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Review Article

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A Review on Piezoelectric and Thermoelectric Nanogenerators

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Abstract

This literature review illustrates the efficient design, basic history, and effective output of piezoelectric nanogenerators (PENGs) and pyroelectric nanogenerators (PyNGs) with the varieties of materials used in both the research to possible real-time applications. The review suggests that the thermoelectric nanogenerator (TENGs) will provide more open circuit voltage and power generated to the current state of art PENGs structure. The Study also discusses the standard circuit used in the generation of electricity during the operation of PENGs. Overall, the effective materials for the future, figure of merit (FOM), Seebeck effect and applications for TENGs and PENGs are studied.

Keywords

Nanogenerators, Piezo, Pyro, Thermoelectricity

Introduction

Energy is the basic necessity to sustain the very intricate infrastructure of our evolution that has been built throughout the centuries. From powering thousands of tons of machinery to the minutest of electrical circuits, energy is a must. Over the decades, multiple methods of energy production and transfer have been innovated to suit our energy needs, along with the restructuring of already present procedures to increase their respective efficiency. Over 400,000 years ago, humanity first started using biomass fuels, usually wood, after which fossil fuels took over as the new dominant fuel during the industrial era. As of 2021, fossil fuels account for up to 83% of the total energy produced throughout the world [1]. But these fuel sources are finite and are responsible for damaging consequences on Earth's general biosphere makeup. It is estimated that conventional fossil fuels such as oil will be depleted as early as the year 2060 [2]. Thus, a need arises for us to come up with another solution to tackle the energy issue, and over the years, specialists from around the world have been trying to come up with innovations to respond to the energy crisis. One such significant innovation is the technology of NGs, which is gaining increasing interest and will be the main focus of our article. These energy-producing sources harvest energy by converting mechanical energy into electricity, and the performance of these devices is mostly dependent on the mechanical and electrical parameters of the materials used.

Piezoelectricity was first observed by the Curie brothers, Pierre Curie and

Jacques Curie in 1880, when they were working as laboratory assistants at the Faculty of Sciences in Paris. What they had observed was that when some sort of mechanical stress or strain was applied to certain crystals such as the quartz crystal, tourmaline crystal and Rochelle salt crystals, a generation of electric charge took place [3].

The reversible phenomenon of the piezoelectric effect was predicted by Gabriel Lippman, a Franco-Luxembourgish physicist and inventor, where any application of an external electric field produced internal mechanical stress or strain inside said materials [4]. The prediction was proven true by the Curie brothers in 1881 through a series of experiments and demonstrations. This discovery led to a massive uprise in the development of crystal physics, and in 1910, Woldemar Voigt was able to create a list of all 20 natural crystal classes in which the piezoelectric effect takes place. NGs found their origins around the workings of piezoelectric effect. The first NG was first invented by Wang et al. in the year 2006. It used ZnO nanowires as the source of the piezoelectric effect. ZnO nanowires were used as opposed to normal ZnO wires as they could withstand more strain and stress, thus yielding higher amounts of piezoelectric current [5].

Now multiple materials such as $BaTiO_3$, PZT, and others are being used as they develop. Again, pyroelectric effect's origin finds itself in Greece, around 2300 years ago, a Greek philosopher Theophrastus pointed out that the mineral tourmaline (it is assumed that the mineral mentioned is tourmaline as his writings contained the Greek word "lyngourion", which is assumed to translate to tourmaline) attracted straws and pieces of wood. For an extended period of time this phenomenon remained unexplained, until the 18th century. In 1717, the first ever scientific description was given by Louis Lemery in the Academy of Sciences in Paris, and Charles Linnaeus, a naturalist, was the first person to find a relation between pyroelectric properties to electric current. In 1756, Dr. Franz Ulrich Theodor Aepinus gave the Royal Academy of Sciences in Berlin a thorough scientific analysis of pyroelectric characteristics [6]. In the 19th century, studies of pyroelectricity skyrocketed, through which the phenomenon found many applications, especially in the field of aerospace and astronomy. PyNGs find their origin among their sister NGs (TENGs and PENGs) and have been heavily researched on. It's a well-known fact that a lot of energy is lost in the form of low heat, and this fact can be efficiently utilized to produce electrical energy (Figure 1).

Over the years, multiple developments have been made in the field of NGs. As of now, three types of NGs are being heavily researched upon, and they are: (1) TENGs, (2) PENGs, and (3) PyNGs. All three utilize energy conversion at a very minute level to generate electricity. TENGs and PENGs translate mechanical energy into electrical energy, whereas PyNGs convert thermal energy generated by temperature variations into electrical energy. TENGs were first introduced by the Wang group in 2012, since then garnering a ton of attention. They function on the principle of the triboelectric effect, thus acting as mechanical energy harvesters. They can utilize constructional vibrations or any sort of wave energy to generate an EMF [7-10]. PENGs work on the basis of the piezo potential produced inside piezoelectric materials. Usually, the electrodes of the piezoelectric apparatus have electrostatically balanced Fermi levels. Due to the application of external stresses, the internal and external contact surfaces have differing Fermi levels. To counteract this imbalance, free charge carriers flow through exterior circuits. The balanced state of Fermi levels is then achieved along with the generation of EMF [11]. In PyNGs, the Seebeck effect is the driving force for the functioning of these NGs. PyNGs can convert heat energy into electricity through the polarization variation that occurs between electrodes of layers, using the temperature alterations happening in the environment of the device [12]. When a relatively hotter surface (assume electrode 1) is kept in contact with a (assume electrode 2) cooler surface, the electrons present in the hotter surface flow towards the cooler one. If such surfaces were connected in a circuit, then an EMF would be observed [13]. This article discusses a review on a novel, innovative, and important application of the triboelectric effect, the Seebeck effect for generating electricity, and NGs' characteristics, working, and output attributes.

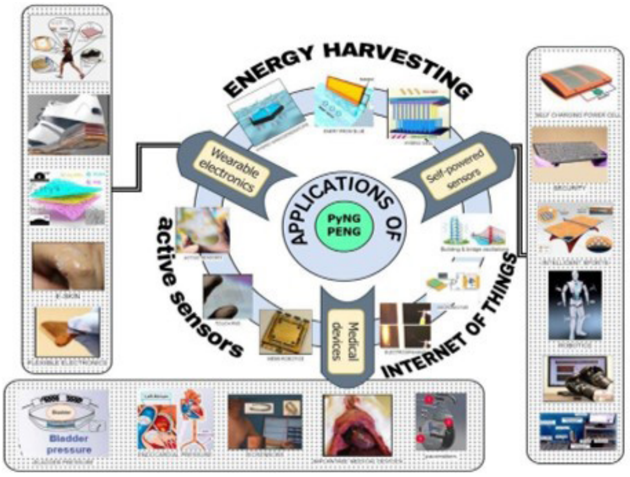

Figure 1: Applications of PENGs and PyNGs.

PENGs

In latest years, biomedical, computing, defense, human health management, synthetic electronic skin (E-Skin), and automation applications have all benefited from the use of stretchable, transportable, ubiquitous, and environmentally benign sensors [14]. Traditional pressure sensors either have to have an external power supply or have a rechargeable battery inside of them, which is dangerous in an emergency and reduces the device's ability to sense pressure. These pressure sensors solely function with various transmission mechanisms, piezo-resistive [15], and piezoelectric [16], because these sensors are capable of detecting any form of environmental stress, including pressure, moisture, and vibration analysis. Due to their self-sufficiency, great sensitivity to micro shocks, good cost efficiency, quick reaction, and sturdiness, piezoelectric pressure sensors are frequently employed. Adopted the piezoelectric effect to capture energy from human motion, such as a jogging energy collector based on a piezoelectric cantilever with a broadband performance at low frequency or low excitation level [17]. Shin et al. [17] conclude that Inorganic ceramics and piezoelectric crystals have a high piezoelectric coefficient and deliver huge power generation density compared to piezoelectric polymers.

Piezoelectric electrets are generally porous, space charges are trapped in the hole walls to form giant dipoles and exhibit a more piezoelectric output comparable to or even greater than that of inorganic piezoelectric and are considered an excellent option for mechanical energy conversion. Polyvinylidene fluoride (PVDF) and its copolymer with tetrafluoroethylene (PVDF-TrFE) are two typical piezoelectric polymers with favorable biocompatibility, piezoelectricity, adaptability, and chemical stability. PENG polymers were designed to harvest energy from walking, breathing pulsing, arm flexing, water flow, acoustic vibrations, roads, bridges, etc. [18].

Energy harvesting

The high-power density and simplistic construction design made the piezoelectric effect generate vibration energy from natural green energy. Hou et al. [18] investigates a piezoelectrically improved TENG for vibration sensing by PDMS and silicone. PDMS films with controllable ultra-small mfa structures were obtained using MEMS technology; thus, P-TPS's output power and sensitivity were notably enhanced. In addition to that, the electrical properties of P-TPS can be enhanced using enhancing the amount of BTO in the piezoelectric sheet. Based on the developed structure, P-TPS made of stretchable polymer neglects non-stretchable materials and shows improved elongation (~187.32%) [19]. In addition, it maintains remarkable output performance in various environmental pressure situations (cycle and frequency). Since no power source is required, which ensures its portability and practicality in multiple situations, the P-TPS can be easily joined to monitor the postural movement of the human body. In addition, movement data can be continuously stored and analyzed over a period by statistical analysis. This can then be evaluated into varieties of motion, such as Flexion movement of ankle, palm, and hand joints [20].

Materials for PENGs

Zinc nanorods

With a direct band gap and an exciton binding energy of up to 60 meV, ZnO has found wide application in solar cells light emitting diodes due to its direct band gap and an exciton binding energy upto 60 meV , and strain gauges In addition, due to its off-center symmetric crystal structure, ZnO exhibits excellent piezoelectric properties under external stress, enabling flexible, controlled electronics that directly utilize mechanical stimuli to generate digital signals, such as PENGs [21].

Fluorine-doped tin oxide was deposited on top of the device and rubbed, made contact with ZnPc (Zinc phthalocyanine) nanotubes to generate friction and produce electricity. The open circuit voltage for ZnPc nanotubes with a thickness of 100 nm and 300 nm is given as 0.524 mV and 968 mV. ZnPc nanotubes are a viable alternative to ZnO nanotubes in nanogenerators because of the simple manufacturing process, lower cost, high initial yield, and biocompatibility [22, 23].

3D ZnO nanosheets improve the stability and robustness of PENG. The fabricated PENG was run continuously for 3 h with no drop in output [24]. Sb-doped p-ZnO showed stability with a continuous interval of more than 18 months. In addition, Sb-doped p-ZnO showed excellent piezoelectric properties in energy sensing and conversion [25]. A negative piezoelectric load can reduce the SBH and increase the current, while a positive piezoelectric load stimulates a current drop. In addition, by using p-ZnO PENG, which works stably and independently and clearly shows the change of gesture, self-powered strain gauges capable of converting mechanical energy into electrical energy have been produced. We believe the device has potential practical applications in intelligent robots, wearable electronics, and medical surveillance systems [26].

SnS_2 nanosheets

SnS_2 nanoparticles are also used for biomechanical energy generation. The typical output power of such a PENG SnS_2 NG has an open circuit voltage of 6 mV and a short circuit current of 60 pA. Also, of note is PENG's innovative design on metamaterials (MM). The MM materials are constructed in a slide cell so that low-frequency excitations cause structural instability (i.e., instability) of the MM piezo. Then the piezoelectric layer is activated to generate current [27].

Highly efficient piezoelectric nanogenerators with silver nanowires (Ag NWs) constructed in a polymer structure are also used to harvest mechanical energy. Here, the stretchable Pyro NG is fabricated by incorporating SmPb polycrystalline piezoelectric ceramic into a (PVDF-TrFE) thin film. The wide aspect ratio g33-Sm-PMN-PT piezoelectric ceramic is selected as the piezoelectric fillers, and the high aspect ratio Ag NWs are integrated as the conductive fillers. Enhanced electrical characteristics are achieved for Ag NWs 15 wt.% with an open circuit voltage and an instantaneous power density of 83.5 V and 7.48 μW/cm^2, respectively. In specific, after two months of aging, excellent mechanical stability is achieved with extreme 6000 bending and releasing cycles of operation [28].

Other materials used in PENGs include Ce-doped barium titanate ($BaTiO_3$, BTO) and BZT- BCT/PVDF-TrFE nanofibers. Finite element analysis simulation shows that the presence of Ag NWs is advantageous for electricity generation. Therefore, due to its high elasticity, robustness, and excellent output parameters, the fabricated PENGS can be a suitable consideration for energy storage in flexible electronic device applications [29, 30].

TENGs or PyNGs

Powering Internet of Things devices requires a lot of energy gathering or scavenging. TENGs (Figure 2), when a waste heat source is available, are thought of as options for power sources in wireless sensor networks due to their capacity to convert heat into energy. Additional benefits for a variety of applications come from their small size, lack of maintenance requirements, adaptability to various environments, and potential interoperability with IC technology (particularly when

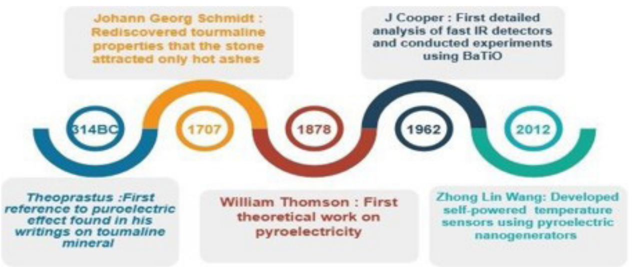

Figure 2: History of TENGs.

implemented in silicon). In order to create thermoelectric nanogenerators, several researchers have used various techniques [31-33].

Pyroelectric or Seebeck effect

In general, the least known electrical characteristic of solids property is pyroelectricity. Even though pyroelectricity has been a phenomenon known to humans for more than 24 centuries, theorizing and continuing research on it in terms of a variation in net dipole moment is a relatively recent development. The tourmaline crystal, which had the capacity to draw straws and pieces of wood, was where this phenomenon was discovered. In the two millennia that followed, scientists and authors were more interested in the stone's origin than in physical justifications for the appealing qualities of the substance it showed. Pyroelectricity was originally described scientifically in an essay published in 1717, but it wasn't until the nineteenth century that quantitative knowledge of this process started to take shape [34-36].

The temperature-dependent spontaneous polarization in particular anisotropic crystals is referred to as pyroelectricity. When exposed to a temperature gradient (dT/dt), materials with non-centrosymmetric crystal structures exhibit this phenomenon, which causes the formation of an electric current or potential [37, 38].

FOM

Based on thermal considerations and the electric circuits utilized for detection, a number of FOM are defined for the selection of material. The designer can choose a material to produce the greatest voltage or current for the specified input power thanks to the often-used FOMs for pyroelectric sensor applications is given in table 1.

High-performance pyroelectric materials frequently consist of complicated oxide systems with ABO_3 chemistry. Because the heat capacity values of these materials often fall within a narrow range (2 - 3.2 $J/cm^3.K$). It is challenging to control these variations in a way that has any real technological impact. The pyroelectric coefficient must be independently increased, and the dielectric permittivity must be suppressed, in order to optimize the pyroelectric performance of materials [39].

Applications

TENGs could be used in many ways where they could convert heat into electricity i.e., in car engines, wearable devices, mobile phones, etc., and hence could help us in a greater and more efficient way than the current energy generating methods.

Table 1: FOM with applications [38, 39].

FOM	Applications
Detectivity, Fd	Pyroelectric point sensor
Current Responsivity, Fi	Fast high-power laser pulsepyro-electric detector
Voltage Responsivity, Fv	Large area pyroelectric detector
Fc	Infrared detector
Vidicon detectivity, Fvid	Material for vidicon detector

Regeneration of heat energy in fuel cells

Fuel cells are electro-filled chemical devices that produce solid electric signal as a by-product. An analysis where they used waste heat recovery for fuel cells using TENGs in their experiment study they found out that a proton exchange membrane fuel cell and geometric energy are incorporated along with a TENGs system (Figure 3). The output analysis shows that the output power is 4 times higher than a combined heat and power system [40, 41].

High-temperature oxidation thermoelectric

The majority of the intermetallic compound thermoelectric materials with the maximum FOMs have low oxidation resistance and high sublimation rates. The oxidation triggers breakdown and the development of a resistive wave. Oxidizing layer that reduces electrical connections' quality and functional stability. If the formation of ZnO is caused by the diffuse of zinc vacancies, it could be challenging to stop it because this would require acceptor doping, which is famously challenging to achieve in ZnO. Instead, alternatively or interstitial Sb^{3+} doping is more likely to occur [42].

Thermoelectric cooler-based dehumidification system

The effectiveness of the dehumidification system must be evaluated. It took a long time to see if the system's output displays a consistent pattern over that time. so that experiment attempts to test the premise that the dehumidification system's behavior can be roughly approximated to be constant over time by examining its performance over a 12-h period. As a result, this experiment was carried out using the identical set-up for

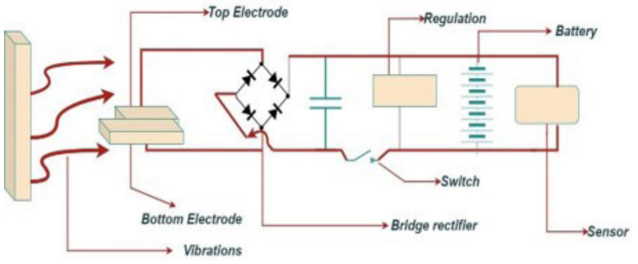

Figure 3: Energy harvesting circuit design for piezoelectric effect from vibration.

12 h, with 3.35 A current being withdrawn. A graduated measuring cup was used to determine how much water was drawn from the system at the conclusion of the experiment.

Materials used for generating pyro energy

Bi_2Te_3 used in TENGs and its properties

Pyroelectric materials have the ability to transfer thermal into electricity, known as the Seebeck effect. An experiment where they used Bi_2Te_3 and skutteramidate and sed them to see if the waste heat generated in a car could generate heat through the experiment. They also figured out that the variation in thermal conductivity of materials in the leg of TENG's provides higher output power and also that segmented power generators could be used to generate more power and hence by choosing the right ratio of TENGs material the output of the generator could increase would improve the amount of output power by the TENGs [43, 44].

Thermoelectric characteristics of X_2AGBII_6

The importance of the researched DPs for thermoelectric applications is increased by the indirect character of the band gap and a high value of the Seebeck coefficient (S). Heat-transfer characteristics, the performance scale is determined by (s, k, S) and its derivatives in terms of the FOM or thermal conductivity, is comprised of an electronic component (ke) and a lattice component (k) [40, 41]. Due to a constraint in the BoltzTraP algorithm, the e is only plotted in the calculations done right now. The k is estimated separately and has extremely low values for the examined DPs [45, 46] in the latter portion, though. The distribution at the Fermi level is controlled by the base elements (K, Rb, and Cs), which alter kE and S [47, 48].

TENGs come in a variety of designs and are made with a variety of materials and technologies. Small-scale TENGs are manufactured using silicon, germanium, bismuth, and antimony are the materials that are frequently employed in the fabrication process [49]. Another technology utilized to create high-density multi-layered TENGs is ceramics-based technology. This approach allows for the fabrication of thermocouples using thin, thick, or combination of thin and thick deposition [50]. Flexible TENGs are produced using polymer technology. The best materials for these technologies include fabric [51], cellulose-based polyimide [52], and fabric [51]. TENGs should be made of materials with high output voltage and high generated power.

TENGs material to transform waste heat into electricity is measured by a dimensionless FOM is known as ZT. Based on the "phonon glass electron crystal" model, ideal TENGs materials must simultaneously have high electrical conductivity like a crystal with high utilized electron mobility and phonon scattering. These properties are required by the "phonon glass electron crystal" model [53, 54]. The fact that these TENGs transport qualities are so intricately linked makes improving ZT more difficult [54].

Conclusion

Here, PENGs and TENGs materials used, and applications of both types are discussed and reviewed. This work also reviewed open perspectives and indexes for NGs study fields that take into account the challenges, constraints, and possibilities. In summary, this research will be useful for future studies on the best design for piezoelectric energy harvesters and thermoelectric energy harvesters based on the intended use and energy source.

Acknowledgments

None.

Conflict of Interest

None.

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