]
Bending	2020	Pdop-$BaTiO_3$@P(VDF-TrFE)	–	–	3	–	–	1460	[299]
Bending	2022	P(VDF-TrFE))-impregnated BaTiO3 nanoparticles network	–	33	2	–	–	2.1	[300]
Pressing	2013	PZT NWs/PVDF	–	371	–	15.8×10^{-3}	–	–	[301]
Pressing	2018	$BaTi_2O_5$/PVDF	–	–	13	–	4	2.11	[302]
Pressing	2018	BCZT/PDMS	164	54	4	–	–	6.5	[303]
Pressing	2018	NiO@SiO_2/PVDF	–	–	4	80×10^{-3}	–	685	[304]
Pressing	2018	ZnO/PVDF	–	50	5	–	–	6500	[305]
Pressing	2019	P(VDF-TrFE)/BNNTs	–	14	2	12×10^{-3}	–	940	[306]
Pressing	2020	Piezoelectric polyimids	–	420	3.5	0.225	1170	1490	[307]
Pressing	2020	BTFs-CNTs/PDMS	–	–	3.5	80×10^{-3}	864	3080	[308]
Pressing	2021	$BaTiO_3$ NPs and Ag NWs doped P(VDF-TrFE)	–	25	2	37.5×10^{-3}	28.4	379	[309]
Pressing	2023	Porous BCZT	–	620	2	12	104	4.3	[310]
Meta	2020	Ceramic	–	820	50×10^3	0.1	2700	–	[243]
Meta	2022	$BaTiO_3$	−274	593	40 800	0.491	710	–	[248]
Cantilever	2022	BTO/P(VDF-TrFE)	–	−7	18	–	–	0.107	[311]
Cantilever	2024	PZT/PVDF/CNTs	–	595	68.1	10.4	129.4	0.183	[312]

[a] Not available.

One of the main types of piezoelectric composites used in energy harvesters is the macro-fiber-composites (MFCs), which have been developed to provide strong electromechanical coupling for energy harvesting while also offering excellent flexibility for various mechanical systems [313–316]. MFCs are made from thin rectangular piezoelectric fibers embedded in an epoxy matrix and sandwiched between interdigitated electrodes, wherein the fibers in the MFCs are typically aligned along a specific direction to maximize the piezoelectric effect. This makes MFCs more flexible and durable than traditional piezoelectric ceramics. The energy output of MFC based piezoelectric energy harvesters is typically greater than that of similar PVDF PEHs, but still less than that achieved with piezoelectric ceramics [317]. Based on the MFCs, Khazaee et al. [214] proposed a concept in geometry and material lay-up toward energy conversion from wideband excitation signals, which utilizes variable cross-sectional area and rotating fiber orientation in the MFC active layer. With the optimum piezoelectric fiber orientation, a 60% improvement in energy density is achieved, while the taper angle also changes the natural frequency of PEHs. By employing different fiber orientations, Lee et al. [318] successfully created a bi-stable lamina energy harvester using two MFCs with fibers aligned at 0° and 90°. In addition, a low frequency PEH using MFCs was developed by Xu et al. [319], in which the combination of the vibration acceleration, electrode spacing and volume fraction of fibers determine the open circuit voltage.

Other composites, integrating nanoparticles or nanowires, have significantly improved properties compared to traditional polymer piezoelectrics. Studies by Yu et al., Fuh et al., and Ahn et al. [296,320,321] demonstrate efficient piezoelectric energy harvesters using graphene, carbon nanotubes, and graphene oxide. For instance, Fu et al. [302] developed a durable piezoelectric energy harvester by aligning $BaTi_2O_5$ nanorods in a PVDF matrix using hot pressing. Similar nanowire-based composite configurations were explored by Jung et al., Xu et al., and Hu et al. [294,301,322]. Additionally, investigation of oxide fillers, such as MgO, ZnO, NiO, and TiO_2, has identified further enhancement of power output [298,304,305,323,324]. It is noted that the advanced manufacturing methods have been introduced to the piezoelectric composites, such as 3D printing, which significantly improved piezoelectric coefficients of the materials [325,326]. These innovations improve the piezoelectric coefficients, sensitivity, flexibility, and density, paving the way for future developments in energy harvesting technology.

2.2.4. Piezoelectric ultra-thin film and porous piezoelectric materials

Recent advances in manufacturing technology have enabled the production of ultra-thin film and porous piezoelectric materials. By reducing thickness (typically less than 100 nm) thin-film electroceramics gain in flexibility, making them ideal for integration into compact devices, such as flexible, wearable, and even implantable electronics [327]. Thin films are also readily integrated into electronic devices [328–333]. Research in this field has used $BaTiO_3$ [334], PZT [335], PVDF-TrFE [336], PMN-PT [337], lead-free BCZT [338], $BaTiO_3$ nanoparticle composites [339], ZnO NW composites [340], and doped ZnO composite [341] in thin-film structures for energy harvesting. Han et al. [342] introduce flexible amorphous thin-film energy harvesters based on perovskite $CaCu_3Ti_4O_{12}$ (CCTO) thin films by room-temperature sputtering on a plastic substrate for highly competitive electromechanical energy harvesting. Surprisingly, the resultant amorphous nature of the films results in an improved power density, breaking the previously reported record for typical polycrystalline ferroelectric oxide thin-film cantilevers. The findings of these studies demonstrate significant potential for robustness and increased cycle energy density. However, it should be noted that the total energy harvested from a device scales with volume, other things being equal. Hence the 2-D arrangement of films inherently constrains the total energy and power output.

The potential benefits of porous piezoelectrics from energy harvesting have recently been recognized. The advantages stem from their relatively low dielectric constant and hence increased effective coupling coefficient [310,343]. The inclusion of pores in the material allows a separation of the transverse piezoelectric coefficient from the d_{31} coefficient of the underlying material, hence increasing the overall hydrostatic coefficient; this leads to improved efficiency. Significant progress in this field has been made by Asadi et al. [344], who achieved a porosity of 45% in PVDF-TrFE. This led to a higher electromechanical coupling coefficient in the piezopolymer and an impressive 500-fold increase in output power compared to the original PVDF-TrFE. Similarly, Roscow et al. [345] developed a porous barium titanate structure with comparable piezoelectric properties to the dense material, while Zheng et al. [346] detailed the development of an exceptional piezoelectric energy harvester utilizing a film made of porous cellulose nanofibril (CNFs) and polydimethylsiloxane (PDMS) aerogel. This energy harvester made use of biomaterial CNFs, offering excellent bio-compatibility and environmental sustainability. The improvements highlight the great potential of porous piezoelectric materials in developing energy harvesting technology, though this field is still in the early stages of development.

3. Ferroelectric energy harvesting

Ferroelectrics have polarization without external electric field below a critical temperature, known as the Curie Temperature (T_c), while other dielectrics normally have polarization only with external electric field due to the dielectric effect. Spontaneous polarization (P_0) is a physical quantity that represents the net dipole moment per unit volume [347]. However, at temperatures above the Curie Temperature, a typical ferroelectric single crystal will show a paraelectric phase with a symmetric structure instead of a ferroelectric state (for example tetragonal, orthorhombic or rhombohedral) [348]. Given its simplicity, the tetragonal example of the perovskite family ABO_3 structure is regarded as a reference to understand the behavior of ferroelectrics, see Fig. 9(a). Here, a lattice having Pb^{2+} or Ba^{2+} at the corners of the unit cell, combines with a Ti^{4+} ion occupying the central cation site and O^{2-} ions at the center of every face of the cubic geometry [349–354]. When the single crystal structure cools below the Curie Temperature, the Ti^{4+} ion in the center moves off center and a tetragonal structure is formed, leading to a dipole moment of the unit cell. The Ti^{4+} ion can be moved along the direction parallel to the edges of the cubic geometry to six symmetrical positions, and this will form six spontaneous variants due to the different direction vectors. Additionally, as the tetragonal state is c in height and a in width and length from a uniform length a_0 after the cooling process, the movement of the central ion gives rise to specific strain change of the lattice, which can be defined as spontaneous strain. Similarly, the orthorhombic and rhombohedral crystals have three equal axes with oblique angles and three unequal axes at right angles respectively [355–359]. The constitutive equations of a typical ferroelectric are as follow [360]:

$$D_i = d_{ijk}\sigma_{jk} + \epsilon_{ik}E_k + P_i^r \tag{3}$$

$$e_{ij} = s_{ijkl}\sigma_{kl} + d_{kij}E_k + e_{ij}^r \tag{4}$$

Where P_i^r and e_{ij}^r are the remanent parts of strain and polarization respectively. Unlike piezoelectrics, the tensorial coefficients in d_{ijk}, ϵ_{ik} and s_{ijkl} are strongly dependent on the material state, and can vary as the material polarization P_i^r changes.

Below the Curie Temperature, ferroelectric/ferroelastic switching occurs with strong electric field or stress, contributing to non-linearity of the material [361,362]. This thermodynamically non-reversible switching process demonstrates a shape memory effect. As for ferroelectric switching, when an applied electric field exceeds the coercive field, it could induce the movement of the central ion and thereby align the direction of polarization towards that of the electric field. In Fig. 9(b), the examples of 180° and 90° switching caused by the electric field are presented. The 180° switching reverses the net polarization vector but has no effect on the strain, while 90° switching changes both the polarization and strain simultaneously. Stress aligned with the polarization vector can only induce the 90° ferroelastic switching, but the new direction of the polarization is uncertain due to the symmetry of the tetragonal cell. There are four possible new directions of the new polarization vector, and Fig. 9(c) gives two of them. The other two possible directions are perpendicular to the in-plane vectors. The result is that cycling stress does not give rise to a cyclic variation of polarization.

Therefore, ferroelectric and ferroelastic switching, which rely on non-linear effects and dielectric hysteresis, can generate large changes in material polarization. These phenomena have gained interest in energy harvesting because the consequent charge flows greatly surpass those produced by piezoelectric materials. This allows for increased energy density, and increased power output, especially at low frequencies. Moreover, ferroelectric energy harvesting devices can be designed using simple configurations, similar to those used in PEHs. This simplicity makes it easier to integrate ferroelectric materials into existing designs without requiring complex modifications. Despite the potential, there have been limited advances in practical devices utilizing ferroelectric switching for energy harvesting. This is partly due to the fatigue issues that accompany ferroelectric switching, and partly due to the intrinsic difficulty in producing a stress (or strain) driven cycle that cyclically changes the material polarization. Mechanical loading alone cannot fully control the polarization of the ferroelectric due to symmetry. For example, typically, a poled ferroelectric can be depolarized by stress but cannot be repolarised by stress alone. Early designs of ferroelectric transducers were thus single-use devices, capable of delivering a substantial pulse of electrical energy, but not a stable

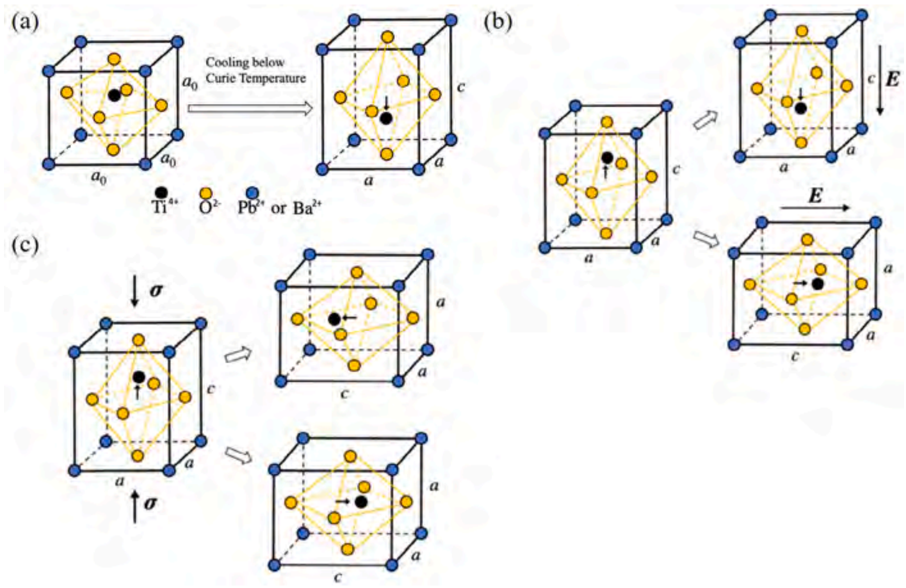

Fig. 9. (a) The lattice structure of an ABO_3 perovskite type oxide with the phase change from paraelectric to ferroelectric state. (b) 180° and 90° ferroelectric switching induced by electric field. (c) 90° ferroelastic switching induced by stress.

power-generating cycle. A central challenge in energy harvesting using ferroelectric/ferroelastic switching is to create a closed and robust working cycle driven by stress. A further challenge is the intrinsically non-linear nature of the ferroelectric material response. This means that variations in load level, frequency or output power demand may result in substantial changes in device behavior that can be difficult to predict accurately. Additionally, ferroelectric hysteresis involves domain switching, a lossy process that can lead to rapid material degradation when operated over large numbers of cycles.

Ongoing research has led to the development of both theoretical models and practical devices using ferroelectric and ferroelastic switching processes [363–370]. These novel ferroelectric energy harvesters show promise for improved reliability and efficiency by addressing, to some degree, issues of power density and fatigue degradation, which are also common in piezoelectric materials. These methods are excellent alternatives for energy harvesting from low-frequency sources (< 20 Hz), and are particularly well-suited for non-resonant mechanical energy harvesting applications.

3.1. Conceptual designs

Several researchers are currently developing theoretical models for ferroelectric energy harvesting technologies, focusing on optimizing efficiency, enhancing reliability, and overcoming technical challenges associated with material design and device integration. These theoretical efforts aim to advance the future practical application of ferroelectric materials in renewable energy harvesting systems.

In 2011, Muench et al. [363] proposed a conceptual design using ferroelectric nanodots as generators. The challenge they addressed was controlling and stabilizing the polarization direction in nanoscale ferroelectric crystals. Strategically placed electrodes stabilized domain structure in a nanodot such that cyclic strain applied to its substrate produced cyclic motion of a domain wall. This theoretical approach, using the stabilizing effects of surface flux closure, was further developed [364] in the form of a ferroelectric film with patterned top electrode. However, the design does not appear to have led to practical devices. In related work, Balakrishna et al. [365] proposed stable operational cycles of ferroelectric energy harvesters using patterned domains in a single crystal thin-film, see Fig. 10(a). The design employs reversible domain wall motion driven by strain. Wang et al. [371,372] suggested an enhanced configuration that stabilizes the energy harvester via a bias field.

Recognizing the need to employ bulk materials for generation of practically useful amounts of energy, Kang et al. [369] proposed an innovative strategy for using ferroelectric switching in ceramics. The approach involves initiating an operational cycle with a strong electric field to achieve complete polarization of the ferroelectric ceramic (Fig. 10(b)). Subsequently, the material undergoes depolarization through transverse tensile stress, while an electric field is applied to facilitate energy output. To re-polarize the electroceramic, compressive stress is applied along with a bias electric field. Behlen et al. [366,373] conducted a detailed exploration of ferroelectric energy harvesting cycles, optimizing for the efficiency and reliability of the energy harvesting device. Although these theoretical analyses have indicated, through conceptual designs, an opportunity to employ ferroelectric switching for energy harvesting, the concepts require experimental development. Future research must also prioritize cost-effective manufacturing, improved system integration as well as the long-term stability and robustness of ferroelectric energy harvesters under various operational conditions. Hence, practical implementation remains a challenge.

3.2. Practical working cycles

Experimental studies are essential to validate energy harvesting concepts and optimize device configurations, addressing issues such as material fatigue and efficiency under cyclic loading. Practical research has focussed on simple thermodynamic cycles that convert mechanical to electrical energy, and variants of these cycles.

3.2.1. Thermodynamic cycles

Energy harvesting using ferroelectric materials can be based on a modified Olsen cycle, which is a pyroelectric energy harvesting cycle used for converting thermal energy to electrical energy. The Olsen cycle comprises two isothermal stages in which electric field changes and two constant electric field stages. The cycle begins at a low temperature, with an increasing electric field. The temperature is then increased at constant electric field, causing charge flow due to pyroelectricity. Next, the electric field is reduced isothermally to its initial level, and finally, the cycle is closed by reducing temperature to the initial level [374–376]. For mechanical energy harvesting, a variant of the Olsen cycle,

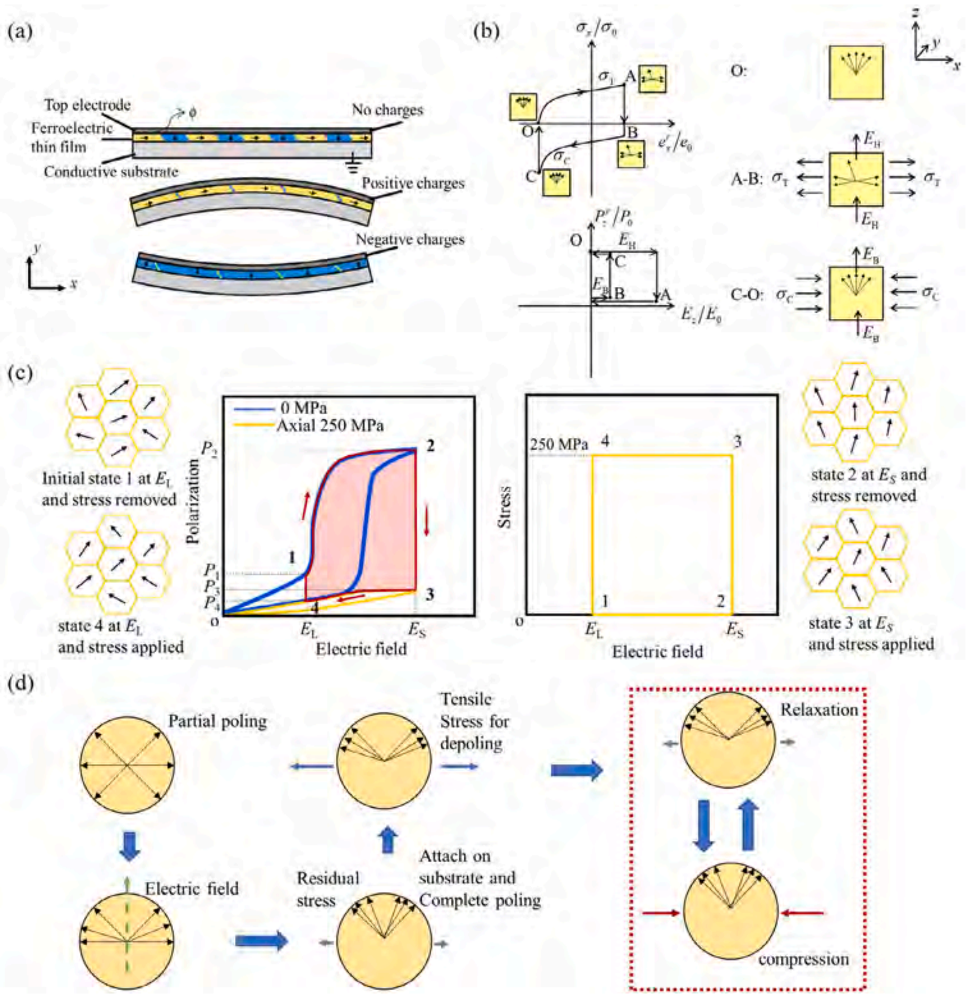

Fig. 10. (a) An operational concept for a single crystal ferroelectric energy harvester [365]. (b) Conceptual working cycle for a polycrystalline ferroelectric/ferroelastic energy harvester [369]. (c) Modified Olsen or Ericsson cycle for ferroelectric energy harvesting [377]. (d) Domain switching during a practical energy harvesting cycle [367,368,370,381].

also sometimes referred to as the Ericsson cycle, can be employed. This uses stress instead of temperature to modify the polarization through switching [377], see Fig. 10(c). The cycle first uses electric field to fully polarize the material. Compressive stress is then applied parallel to the polarization direction to cause depolarization under constant electric field. The cycle is completed by reducing the electric field at constant stress, and then removing the stress. The cycle energy densities achieved with this method are significantly greater than those possible with PEHs. However, despite the simplicity of the harvester's structure, the system design is complicated by the need for external circuits that apply electric fields synchronized with the stress cycles. Various device designs have been proposed [378,379]. Future research directions include simplifying the external circuitry, optimizing the mechanical load conditions, and developing robust prototype devices that can be scaled up for practical use.

Taxil et al. [380] characterized the Ericsson cycles of various ferroelectric materials, including PZT C203, PZT C6, PZN-8PT, PMN-25PT and PMN-15, for mechanical energy harvesting subjected to high electric field, high uniaxial stress, and varying temperature. The results show that the optimal performance is attained at the temperature at which the crystal becomes fully tetragonal. A Bennet doubler was used to achieve synchronization of the different steps of Ericsson cycle.

In a variant of ferroelectric energy harvesting, Dong et al. [382–384] used the phase transition between rhombohedral to orthorhombic states in ferroelectric single crystals to develop an Ericsson-type cycle with high polarization change. Power density was increased by 10^2–10^3 times relative to piezoelectric materials. The operational cycle involves applying alternating high and low compressive uniaxial stresses to the ferroelectric, exceeding the coercive stresses for the forward and reverse phase transitions. Initially, a modest compressive stress starts the energy harvesting cycle. This stress increases to a higher value, creating an electric field that stabilizes the rhombohedral phase. The circuit is then closed while maintaining constant stress, allowing the accumulated electric field to decrease and charge to transfer through an external circuit. Subsequently, the stress level is reduced back to its original low level with the circuit open, generating an electric field that stabilizes the orthorhombic phase. Finally, the closed circuit enables the return from the orthorhombic phase back to the rhombohedral phase. Experimental findings confirm that this cycle can operate at a frequency of 100 Hz, with peak efficiency potentially reaching around 40% using optimized mechanical loads.

3.2.2. *Transverse stress-driven cycles*

Ericsson-type cycles have mainly been developed with the axis of uniaxial stress parallel to the polarization. However, in many practical energy harvesting arrangements, such as bending beams, the stress axis may be transverse (perpendicular) to the polarization direction. Ericsson-type cycles can still work in this arrangement. Kang et al. [367,368,370,381] introduced a ferroelectric/ferroelastic energy harvester in this transverse arrangement, without the requirement for a synchronized external electric field. The method exploits a "memory" effect in polycrystalline ferroelectrics, in which polarization is biased in a preferred direction during a partial-poling step (see Fig. 10(d)). Subsequently, a substrate is used to stabilize this biased state. This arrangement enabled cycles of partial depolarization under tensile stress and subsequent repolarization under compressive stress, yielding significantly greater energy densities than PEHs [226,238,239,281,286,297,299,346,385–388]. The resulting performance is comparable to that of triboelectric generators [389–403]. The innovation in this work lies not in the adoption of new materials or structures but in the strategic manipulation of the material state of electroceramics to enable a stable ferroelectric/ferroelastic energy harvesting cycle using only cyclic compression. Specifically, the approach involves bonding a partially poled electroceramic layer to a rigid substrate, after which the poling process is completed. This creates residual stress within the electroceramic layer. By applying bending loads, the electroceramic is brought into a partially depolarized state, where its polarization can be easily influenced by stress. Then, cyclic compressive stresses are introduced by bending loads that leverage the curvature of the substrate. This induces a reliable cycle of polarization changes under mechanical load, which is harnessed to establish an energy harvesting cycle.

Building on this concept, Kang et al. [368] further identify two types of energy harvesting cycles in the quasi-static tests with various pre-poled states, where the energy harvesting cycles are driven by tensile stress and compressive stress on the ferroelectric wafer. The results show that the cycle energy density can reach 11 mJ/cm^3 under tensile loading and 3.2 mJ/cm^3 under compression, demonstrating great potential for practical applications. However, although the tensile stress-driven energy harvesting cycles show greater energy output, degradation by cracking occurs after several cycles. Thus, A 30% pre-poled sample gave a good balance of high energy output whilst avoiding degradation by cracking with the compression operation mode. Then the impact of resistive load and operating frequency on energy harvesting cycles driven by compressive stress were investigated by Kang et al. [367] further. By adjusting the operating frequency between 1 and 20 Hz and varying the electrical load, the optimal energy output was identified, showing better performance than conventional piezoelectric transducers at low frequencies. The ferroelectric/ferroelastic device displays a load-power relationship similar to that of piezoelectric harvesters, it exhibits a significantly higher effective piezoelectric coefficient. However, prior research has not explored the ideal engineered material state for these energy harvesting devices or the connection between fabrication success and pre-poling levels. Therefore, the energy harvesting devices were further optimized by systematically examining the precise pre-poling of an electroceramic material, with pre-poling levels between 20% and 40%, allowing a comparison of their durability and energy harvesting performance across the 1–20 Hz frequency range [370]. A correlation was found between the level of pre-poling and the device's robustness, with lower pre-poling levels resulting in higher residual tensile stress. Interestingly, lower pre-poling levels also enhanced power density, creating a trade-off between power output and device durability. This balance is crucial for real-world applications and warrants further investigation. Modifying the device design, such as adjusting the choice of active material and refining the poling process, could help address this issue.

The fatigue tests show that the devices exhibited gradual decline in performance over 10^7 working cycles, demonstrating promises in repeatable practical applications. To mitigate fatigue issues in ferroelectric energy harvesting devices, several strategies can be adopted in future investigations to enhance durability and extend operational lifespan. Optimizing pre-poling levels, typically around 25%–35% of full polarization, helps balance energy output with robustness, reducing residual stress that contributes to fatigue. Besides, by utilizing composite ferroelectric materials, which can increase resistance to micro-cracking, the devices' fatigue performance can be significantly improved. Additionally, advanced fabrication techniques like graded poling or layered structures improve stress distribution across the device, minimizing fatigue-induced damage. Finally, operating within an optimized frequency and loading range tailored to material properties can maximize performance while minimizing degradation. By combining these approaches, devices achieve a better balance between high energy output and extended durability.

While the performance of ferroelectric energy harvesters in earlier studies surpasses that of previous technologies, there is still a need to improve energy output and adaptability for harvesting mechanical energy from sources like human motion, vehicle vibrations, or fluid-induced excitations. The ferroelectric energy harvester has not been optimized so far for a specific application, allowing the strategy to be broadly applicable across various energy harvesting applications, including wireless sensors, medical devices, and mobile electronics through tailored designs. Energy output could potentially be improved by customizing these designs to meet the specific needs of each application. Future research offers several opportunities to enhance performance, and five key factors for improvement provide opportunities, including material selection, structural optimization, frequency adaptability, fatigue resistance, and performance in extreme conditions. These areas should be explored in future research, with a focus on specific practical applications such as flexible electronics and implantable devices. There is substantial potential for further development, for example, by selecting ferroelectric single crystals or ceramics to enhance energy output. The choice of substrate and adhesive materials for device fabrication will also play a critical role. Additionally, the fatigue resistance and ability to function in extreme environments are closely linked to material selection. Considering these factors in the development of ferroelectric energy harvesters will be crucial for advancing towards the commercialization of this technology.

Fig. 11 compares the power density, operating frequency and energy density characteristics of various piezoelectric, ferroelectric and triboelectric energy harvesters. Ferroelectric devices exhibit superior energy density when compared to piezoelectrics and similar performance to triboelectric nanogenerators. However, piezoelectrics can typically operate at higher frequencies. Direct performance comparisons remain challenging due to varying loading conditions and the complexity of the individual energy harvesting technologies that have been reported. Research into ferroelectric energy harvesters is still at an early stage, with several proposed designs, but further improvement, optimization, and practical implementation are needed. Research is also needed to optimize fabrication processes, enhance efficiency, and explore scalability for practical applications.

4. Conclusions and outlook

From the piezoelectric effect to ferroelectric switching, this review has highlighted the substantial advances made in mechanical and vibration energy harvesting in recent years. Theoretical insights and creative approaches have established a strong foundation, paving the way for new technologies with the potential for widespread application. However, further work is needed, with the majority of energy harvesting concepts reaching laboratory demonstration stage, rather than commercial technology.

Piezoelectric energy harvesters, converting mechanical vibrations to electrical energy, have become popular due to their simplicity, with solid state, direct energy conversion. The main challenges lie in enhancing the energy generation, as energy density is low, and accommodating broad-band excitation, especially including the low frequencies typical of ambient mechanical vibrations. To address these goals, research has focussed on innovative structural designs and optimization of the active material. Additionally, the use of advanced materials, including metamaterials, either as the active component, as a substrate, or as an energy collection system, has been explored. Among the advanced materials, piezoelectric composites are particularly promising, combining the flexibility of polymer composites with

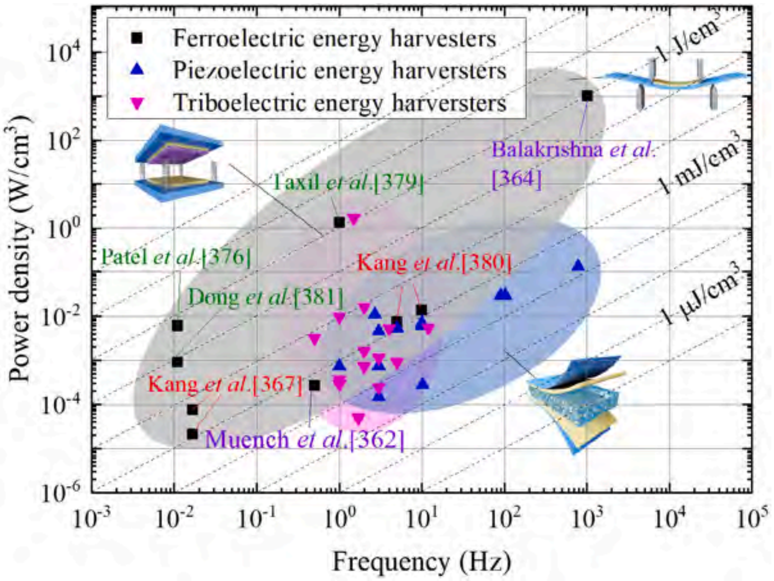

Fig. 11. Frequency–power density characteristics for various energy harvesters. Lines of constant cycle work density are shown. Text color coding: green = ideal/theoretical cycles; purple = theoretical device models; red = experimental devices.

the high coupling of electroceramics. This offers great potential in fields such as wearable and implantable technology. However, limited energy/power density continues to be the main obstacle to widespread adoption, with typical energy harvesters unable to meet the growing power demands of portable electronic devices. Advanced materials, including metamaterials, composites and porous materials, offer potential solutions to some of the technical problems that limit application.

This study also tracks the development of ferroelectric energy harvesters, that use polarization switching to greatly increase energy density. They are regarded as one of the promising alternatives to PEHs. These devices, though still in their early stages of development, attain energy density levels that potentially open up a wider range of applications. The fundamental problem of providing useful energy harvesting cycles driven by stress has been tackled, but further work on robustness, lifetime and stability is needed. The non-linear nature of these ferroelectric devices also presents a significant barrier to their application wherever there is uncertainty over load levels, frequency, or external power demand. Yet, with energy density comparable to, or superior to triboelectric systems, the ferroelectric energy harvesters show great potential.

In conclusion, while piezoelectric and ferroelectric energy harvesting show promise, progress must be made in multiple areas. Five key technical aspects needing further research are: (1) material optimization, (2) structure optimization, (3) frequency adaptability, (4) fatigue performance, or lifetime, and (5) performance under extreme conditions. In addition to these aspects, commercial viability will depend on optimizing fabrication to reduce cost, and appears likely to develop around niche applications at first.

CRediT authorship contribution statement

Wenbin Kang: Writing – review & editing, Writing – original draft, Conceptualization. **Guosheng Ji:** Writing – review & editing, Writing – original draft. **John E. Huber:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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