SOP Report

Electrospun Nanofibers in Wearable Sensors

Oindrila Ghosh
2018A1PS0080G
B.E. Chemical Engineering
BITS Pilani, K.K. Birla Goa Campus

Under the Guidance of:
Dr. Richa Singhal
Department of Chemical Engineering
BITS Pilani, K.K. Birla Goa Campus

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ABSTRACT

A sensor is a device that is responsible for detecting certain changes in the immediate environment and converting the signals obtained to readable and interpretable form. They are generally classified based on the application, that is, the property corresponding to which changes are being detected. Biosensors, thermal sensors, optical sensors and piezoelectric sensors are some such examples. Piezoelectric materials are capable of converting mechanical stress or force exerted on it to electrical potential, and vice versa. This property is widely utilised in developed and developing fields of sensors, actuators and harvesters. These devices can be used in wearable harvester technology, tattoo-like sensors for health monitoring, large scale energy harvesters on stretches of roads and other traffic-rich pathways, small scale harvesters embedded in wearables to enable the working of passive wearable sensors, wearable human machine interfaces, etc. Most of these make use of nanofibers made of piezoelectric materials like PVDF-TrFE and PAN, of which, recent researches in the field establish PAN as the best option. The nanofibers are synthesized using a process known as electrospinning. In fact, recent advances in the avenue also prove that electrospinning, especially in the case of PVDF and PAN, improve the piezoelectric properties, thereby enabling us to fabricate more sensitive sensors. Wearable sensors and materials used in them can be judged on the basis of certain characteristics that are referred to as performance parameters. Often, the fabrication of the sensor, the parameters of the electrospinning process, the structure and the other materials used, the additional circuitry involved and the impedance offered have a major impact on the use-cases and benefits of using the developed sensor.

1. INTRODUCTION

A sensor is a device that is responsible for detecting certain changes in the immediate environment and converting the signals obtained to readable and interpretable form. They are generally classified based on the application, that is, the property corresponding to which changes are being detected. Biosensors, thermal sensors, optical sensors and piezoelectric sensors are some such examples. In recent times, nanomaterials have found a prominent place in this field. In fact, most wearable sensors make use of electrospun nanofibers due to the many favourable properties possessed by them.

2. NANOTECHNOLOGY

Nanotechnology involves the development and use of devices in the range of 1-100 nm. This avenue of technology requires manipulation of materials at an atomic or molecular scale. The nanometer scale is smaller than the wavelength of visible light and it is necessary to opt for alternative measures to view them. This has led to the rise of different microscopic techniques - scanning tunneling microscopy (STM), scanning electron microscopy (SEM), transmission electron microscope (TEM), etc.

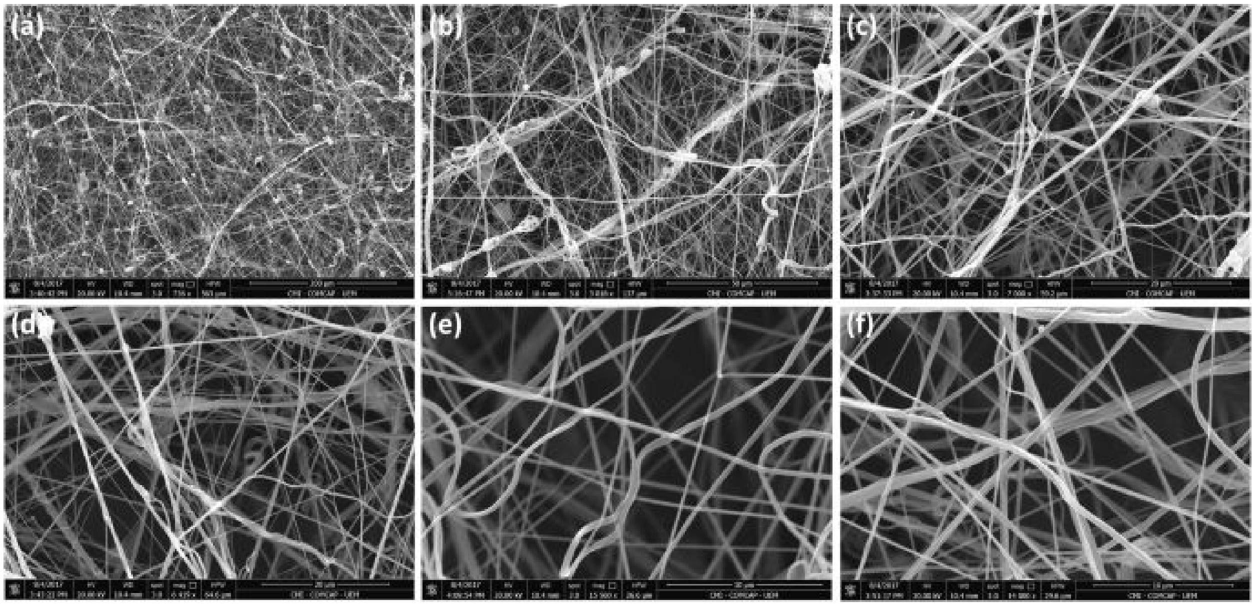

Figure 1: Scanning Tunneling Microscopy image of electrospun PVDF nanofibers

Nanotechnology often involves miniaturisation of already existing devices. For the purpose of miniaturization, it is necessary that physical laws are applicable at nanoscale. However, this is not a given. It is possible that nanoscale physical laws are not applicable or differently applicable for much smaller scales. A study in 2012 established that, contrary to expectations, the Ohm's Law is in fact still valid when the wires are just one atom high and four atoms wide. It is believed that the high level of doping and the absence of surface effects are responsible for the Ohm's Law's survival down to the atomic scale.

Today nanotechnology is a rising and very promising field. The government of the USA put forward a budget of $ 1.8 billion in 2013 for the US National Nanotechnology Initiative.

2.1. NANOMATERIALS

"Nanomaterials are an arrangement of molecules and atoms, that when combined, form stable building blocks that can be made into larger and more complex materials and structures."

Everything is made up of nanomaterials. In nanomaterials, the surface, boundary or interface plays a very important role. Taking the example of catalysis, we know that the surface are to volume ratio is an important characteristic. As this value increases, the catalytic activity increases as catalytic phenomenon occurs at the surface. In general, as characteristic dimensions decrease, the surface area to volume ratio increases. This implies that more units (atoms/molecules/ions) are found on the surface compared to that in the bulk resulting in a greater contact with the reacting medium. This increases the catalysis. Clearly, nanomaterials are favourable in catalytic phenomenon. Large surface area also makes nanostructured membranes and materials ideal candidates for applications like water treatment, drug delivery, desalination, clothing insulation, etc.

Thus, we can conclude from this that nanomaterials are far more active compared to micro/macro scale materials. Almost all types of nanomaterials are capable of catalysing reactions and free nanomaterials tend to agglomerate into bigger particles.

2.2. NANOSTRUCTURES

A nanostructure is simply a structure that has at least one dimension in the nanoscale range, that is 1-100 nm. Nanostructures can be subcategorized into four types:

1. **Nanoclusters:** These are nanostructures that are in the nanoscale range in every spatial dimension. These are also referred to as 0 - dimensional nanostructures.
2. **Nanotubes/fibers/rods/wires:** These are 1 - dimensional nanostructures with a diameter in the nanoscale range, while the length can be much greater.
3. **Nanocomposite surfaces/films/coats:** These are 2 - dimensional nanostructures with a thickness in the nanoscale range and two other dimensions being much larger.
4. **Polycrystals:** These are bulk materials with all dimensions greater than the nanoscale range but composed of 0/1/2 - dimensional nanostructures. They are also referred to as 3 - dimensional nanostructures.

2.2.1. 0-D NANOSTRUCTURES

This category consists of nanoparticles. Nanoparticles are small structures with radius in the nanoscale range, that act as a whole unit with respect to its transport properties. These rea dependent on the size, implying that the properties change with change in the size of the nanoparticles. This is primarily because of the change in the number of particles present on the surface compared to that in bulk for reasons explained previously.

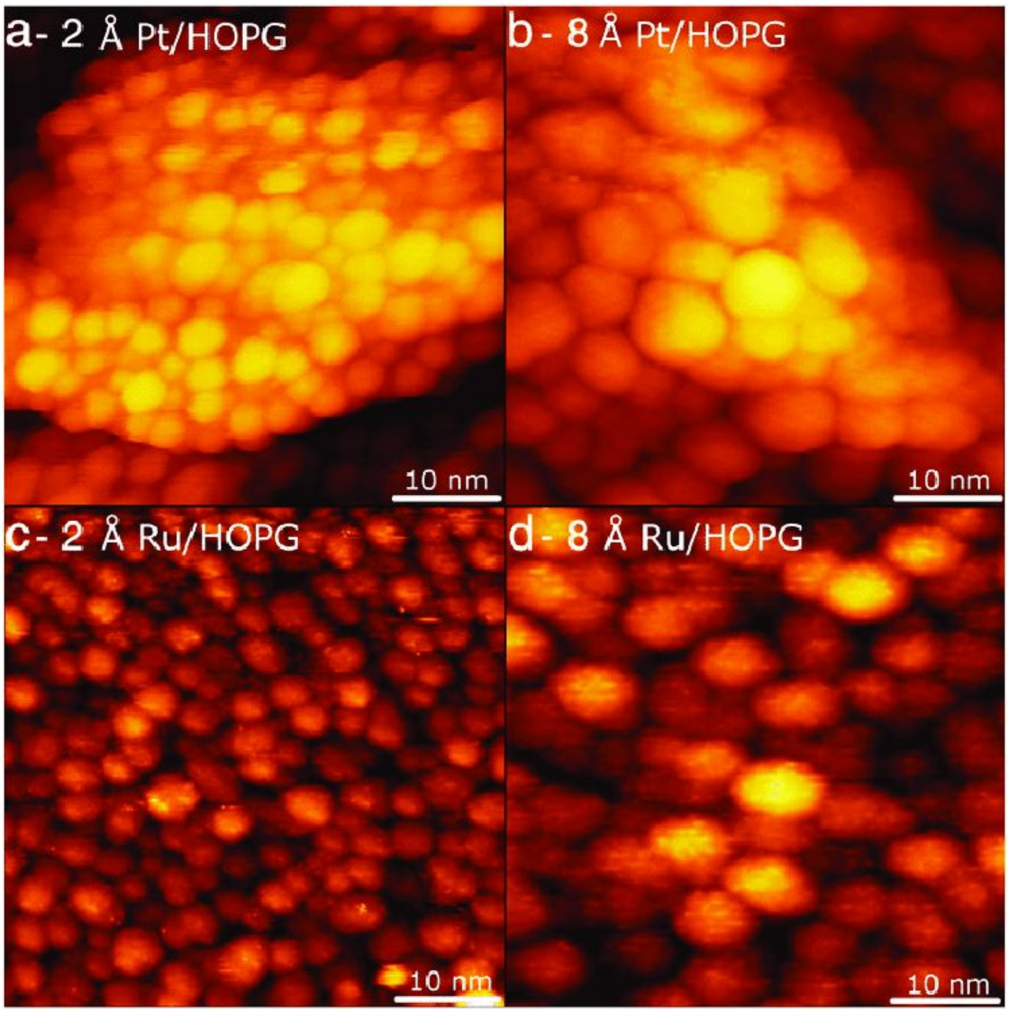

Figure 2: Scanning Tunneling Microscopy images of Platinum nanoparticles

Nanoparticles are small enough to confine electrons and produce quantum effects, and thus, possess various optical properties. There are less than 10^6 atoms per nanoparticle. Other size dependent properties include quantum confinement in semiconductor particles and surface plasmon resonance in certain metal nanoparticles. Some applications of the same are as follows:

1. **Stained Glass:** small metal oxide nanoparticles of the size comparable to the wavelength of light are used to impart a glittery effect to decorative glass.
2. **Photography:** Earlier, small colloidal silver particles used to be used for image formation.

2.2.2. 1-D NANOSTRUCTURES

These nanostructures generally have diameter in the nanoscale range and a length that is much larger. The two most commonly used subcategories are nanowires and nanotubes.

1. **Nanowires:** These have unconstrained length. They can be conducting, insulating or semi-conducting depending on the requirement. They also are crystalline. Molecular nanowires are composed of repeating molecular units, which may be organic, like DNA or even inorganic. The newest types include core-shell and superlattice nanowires. At the nanometer scale, quantum mechanical effects are important and thus, we also have quantum nanowires. Nanowires exhibit quantum confinement effects. Changing the wire diameter affects the bad gap and the thermal conductivity. Nanowires have two quantum confined directions while still possessing one unconfined direction for electrical conduction. This makes it possible to use nanowires in applications where electrical conductivity is a necessity. Due to the unique density of electron states, smaller diameter nanowires exhibit different optical, magnetic and electrical properties compared to the bulk 3-D crystalline nanostructures.

2. **Nanotubes:** Nanotubes can be subcategorized into organic and inorganic. Among the organic examples, carbon nanotubes are by far, the most popular and commonly used. Carbon nanotube is made up of a sheet consisting of a hexagonal network of carbon atoms, which is rolled to form a tube like structure with a diameter in the nanoscale

range. The two ends are capped with half Bucky-Ball like carbon structures. There may be single or multi walled nanotubes. Generally, the walls of carbon nanotube are made up of a single carbon atom thick sheet. The sheets are rolled in specific chiral angles. The properties of the nanotube are decided by the chiral angle as well as the radius. Individual nanotubes generally align themselves naturally into ropes held together by forces like the Van der Waals force or pi-stacking.

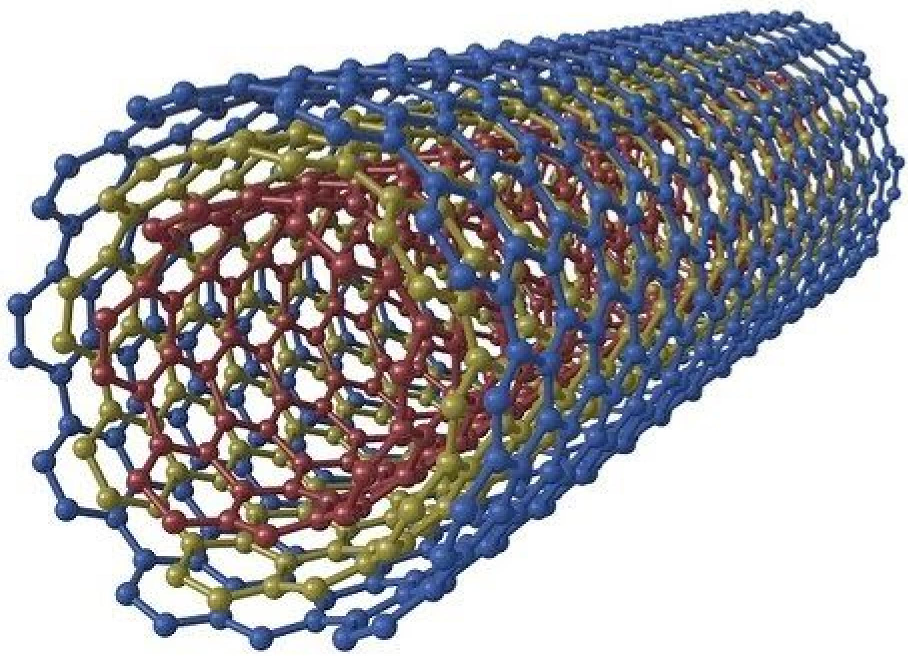

Figure 3: Structure of multi-walled carbon nanotube

Carbon nanotubes have extraordinary thermal conductivity, mechanical properties and electrical properties. In fact, they are 100 times stronger than and only 1/6th the weight of steel. This is the reason why they are often used as additives in structural materials. For example, in carbon fibers, basketball bats, golf clubs and car parts. Most inorganic nanotubes are made of metal oxides. They posses the following properties:

a. High crystallinity
b. Easy synthetic access
c. Pre-defined electrical conductivity

d. Good adhesion to a number of different polymers
e. Dispersion
f. High impact resistance
g. Good uniformity

Clearly, they are good candidates for use in impact resistant applications and for the making of polymer composites with superior thermal, mechanical and electrical properties. However, inorganic nanotubes are heavier than carbon nanotubes. Some examples of inorganic nanotubes are:

a. Boron nitride (BN) nanotube: They are:
    i. Resistant to oxidation
    ii. Semiconducting
    iii. Young's Modulus = 1.22 TPa
    iv. Predictable electronic properties
    v. Suitable for high temperature applications
b. Silicon Carbide (SiC) nanotube: They are:
    i. Resistant to oxidation
    ii. Suitable for application in harsh environments
    iii. Capable of functionalising surface Si atoms

2.2.3. 2-D NANOSTRUCTURES

This category of nanostructures include thin films, planar quantum wells, nanocomposite surfaces and coatings, etc. thin films refer to single two-dimensional films made of nanomaterials and with a thickness within the nanoscale range, that is, between 1 - 100 nm.

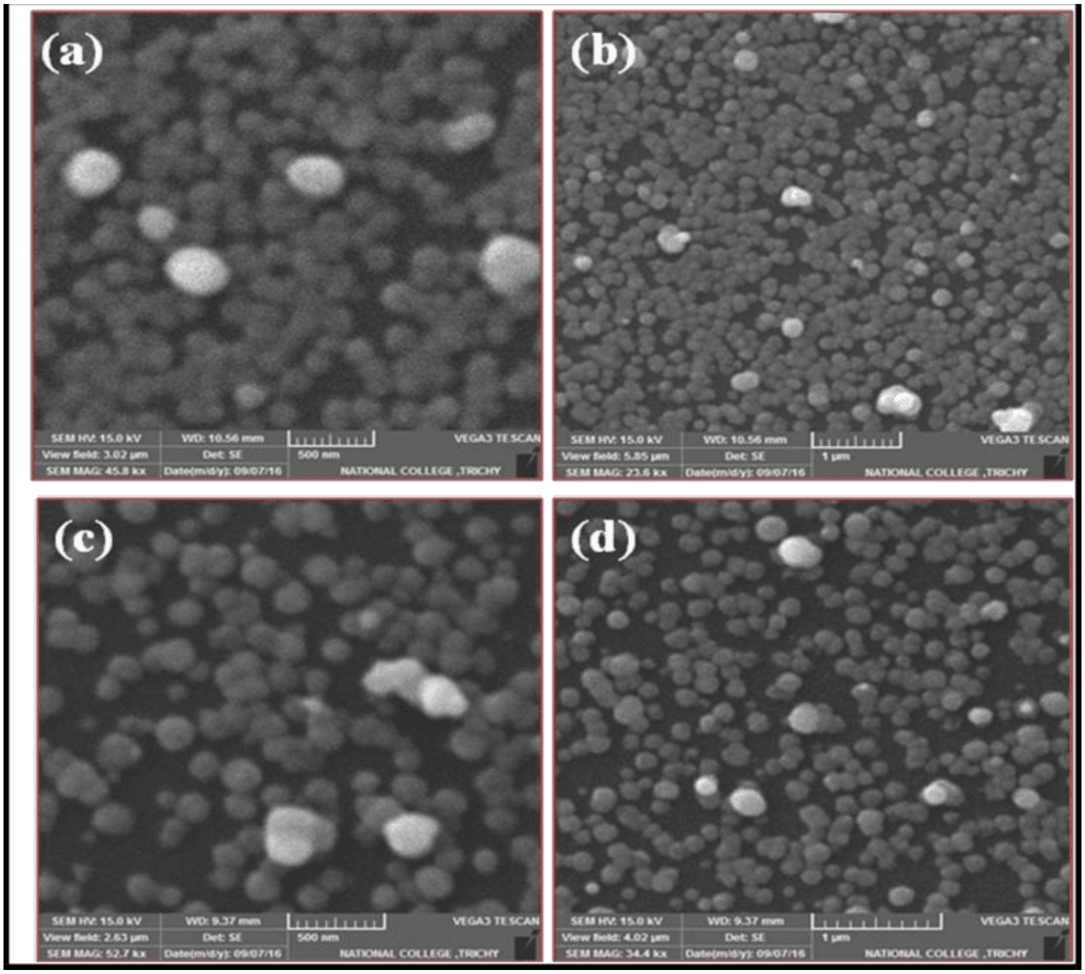

Figure 4: Scanning Electron Microscopy image of CdS thin film

Electronic and optical properties of thin films are widely different from those of the bulk materials. As materials approach the nanoscale range, the confining dimensions decrease. Both electrons and phonons are thus confined in one direction, and this affects the various properties. The energy spectrum in this case is discrete, in stark contrast to the continuous spectra of bulk materials. The measurement is thus done by quanta and the characteristics are not defined as average by bulk. The confinement of electrons also affects the interaction with electromagnetic radiation. Electrons are confined in a direction perpendicular to the substrate and this affects the wave function as well as the density of the states. The confinement of phonons in a direction perpendicular to the substrate affects the thermal properties. The transport phenomena in 2 - D structures are affected by the fixed boundaries and interfaces that may or may not exist in or in the vicinity of the thin film.

2.2.4. 3-D NANOSTRUCTURES

This category of nanostructures consists of bulk nanocrystalline films and nanocomposites. Nanoscale based bulk materials often have different chemical, physical and mechanical properties compared to macroscale materials. They may be classified into three main categories:

a. **Crystalline or multi-layer nanoscale thin films:** The atoms/molecules/ions that make up the material are arranged in an orderly fashion through a pattern that repeats itself. This arrangement has a large range order. For example, diamond (each diamond is a single crystal).
b. **Polycrystalline materials with nanostructured grain sizes (<100 nm):** Materials that are large enough for us to see using naked eyes are seldom composed of a single material. They are composed of a large number of crystallites (singular crystals). The size of these crystallites may be very small (nanoscale range) or large (several metres). Almost all metals and ceramics are crystallines.
c. **Amorphous/Glassy materials:** These are non-crystalline solids and have short range order. Glass, plastics and gels are examples under this category. It may possess order, for a short range, at the atomic length scale due to various types of chemical bonding.

Nanocomposites are composed of materials, of which at least one possesses dimensions in the nanoscale range. They can include combinations of organic and organic, inorganic and organic, inorganic and inorganic materials. Generally, the term "nanocomposites" refer to a solid combination of a belt matrix and a nano dimensional phase differing in properties. The mechanical, electrical, thermal, optical, electrochemical and catalytic properties of the nanocomposite differ widely from those of its constituents. Generally, the properties are enhanced. The size limits for various effects currently exist in literature. For example:

1. **Less than 5 nm:** used for catalytic activity
2. **Less than 20 nm:** used for making hard magnetic materials
3. **Less than 50 nm:** used in applications involving changes in the refractive index

4. **Less than 100 nm:** used for achieving superior mechanical strength or for restricting matrix dislocation movements

Addition of carbon nanotubes increases the electrical and thermal conductivity. Other kinds of nanoparticles may enhance the following properties:

a. Dielectric properties
b. Heat resistance
c. Optical properties
d. Mechanical properties
    i. Stiffness
    ii. Strength
    iii. Resistance to wear and tear

3. SENSORS AND THEIR CONSTRUCTION

"A sensor is a device, module, machine, or subsystem whose purpose is to detect events or changes in its environment and then, send the information to other electronics, frequently a computer processor."

Sensors are actually pretty diverse and are used extensively on a day to day basis. However, many of these setups are still not portable and this is primarily due to the large size of the devices.

"Nanosensors are nanoscale devices that measure physical quantities and convert these to signals that can be detected and analysed."

A typical sensor has primarily 3 parts:

a. **Receptor:** Receptor, also called a recognition element, is capable of interacting with the target molecule/analyte and producing a recognition signal.

b. **Transducer:** Converts one type of signal to another, generally electrical signal. The reason is that variation in certain kinds of signals are easier to read and analyse. There are several different types of transducers like pressure transducer and optical transducer.

> *"Transducers are devices that convert variations in a physical quantity, such as pressure or brightness, into an electrical signal, or vice versa."*

c. **Amplifier/Transmitter:** Often the signal obtained is too mild. An amplifier/transmitter amplifies the signal or conditions it. This step is optional and depends on the application. Often they are converted to an industry standard signal (4 - 20 mA).

The signal is then recorded and processed to get the results, analyse them and draw inferences.

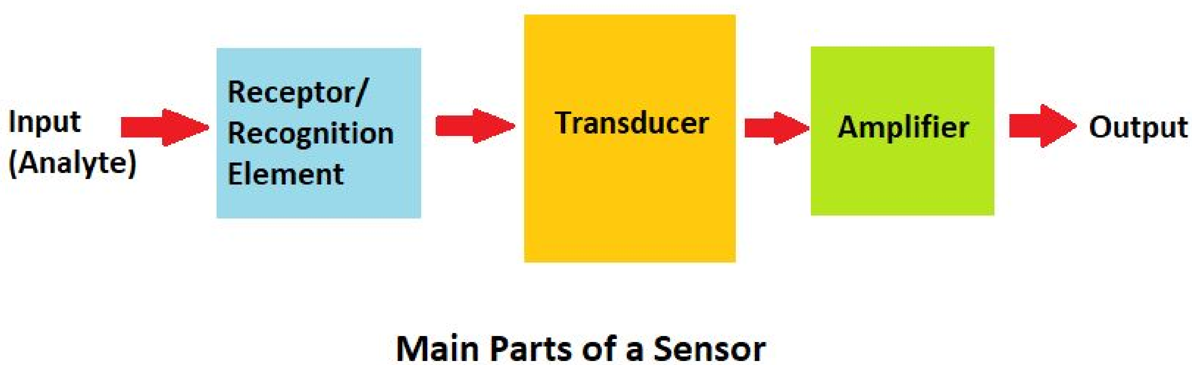

Figure 5: The main components of a typical sensor

Some applications of sensors are as follows:

1. Traffic lights change signals based on responses from the signals sent to it from sensors embedded in roads.
2. Automatic doorways in departmental stores.
3. Pressure and temperature sensors used in plants for process regulation.

Sensors generally detect different physical properties as follows:

1. Level
2. Flow

3. Temperature
4. Pressure
5. Speed
6. Position

Sensors can generally be subcategorized into the following two categories:

1. **Active:** This does not require an external source of power to operate. Examples:
    a. Thermocouple (the voltage changes on change in temperature and no external power source is required in the process).
    b. Piezoelectric sensor
2. **Passive:** Requires an external power supply. Examples:
    a. RTD (Resistance Temperature Detector). In this example, the resistance changes with change in temperature but to take advantage of this, an external source of power or excitation circuit is connected to obtain a change in voltage.
    b. Strain Gauge

Most sensors return electrical signals as these are the easiest to read. Such signals are of two main types:

1. **Digital Signal:** on/off signal
2. **Analog Signal:** range of values within specific limits

Digital/Binary sensors are among the most commonly used sensors. These often make use of limit switches, that switch on/off and thereby, return a signal when the element being sensed reaches extreme values defined beforehand. For example, proximity sensors are used to detect metal objects close by using magnetic fields. They have only two responses: yes or no. Most optical, capacitive, ultrasonic and auxiliary sensors come under this category. Most temperature, pressure, humidity, distance and speed sensors are analog sensors.

3.1 TRANSDUCERS

A transducer is a device that converts one form of energy/signal to another. It converts the measured signal to a usable signal. Generally, the output signal is an electrical quantity like voltage, frequency or current. The reason is that it is easier to analyse and read electrical signals due to the huge advancement in the relevant fields till date. Transducers are of two main types:

a. **Active transducers:** These are self generating type and do not need an external source of energy to run. Some examples are as follows:
    i. Photovoltaic transducers
    ii. Thermoelectric transducers
    iii. Electromagnetic transducers
    iv. Piezoelectric transducers
    v. Photoelectric transducers
b. **Passive transducers:** These require an external source of power for their operation, that is, they are not self-generating types. These are more common than active transducers. Generally an energy harvester is designed to generate the power required for the operation of the sensors.

Wearable sensors are today used and are being developed for various medical applications, among others. As the sensor itself is small and the overall set up has to be portable and wearable, compact harvesters that store energy obtained from renewable and clean sources, and supply to the wearable sensors for operation, are being developed.

3.2. PERFORMANCE PARAMETERS

The performance of a sensor can be characterised by a number of parameters that are referred to as the Performance Parameters. Some of the performance parameters are as follows:

1. **Specificity:** This refers to the ability of a particular sensor to detect a specific analyte in the presence of other analytes, that may or may not be structurally and functionally similar to the target molecule (required analyte). The recognition element may possess

group specificity, meaning it is capable of recognising a set of analytes. Generally, we require high specificity, especially for research purposes.

2. **Sensitivity:** This is an indication of how much the sensor's output changes with a small change in the input quantity. Thus, if we plot a graph of the signal versus the analyte, higher slope indicates a high sensitivity. High sensitivity allows us to detect the smallest changes in the signal and helps us to differentiate between two very close signals very easily. Generally, high sensitivity is preferred in a sensor.
3. **Dynamic Range:** It is the range of the input quantity, over which the output signal of the sensor varies in a monotonic manner with changes in the input signal. The output in this range is highly predictable.
4. **Reusability:** It is the ability to use a particular sensor multiple times, without loss in efficiency. Reusability is preferred over use-and-throw sensors. The reasons behind this are multifold. The most important reasons are the fact that reusable sensors are cost-effective and are more environmentally friendly compared to non-reusable sensors.
5. **Reproducibility:** This is the ability to obtain the same response corresponding to the same input signal under the same conditions, at different points of time and different places.
6. **Limit of Detection (LOD):** This refers to the minimum input signal to which a response signal can be obtained from the sensor at a specific confidence level. Lower LOD implies smaller signals can be detected and this is generally preferred.
7. **Limit of Quantification (LOQ):** It is the lowest input signal level at which the output is quantitatively meaningful. Generally, LOQ is greater than LOD.

As far as wearable sensors are concerned, we need them to be reusable and their performance should not drop a lot with wear and tear. In medical and other precise applications, the LOD, LOQ, sensitivity and specificity are also high. Reproducibility is a necessity for commercial production and making sure that high batch to batch variation in the sensors performance does not exist. Reproducibility thus helps us have a level of confidence in the sensors. In addition, specifically for wearable technology applications, the sensors used should be flexible, that is, its performance should not degrade drastically with repeated folding/bending/stretching. It should also not be toxic to the skin and should be able to conform to it, if required, depending on the application.

4. ELECTROSPINNING

As mentioned previously, nanofibers are materials that possess a large length to diameter ratio. Nanofibers possess various favourable properties such as follows:

a. Large surface area to volume ratio
b. High porosity
c. Small pore size
d. Low density
e. Excellent mechanical properties
f. Thin and lightweight

These properties make nanofibers a good choice for applications in tissue engineering, drug delivery, wearable sensors and other related fields. There are various ways for fabricating nanofibers:

a. Electrospinning
b. Melt Processing
c. Interfacial Polymerisation

Electrospinning is a process for electrostatic production of nanofibers. It uses electric force to draw charged threads of polymer solutions or melts. The process was patented by F.J. Cooley in May 1900 and February 1902 and by W.J. Morton in July 1902. The process is largely applied to the production of fibers with diameters in the nanoscale range using large and complex molecules. While often polymer solutions are used for the purpose, polymer melts are also used as this ensures that none of the solvent molecules are present in the final product. Electrospinning is highly preferred because it does not require high temperatures or coagulation chemistry. The process itself has characteristics of the conventional dry spinning of fibers as well as electrospraying.

4.1. APPARATUS REQUIRED

For the purpose of electrospinning, the setup has three main components:

a. High voltage power supply (5 - 50 kV)
b. Syringe pump with a metal needle (spinneret)
c. Collector (which is grounded and may or may not be rotating, in order to collect the fibers)

The material used is generally a polymer solution, particulate suspension, sol-gel or melt.

The main forces involved are:

a. Electrostatic repulsion
b. Surface tension
c. Molecular cohesive forces

4.2. PROCESS

When a high voltage is applied to a liquid, it becomes charges. In any drop of this liquid, two opposing forces act: the electrostatic repulsion force and the surface tension. The integrity of the drop is maintained while the surface tension is much larger than the opposing force. As the values approach each other, the droplet tends to distort and elongate. At a critical point, when the repulsion xceeds the attractive force of surface tension, a stream of the liquid erupts from the surface. At this point and onwards, the base of the stream appears as a cone, commonly referred to as the Taylor Cone. If the molecular cohesive force among the particles of the liquid is high, the stream does not break up and a charge liquid jet is obtained. Otherwise, droplets are electrosprayed.

This property is used in the electrospinning process. A voltage is applied to the polymer solution/melt causing it to get charged. The injection pump is capable of pumping the polymer solution into the metal needle. The high voltage power supply generates an electric field between the needle and the grounded collector. When the force of the field exceeds the surface tension of the solution/melt, a Taylor Cone is formed at the tip of the needle and an electrically charged jet is obtained from its tip, which travels towards the collector. Often the collector is a grounded rotating drum and the fibers get collected around it.

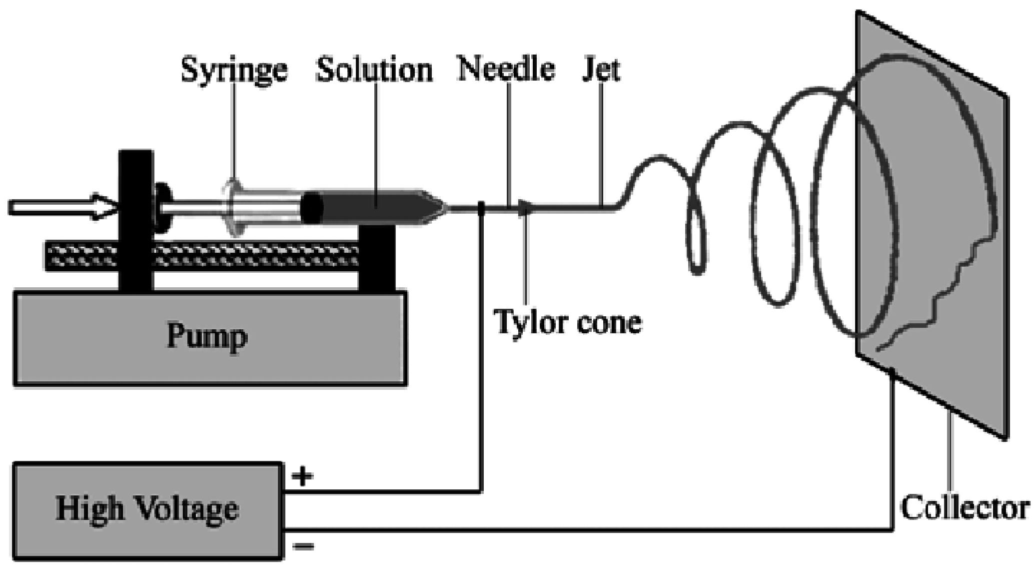

Figure 6: Setup required for electrospinning

The jet dries in flight and this causes the mode of current flow to change from Ohmic to convective (the charges migrate to the surface of the fiber). Before being collected on the collector, the jet is elongated by a whipping process caused by the electrostatic repulsion initiated at the small bends in the fiber. This elongation/thinning process results in uniform nanofibers.

4.3. PARAMETERS

The various parameters that affect the process are as follows:

a. Physical properties of the polymer solution/melt (molecular weight, intermolecular bonding/forces, viscosity, conductivity, surface tension, etc)
b. Electric potential applied
c. Distance between the spinneret and the collector
d. Size and motion of the collector
e. Ambient conditions (temperature, humidity, air velocity, etc)
f. Needle properties

By controlling these parameters, we are capable of regulating the efficiency and scaling up the process. There are thus, various variations on the conventional electrospinning process, which are employed based on the application. Some examples are as follows:

a. Coaxial electrospinning
b. Emulsion electrospinning
c. Melt electrospinning
d. Needleless electrospinning
e. High speed electrospinning
f. Rotating roller electrospinning

4.4. APPLICATIONS

Nanofibers produced by the process of electrospinning possess the following properties:

a. Enhanced physical properties. For example, electrospun PVDF or PAN nanofibers show higher piezoelectric effect than dense films.
b. Relatively defect free structure at the molecular level and this allows the nanofibers to reach the theoretical maximum strength of the spun material thus, allowing high mechanical performance.
c. Very high surface area to volume ratio and thus, beneficial in applications requiring physical contact.

These properties make electrospun nanofibers favourable for applications in various fields, including but not limited to:

1. Nanofiber webs as filtering medium
2. Textile manufacturing (used in wearable sensor applications)
3. Nanofibrous wound dressing, tissue engineering and other medical applications
4. Making of surfaces to immobilize enzymes and use as catalysts.

Figure 7: Applications of electrospun nanofibers

5. WEARABLE SENSORS

Wearable sensors refer to sensors on wearable technology, often used or envisioned to read important clinical data. They are incorporated in wearable items like glasses, watches, shoes, shirts, etc. Currently there are pressure, temperature and strain sensors available that can realise full body motions.

"Wearable and flexible electronics are popular because of their combination of related base functions with stretchability and foldability."

The main necessity in such applications is that the performance of the sensor should not decrease considerably on being subjected to repeated bending/folding or stretching.

Wearable/flexible sensors are used in:

1. Roll up displays, touch screens and electronic papers
2. Active radio frequency identification tags and other military garment devices
3. Biomedical devices and nanoengineered flexible textiles

5.1. SMART TEXTILES

"Smart textiles are textile products such as fibers, filaments and yarns together with woven, knitted or non-woven structures, which can interact with the environment or the user."

The use of nanomaterials in smart textiles helps give it function without altering the comfort properties of the substrate. Textiles, especially those which are cotton-based, are ideal substrates for integration of nanomaterials and other devices. They mabe be built-in or embedded.

The final product is:

1. Comfortable and can be worn
2. Lightweight
3. Flexible

The benefits of the use of each of the two components, that is, the flexible electronics and textiles, are as follows:

1. Modern electronics: computational capacity and speed
2. Fiber assemblies: flexible, wearable and continuous nature

Thus, the selected material must satisfy weight, performance and appearance properties for use in wearable/flexible electronics.

5.2. EPIDERMIS AS AN INFORMATION BARRIER

The epidermis is the first line of defence in our immune system. It:

a. Prevents the entry of foreign particles that may be potentially harmful
b. Prevents the loss of bodily fluids and water
c. Protects that underlying tissue from injury and UV rays of the sun, etc

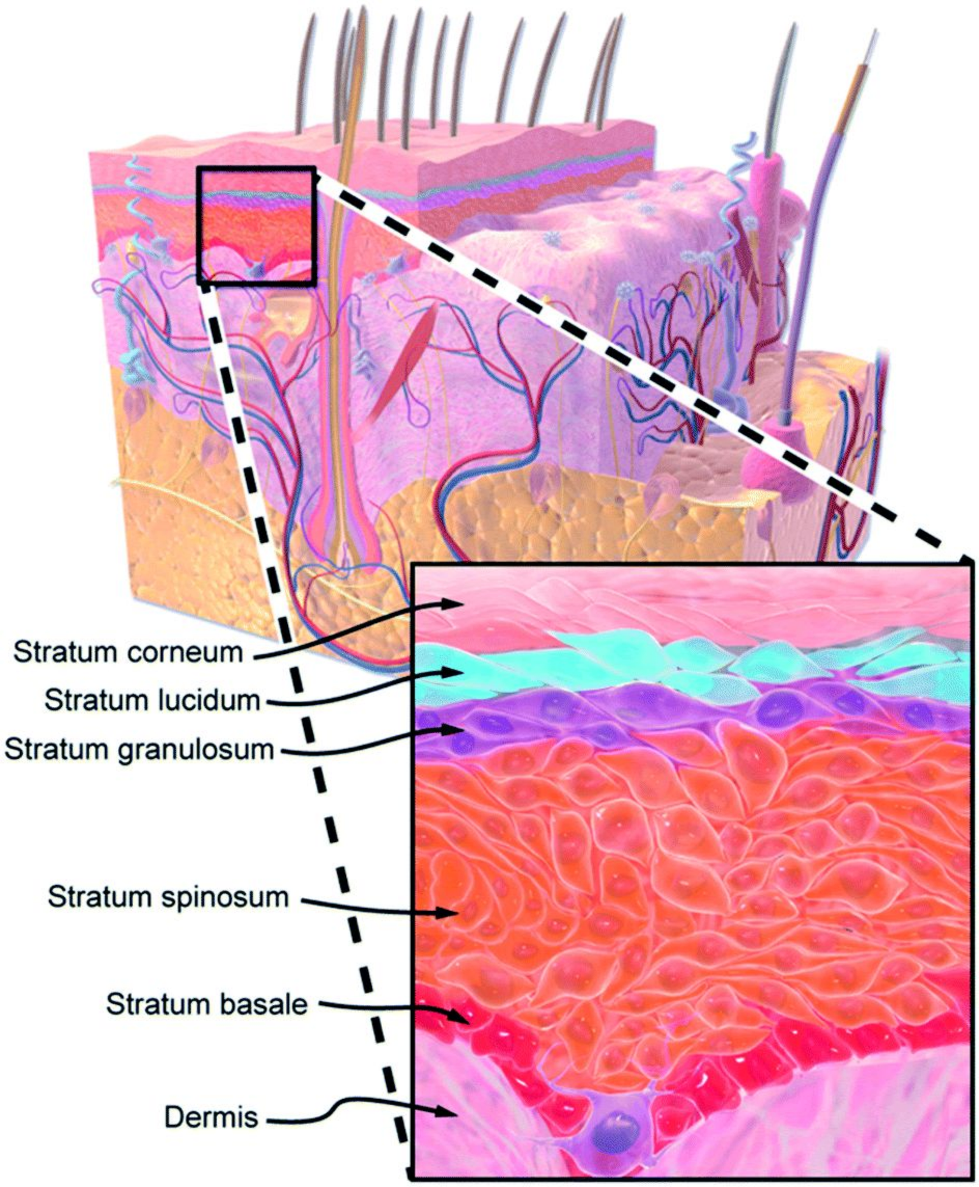

Figure 8: Diagrammatic cross section of the human skin

The stratum corneum, which is the top most layer, is dry and oily. Thus, it is electrically resistive. The epidermis is "soft and stretchy" and can slide over the organs lying underneath. This leads to dampening of the mechanical effects inside the body. This is the reason why, when it comes to wearable sensing, the epidermis is an information barrier and not an information source.

There are certain applications, however, wherein the epidermis is not a barrier. This includes applications like wound healing and transdermal needle based glucose monitors. Nevertheless, these are partially invasive in nature as they involve a non-natural opening through the skin. Wearable sensors are generally non-invasive.

5.3. COUPLING TO THE SKIN

For a wearable sensor to work for a wide range of applications, it should be possible to couple the equipment to the skin. For this, the main requirement for the material that the sensor is composed of is to match the modulus of elasticity of the skin. The two most commonly opted for choices are as follows:

1. **PDMS (Polymethylsiloxane):** This is a very common silicone elastomer. The Young's modulus of this material is 3 MPa. This implies that it is way too siff, when compared to the human skin. Thus, if the wearable sensor is made of PDMS, it can lead to delamination.
2. **Ecoflex (Smooth-on):** This is a silicone elastomer too. However, this is much softer compared to PDMS. In fact, the Young's modulus is around 125 kPa and this almost matches the value associated with the skin. Thus, a wearable sensor made of ecoflex could easily maintain conformal contact with the human body without getting delaminated.

Clearly, Ecoflex is the better option among the two.

5.4. MECHANICAL IMPEDANCE

The human skin is complex and highly anisotropic and produces a non-linear stress-strain curve when elongated. The deformation is limited. The collagen fibers of the dermis align at around 30% strain and this prevents further deformation. The Langer Lines are specific directions on the human skin, along which the modulus of elasticity is the least. Thus, the mechanical properties of the skin are also orientation specific.

In addition to these, the Young's modulus of elasticity of the skin varies with age, hydration and location on the human body. The skin is frequency dependent too and thus, can be modelled as springs, dampers and masses. When the skin is stimulated with a variable mechanical input, the mechanical impedance offered by the skin varies as a function of frequency. As the frequency of the normal force increases, the mechanical resistance offered by the skin and its elasticity consequently increases. This implies that the skin becomes stiffer.

In order to evaluate the shear wave attenuation along the skin elastic wave propagation systems are used. The conclusions are as follows:

a. Shear waves propagate along the surface of the human skin when the frequency is low.
b. Shear waves propagate through the bulk of the dermis, which contains mucopolysaccharide (water-gel components)at higher frequencies.

Shear waves are transmitted through viscous coupling within the human skin. Water affects the viscosity of the stratum corneum. This can affect the mechanical properties of the human skin.

These effects are especially important in mechanical sensors. The different modalities of the same are as follows:

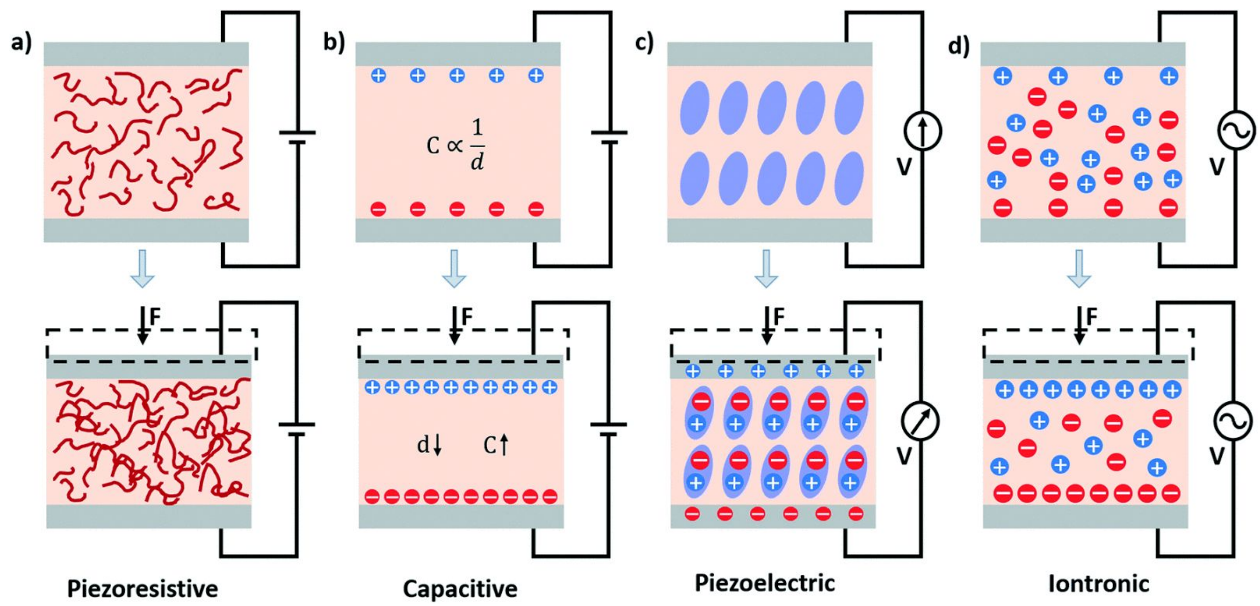

Figure 9: The different modalities of mechanical sensors

5.5. MECHANICAL NOISE

The mechanical noise present can be of two main types:

a. **Motion induced noise:** This highly affects the use cases, especially in wearable technology applications. Motion induced noise is due to body movements due to various bodily functions and life-supporting processes, for example respiration (inhalation and exhalation). Activities like bending also contribute to the noise. The noise in these cases can be reduced by making use of a redundant sensor. Algorithms are applied to pick out the real signal from all the noise.
b. **Sensor intrinsic noise:** These are of various kinds and negatively affect wearable mechanical measurements. Some examples are: temperature noise (especially in the case of resistive sensors) and parasitic noise (in case of capacitive sensors).

5.6. STRETCHING

In most wearable applications, stretchability is a necessity. We know:

$$\xi = d/2r$$

where, ξ = bending strain

r = thickness

The main conclusion that can be drawn from this is that very thin materials tend to be able to withstand much higher bending strains. However, these materials fracture at tensile strains of around 1%.

5.7. ELECTRICAL IMPEDANCE

The naturally occurring ionic flows and pulses in the human body can easily be picked up by sensors and transduced to measurable signals. These interfere with the desired signals. The ionic flows are time dependent and can be easily seen in the outputs of the wearable sensors. Actuators face a similar issue- they get stimulated by alternate causes of motion on the skin surface. Clearly, the quality of the recordings obtained from wearable electronics and the efficiency of stimulation depend on the electrical impedance offered by the skin interfaced electrodes used on the human body.

In order to reduce these effects, we can make certain simple changes to the electrode-skin-body interface. It is possible to achieve a “wet” electrode contact using a hydrogel or electrically conductive adhesives. These contain electrolytes and are the best kind of interfaces possible. An additional benefit of this kind of a setup is that its prolonged use can hydrate the skin which thereby reduces the impedance offered by the skin. The electrical impedance offered by the skin when a dry electrode is used varies with the smallest changes in the pressure of electrode contact.

For calculation and modelling purposes, we can evaluate the impedance offered by the skin by approximating using equivalent circuits. The behaviour of the different structures and the properties of the different layers of the skin can be represented as resistors, capacitors, etc depending upon their net effect.

5.8. ELECTRICAL NOISE

Electrical noise often hinders electrical measurements in wearable sensors. They can have various origins. Four such noises that are often detected and are commonly known are as follows:

a. **Body noise:** This kind of noise is unavoidable and is due to various kinds of muscle movements which may or may not be voluntary. Body noise is not dominating and can be easily regulated using data processing techniques.
b. **Skin-electrode interface noise:** This is among the most significant sources of electrical noise. As already mentioned, this kind of noise can be significantly reduced by using a wet electrode.
c. **Motion artifacts:** These are caused due to the relative motion between the electrode and the electrode. This kind of noise can be reduced by making some design changes. The sensor must have robust mechanical attachment to the skin. Generally, materials with Young's Modulus similar to that of the skin are used for construction to accomplish this.
d. **Environment noises:** There may be interferences from various external sources like charges in the air, other electronic appliances nearby, wiring, etc. Most of these kinds of noises can be dealt with by insulating cables and shielding appliances, electrodes, etc.

5.9. MEASUREMENT OF IMPEDANCE

The impedance offered by different structures including the human skin can be approximated using equivalent circuit models. The electrically conductive areas can be modelled as electrical wires and based on the characteristics and effects of the different structures or "zones", they can be approximated as resistors (R), capacitors (C) or inductors (I). All of these are associated with a definite va;ue of impedance. They are arranged in series or parallel to better simulate the actual effects. The net impedance can then be calculated.

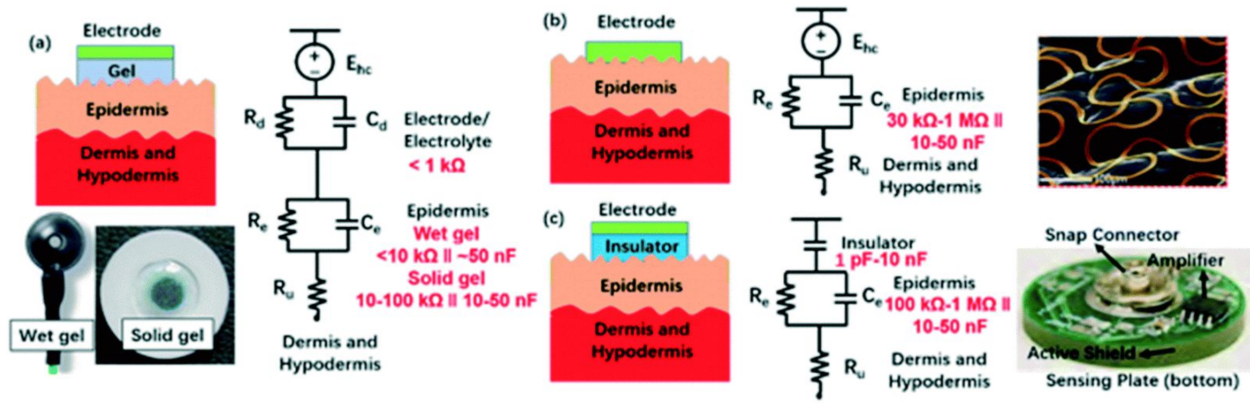

Figure 10: Equivalent circuits for skin-electrode interfaces for different designs. (a) Wet electrode contact (b) Dry electrode contact

In this picture, we can see how it is possible to model the extremely complex structures and layers of the skin as an equivalent circuit to evaluate the impedance with ease.

In general, when a piezoelectric crystal is employed in a circuit, it can be represented in the form of a voltage source/ signal generator/ charge source that is in parallel with a resistor (R_{cry}) and a capacitor (C_{cry}) as shown below.

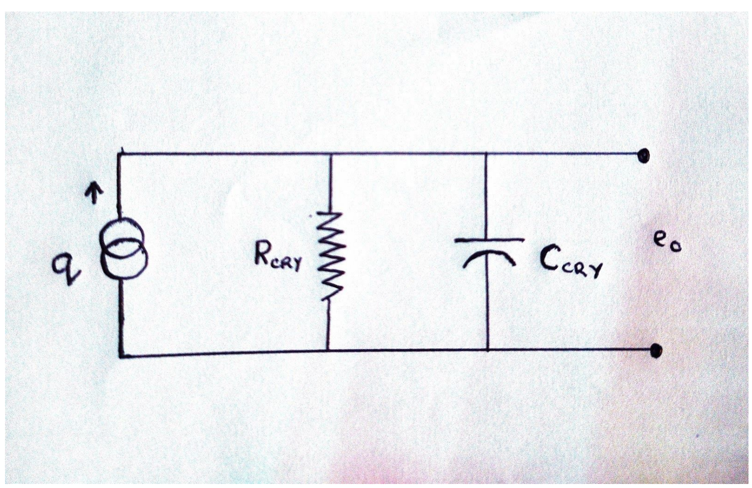

Figure 11: Equivalent circuit of the piezoelectric crystal

Usually when piezoelectric crystals are employed, the output signal needs to be amplified before it can be measured or analysed. For this, an amplifier is required, which offers its own impedance in the form of a parallel arrangement of a resistor (R_{amp}) and a capacitor (C_{amp}). The amplifier is connected to the crystal by the means of cables, which offer a net capacitance (C_{cab}). This can be represented as follows:

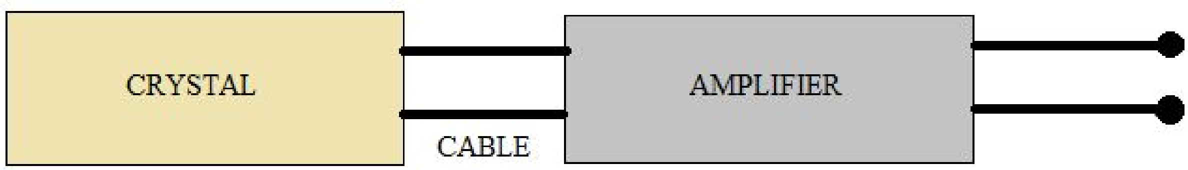

Figure 12: Components of the circuit

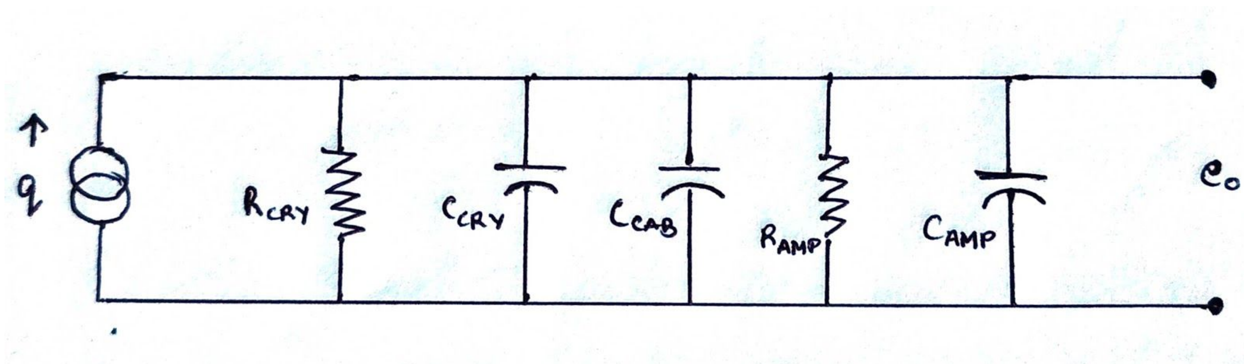

Figure 13: Equivalent circuit of the crystal-amplifier combination

It is possible to simplify it further and the resultant equivalent circuit would look something like this:

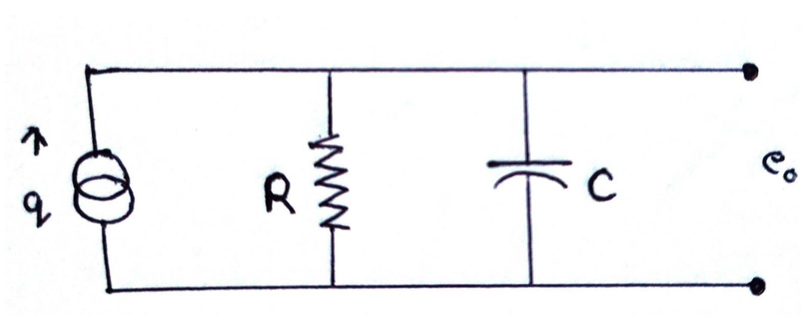

Figure 14: Final equivalent circuit

Clearly, C = $C_{cry} + C_{cab} + C_{amp}$

And, C = $R_{cry} \parallel R_{amp}$

Circuital analysis gives us the following,

$$e_o = iR = (\frac{dq}{dt} - C\frac{de_o}{dt}) * R$$

or, $RC\frac{de_o}{dt} + e_o = R\frac{dq}{dt}$

We know, q = d * f

Thus,

$$\frac{e_o}{f}(s) = \frac{dRs}{RCs+1} = \frac{(d/c)\tau c}{1+\tau s}$$

Where, τ = RC

We know that (d/c) is the static sensitivity and this value clearly changes with the capacitance offered by the cable or amplifier. So, we make use of a charge amplifier (which makes use of a feedback mechanism) to improve the design and enhance the sensitivity:

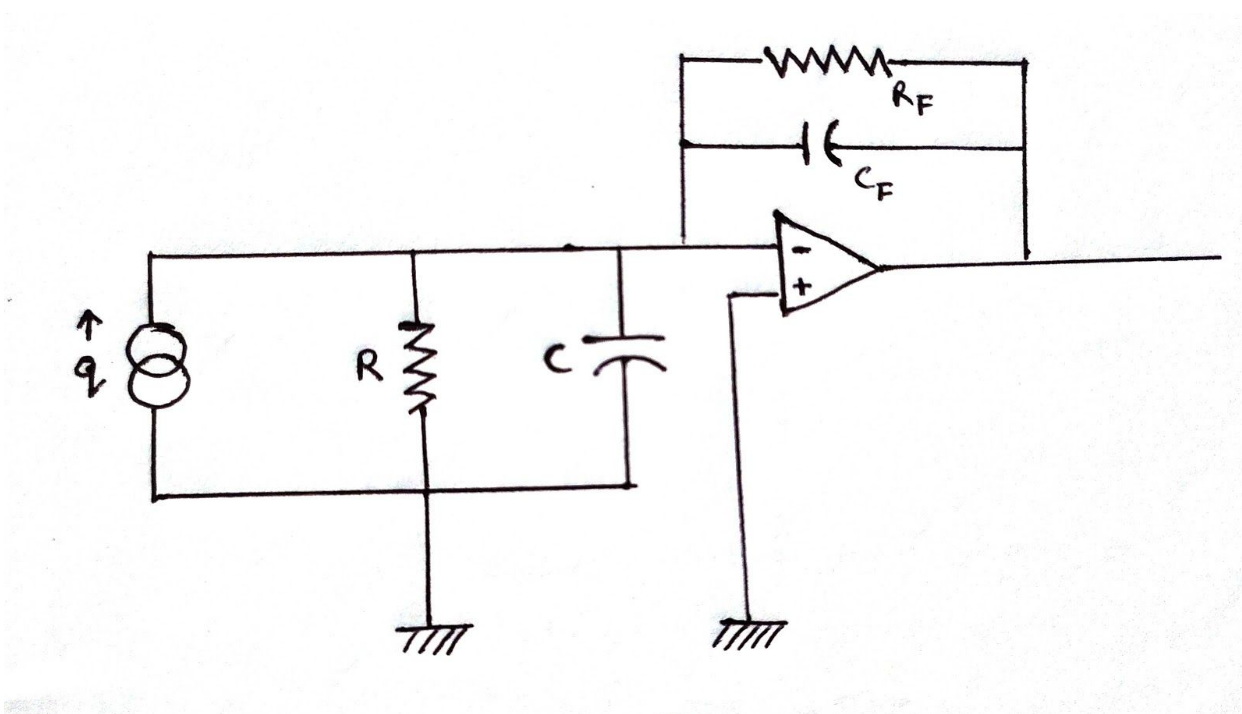

Figure 15: Equivalent circuit with the charge amplifier setup including the feedback mechanism

5.10. DEALING WITH NOISE

It is possible to reduce or regulate the noise such that it does not hinder the process of analysing signals and drawing conclusions. Generally, it is prefered to have a signal to noise ratio of 3:1. The following methodologies can be implemented to achieve this:

a. Various digital or signal processing techniques can be implemented to reduce the effect of noise.
b. Certain design changes can be made to ensure a reduction in the impact of noise. For example, it is possible to use materials that have Young's Modulus similar to that of the skin to ensure good conformation to the skin which will reduce motion artifacts.
c. Various environmental noises can be reduced by insulating nearby electrodes and cables and shielding other electrical appliances.
d. Use of a buffer at the electrode site and using a wet electrode over a dry electrode can be used to reduce effects on and in the skin.
e. A redundant sensor, which acts as a control, can be used and various algorithms can be implemented to separate the real signal from the noise.

6. BIOSENSORS

"Biosensors are analytical tools for the analysis of bio-material samples to gain an understanding of their bio-composition, structure and function by converting a biological response into an electrical signal. The analytical devices composed of a biological recognition element directly interfaced to a signal transducer which together relate the concentration of an analyte (or a group of analytes) to a measurable response."

Biosensors find applications in various fields:

a. Drug development
b. At home medical diagnosis
c. Crime detection
d. Study of biomolecules
e. Food analysis
f. Environmental field monitoring
g. Quality control
h. Disease detection

These are only some of the numerous applications of biosensors today. Biosensors can be primarily categorized by the type of biological recognition element that is used for its working. Enzyme electrodes (biosensors) make use of enzymes and other proteins, immunosensors make use of antibodies, DNA sensors make use of DNA, RNA or aptamers and microbial sensors make use of microbial cells, plant tissues or animal tissues.

Most of the detection and sensing work can be done using conventional laboratory based methods. However, sensors are preferred. The main advantages of using biosensors are as follows:

a. **Rapid analysis:** Conventional methods generally have a long analysis time, making their use disadvantageous when the requirements are urgent. An example of this can be the diagnosis of diarrhoea. Diarrhoea is caused by e-coli bacteria. Conventional methods of detection take about 48 hours for the results to arrive. However, infants can die due to the disease in a few hours. In such a scenario, using biosensors with very small analysis time is beneficial and preferable.
b. **Cost effective:** Conventional techniques generally involve higher costs.
c. **Scope of miniaturisation:** A research in 2012 revealed that Ohm's Law is valid even when wires are just one atom high and four atoms wide. In general, it is possible to make nanosensors. Conventional methods are not always appropriate for field measurements. The equipment is almost never portable, a tedious sample preparation phase is involved

and often requires highly trained professionals to operate. Sensors can easily be used for field measurement purposes and often require very small sample volumes.

The main types of biorecognition elements that are used in biosensors today are as follows:

a. **Bio-catalysis Biosensors:** The biosensing elements used are proteins, especially enzymes.
b. **Bio-affinity Biosensors:** The biosensing elements used are antibodies.
c. **Cell Biosensors:** The biosensing elements used are microorganisms.
d. **Nucleic Acid Based Biosensors:** The biosensing elements are DNA or RNA, or artificially prepared species like aptamers.
e. **Molecularly Imprinted Polymer (MIP):** MIP is a polymer with a memory of the shape and functional groups of a template molecule.

6.1. PERFORMANCE PARAMETERS

In addition to the already mentioned performance parameters, specificity plays a very important role in biosensors. This is primarily a property of the biorecognition element. It refers to its ability to identify a specific target molecule(s) from a pool of similar molecules. If a bioreceptor is capable of recognising a single molecule, it is considered to be highly specific. If it is capable of identifying a group of analogous molecules, it is considered to possess group specificity.

In natural bioreceptors like enzymes and antibodies, the specificity is by the virtue of structures like active sites and complementary determining regions (CDRs). Active sites have a specific shape which is complementary to the target molecule. If a similar molecule binds to the active site or if the shape of the active site is altered by any means like the presence of an inhibitor at the allosteric site, the recognition capability of the enzyme is diminished or completely inhibited.

6.2. ANTIBODY BASED SENSOR TECHNOLOGY

Essentially, antibodies are proteins that are generated by the body's immune system in response to the introduction of a foreign substance, with the aim of rendering them inactive or neutralising them. There are two main subcategories of antibodies: monoclonal (mAb or moAb) and polyclonal (pAb or poAb). Monoclonal antibodies are highly specific and are capable of binding to a very specific target molecule, which is generally an antigen. Polyclonal antibodies recognise multiple analogous or related structures.

6.2.1. STRUCTURE OF ANTIBODIES

For any protein, their functionality is encoded by its 3-D structure. Often, protein crystallographic methods are employed to decipher the structure of proteins. Antibodies are naturally found as aggregates and under this condition, they appear globular. Each antibody is Y shaped with two main regions: Fab and Fc.

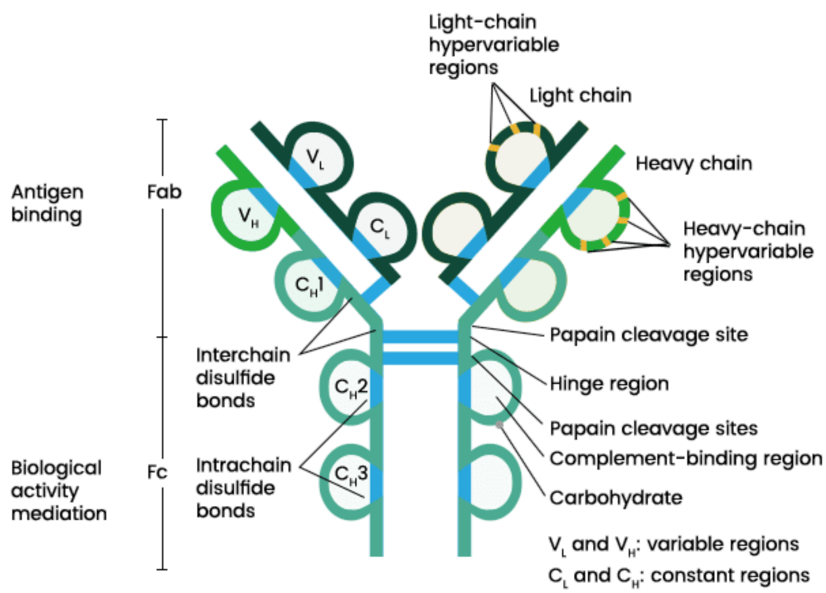

Figure 16: Basic structure of an antibody

From the picture given above, it is possible to divide the antibody into various regions based on their functionality. The Fab portion, which stands for Antigen Binding Fragment, is responsible for recognising the antigen and binding to it. This domain consists of two variable and two constant domains. The variable domains are designated collectively as the Fv or Variable

Fragment. The Fv has three hypervariable loops which are referred to as the Complementary Determining REgions (CDRs). The CDRs provide an antigen recognition site which makes it possible to bind with a specific antibody. The Fc domain, which stands for Crystallizable Fragment, is capable of interacting with the other elements of the immune system.

6.2.2. IMMUNOASSAY

Due to the specificity of the antibody, it is possible to utilize them for the recognition of various complementary structures. The way this is done is through an immunoassay. For this, we require a surface- we can use a chip coated with a inert metal like gold or we can employ the use of a microwell plate. The antibodies, in an upright condition, are coated onto the surface. This is done by either physical adsorption or by covalent coupling. Crosslinkers help in making this connection, especially when a chip is used.

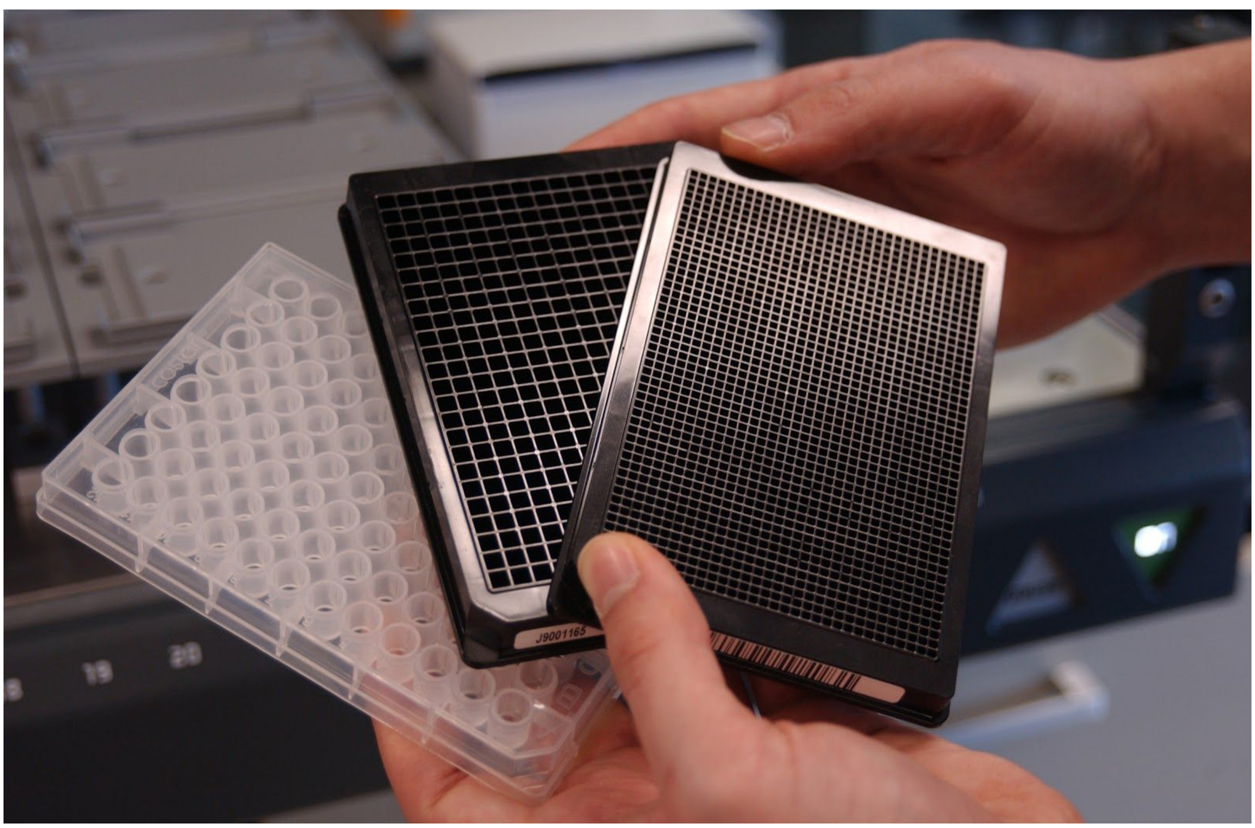

Figure 17: Microwell Plates

Generally a mAb (monoclonal antibody) is used and this process is referred to as immobilisation of the antibody. The monoclonal antibodies act as primary or 1º antibodies, that is, as bioreceptors. A blocking agent like BSA prevents the analyte/target molecule from settling at the base of the antibodies. The analyte is then passed over this set up. Some of these are recognised by and bind to the antibodies. Some of the antibodies do not undergo the binding process. To remove the excess molecules (unadsorbed antibodies and unbound analyte), washing is carried out. The setup is then incubated with polyclonal antibodies (pAb) which act as secondary or 2º antibodies. These are in an inverted form and recognise the analyte. The unbound secondary antibodies are washed away. This step is usually followed by labelling. The labelling is done using various substances like luminescent substances or chromophores whose intensity of light emitted or colour obtained can be quantified, allowing us to indirectly quantify the interaction between the antibodies and the target molecules. This method is thus referred to as indirect or label technique.

6.2.3. CL-ELISA

CL stands for Chemiluminescence and ELISA stands for Enzyme Linked ImmunoSorbent Assay. The same procedure as above is implemented. The main difference is that instead of a secondary antibody, an enzyme is used for the labelling process. The label is a chemiluminescent material. These substances, for example, luminol generate electromagnetic radiation in the visible region due to the occurrence of a chemical reaction. Luminol in specific, results in the formation of a dianion in the presence of OH- ions. This dianion reacts with an oxygen molecule to produce an unstable peroxide. This excited state is highly unstable and short lived. It quickly gives out the ground state dianion accompanied by photon emission. The energy carried by a photon is given by the equation:

$$E = h\nu = hc/\lambda$$

Thus, a EM radiation of wavelength λ is produced and if it is in the visible region, it is perceived as a specific colour. The number of photons emitted can be quantified using signal detectors like Photomultiplier Tubes (PMTs) and Charge-Coupled Devices (CCDs).

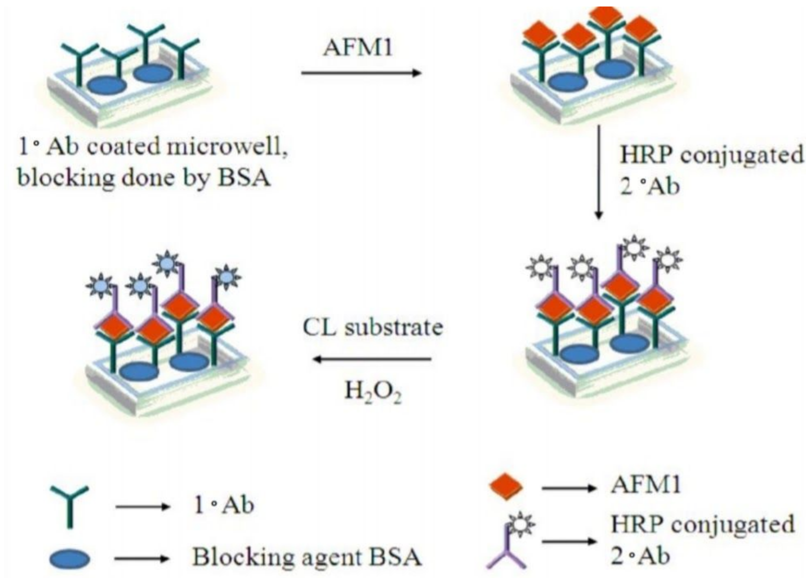

Figure 18: CL-ELISA Procedure

It is possible to perform ELISA using other kinds of labels like fluorophores or chromophores. There are various subcategories of ELISA too, depending on the mechanism employed. The one discussed here is the most commonly used and is known as the Sandwich ELISA. In Competitive ELISA, the capture probe and target molecules are mixed together. They compete for the unoccupied positions. After the washing is done, based on the number of bound structures, the percentage of binding can be obtained. In Direct ELISA, direct measurement takes place as the binding itself produces some physical change, for example, a colour change, whose intensity is proportional to the percentage of binding.

6.3. PROTEIN AND NUCLEIC ACID BASED SENSOR TECHNOLOGY

The use of proteins like enzymes and nucleic acids like deoxyribozymes is very similar to the assay mentioned before. These can also be used instead of the secondary antibodies in immunoassay.

Metalloproteins have a metallic active center. When the metal is removed, it forms an apoprotein. This has a very high affinity for the specific metal or other related metals. An example of this is urease.

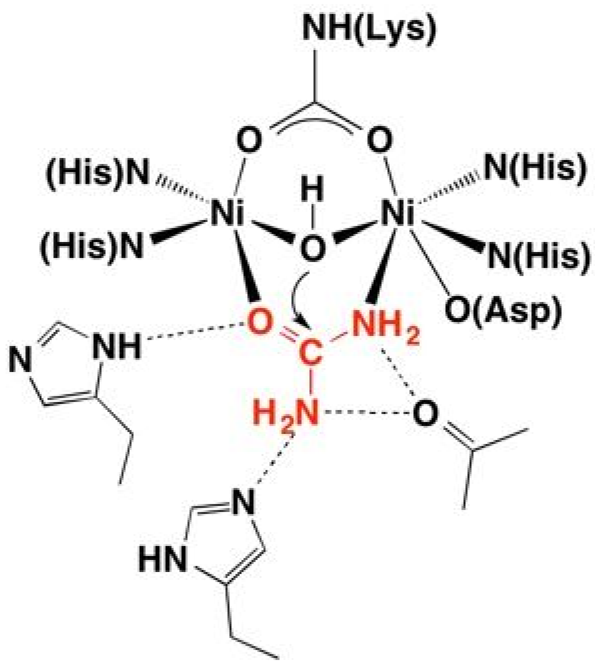

Figure 19: Structure of urease

Urease is an enzyme found in jacki beans which have two Ni centers, surrounded by histidine and aspartate. When the Ni is removed, it develops a very high affinity for Ni or other related metals. Thus, they can be used as metal sensors.

In DNA based sensors, oligonucleotides are used as the biorecognition element. It is capable of binding to complementary single strands of DNA, thereby allowing us to recognise a specific structure of DNA. This is the basis of DNA hybridisation too. Similar functionality can be obtained for RNA too.

The main issues associated with these types of sensors is that proteins get denatured beyond a particular range of temperature and pH. The structure of proteins is responsible for its functionality and beyond the optimal range of temperature and pH, the quaternary, tertiary and sometimes even the secondary structure of proteins get affected. This is known as denaturation.

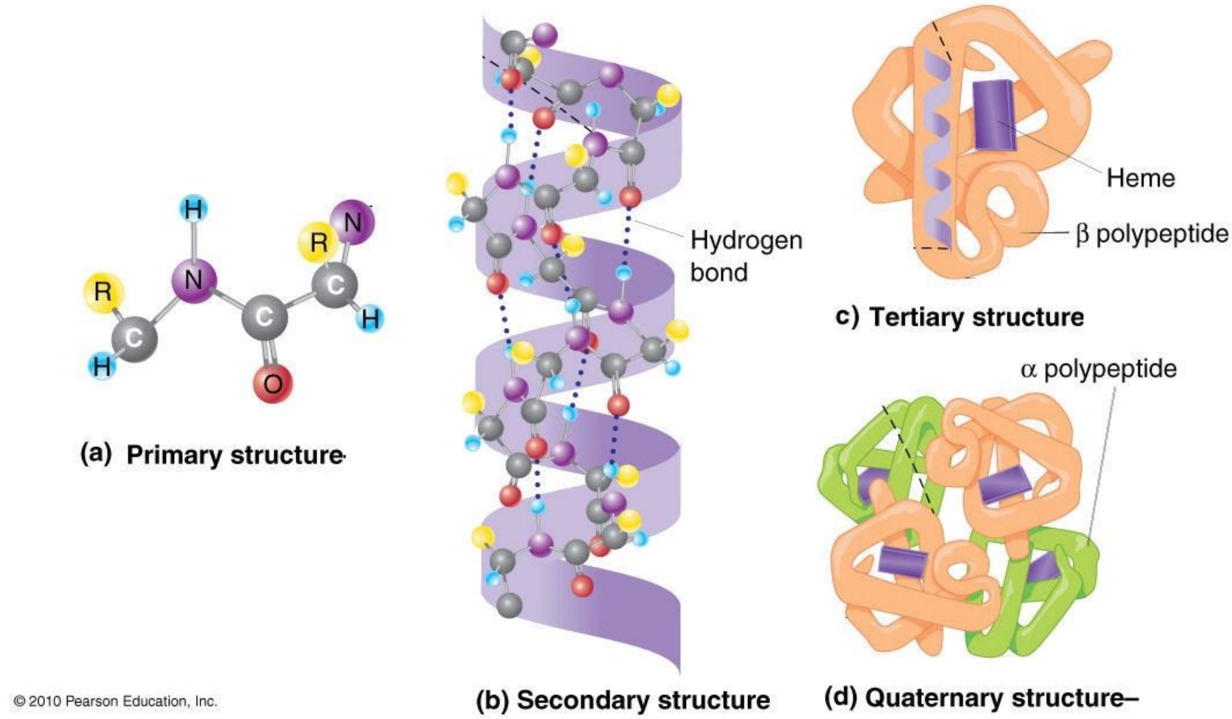

Figure 20: Structure of proteins.

In addition, they need to be stabilised to ensure there are no conformational changes which will change the position of the active site. Apart from that, they are generally liquids making the handling and the fabrication process of the sensors very difficult. In order to overcome these drawbacks, artificial bio-recognition elements are employed.

6.4. ARTIFICIAL RECEPTORS AND MIMICS

Protein crystallography is often used to decipher the structure of proteins. The knowledge of the structure of the active site is important in being able to artificially mimic it to make a less temperature/pH sensitive artificial recognition element. Artificial receptor sites can also be obtained using molecular imprinting. Artificial receptors are not perfect alternatives and do have an operating range. However, this range is larger than that for natural receptors improving the use-cases for artificially prepared receptors.

6.4.1. APTAMERS

Aptamers are synthetically prepared stable DNA/RNA ligands that bind with extremely high affinity and specificity to target molecules. They are very highly sensitive and have an optimum temperature and pH range larger than their natural counterparts. They can actually be handled under ambient conditions thereby improving the use cases. Denatured aptamers are not useless like denatured natural proteins and nucleic acids. Instead, the aptamers can be regenerated within minutes. It is possible to use aptamers everywhere a nucleic acid based bioreceptor is required and many more. Apatmers also possess long term inherent stability. Due to the single strand structure of aptamers, it is easy to couple them with fluorophores, quenchers or amines and thus, are used in labelled techniques. The binding capacity of aptamers remains largely unaffected on labelling. Aptamers are identified through the SELEX process (an in-vitro process). This ensures little to no batch to batch variation which allows it to be successfully commercialised.

6.4.1.1 SELEX PROCESS

The SELEX process is an aptamer selection scheme. A very large library of single stranded molecules is required for the process. The idea is to go through multiple passes of checking binding capability and rejection, allowing one to reject thousands of choices at every step to narrow down to a small selection of molecules. This technique is often implemented in high throughput screening and drug discovery.

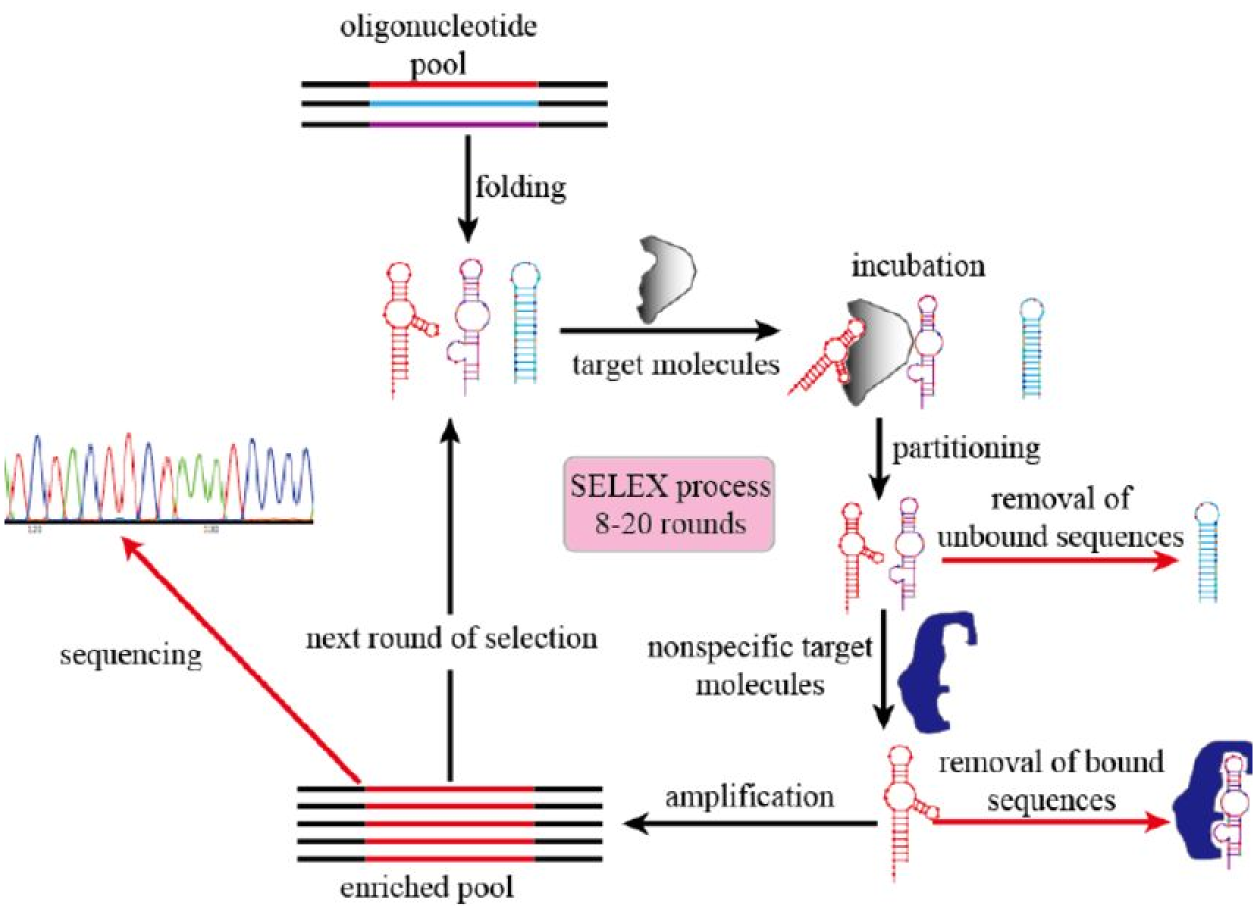

Figure 21: SELEX process

For making the oligonucleotides, an oligo synthesizer is used. It is then exposed to target molecules. The unbound molecules from the library are washed away or discarded. Several iterations of this is down to narrow down to a small selection of possible complementary molecules. Thus, the SELEX process is a selection by rejection process.

6.4.2. MOLECULARLY IMPRINTED POLYMERS

MIPs are synthetic receptors that are created by making a mimic of an active/binding site. We need to possess a knowledge of the target molecule and its structure (most importantly, the surface functional groups). A template is prepared in accordance with the functional groups that can recognise the surface functional groups of the target molecule. An initial binding process called the assembly step allows the functional to bind to the template. After this, a crosslinker like methacrylic acid (MAA) or acrylamide (AAm) is added in a porogenic solvent. A polymerisation process results which helps in the formation of the MIP structure. This step is followed by a re-binding step which involves removing the template. The functional groups are bound to the template through strong covalent forces making it difficult to remove the template. This process often results in the destruction of the crosslinker, partial removal of the template or breaking of the MIP as harsh solvents are utilised for this purpose. Once the template is removed the MIP can be used as a recognition element in biosensors.

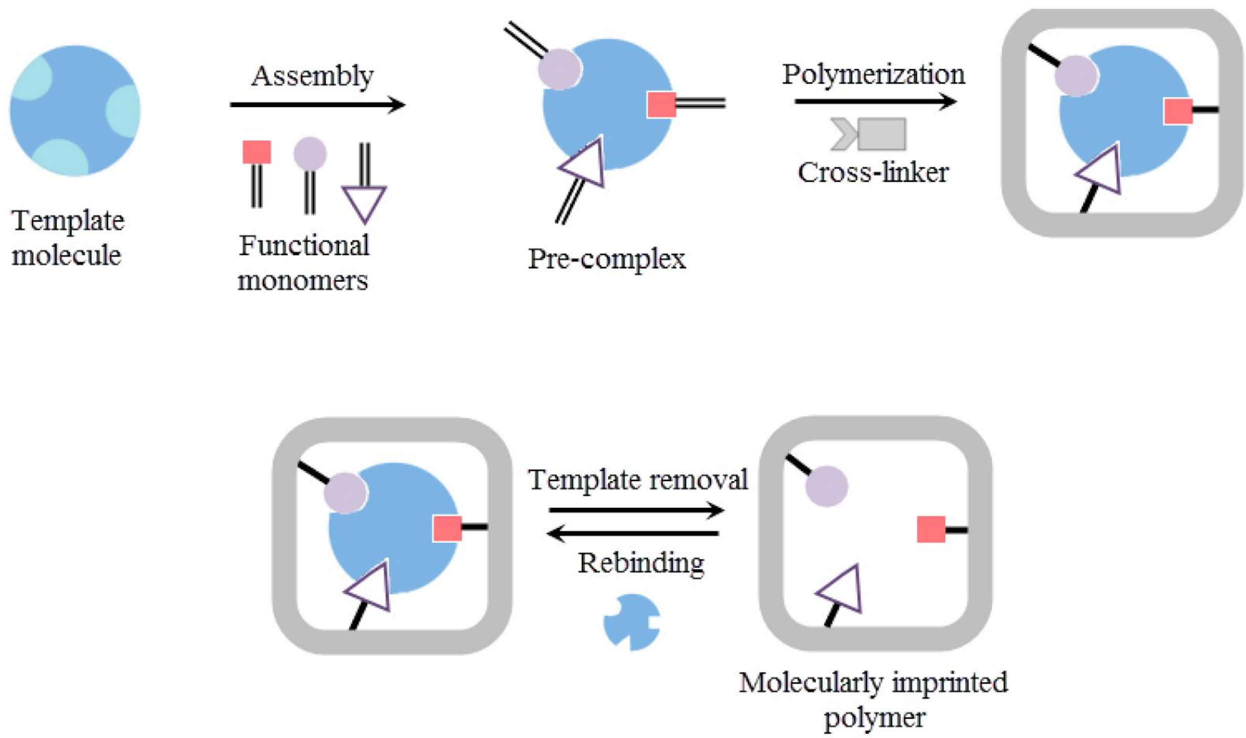

Figure 22: Making of a MIP

7. THERMAL SENSORS

Thermal sensors help to detect changes in temperature. This field of sensor technology is pretty well developed. There are many different options currently, commercially available:

a. Resistance Temperature Detector (RTD)
b. Thermistor

c. Thermocouple
d. Pyrometer
e. Langmuir probes
f. Various types of thermometers: infrared thermometer, bimetallic thermometer, liquid thermometer, digital thermometer, tympanic thermometer, etc

Generally, the output signals are very weak, that is, they are very small in magnitude, making it difficult to read and analyse them. Consequently, amplifiers are used to convert the signals obtained to a signal within a globally accepted range: 4 - 10 mA, 1 - 5 V, 0 - 10 V, etc.

7.1. PERFORMANCE PARAMETERS

There are two main performance parameters:

a. **Response time:** Response time is the time required to reach about 99% of the final, steady state response of the sensor from the onset of operation. Generally, a low response time is highly preferred.
b. **Time constant:** Time constant is indicative of the speed of the system to respond to changes in the input signal. It is measured as the time required to reach 63.2% of the final, steady state response. It is represented using τ.

$$T = (T_2 - T_1)(1 - e^{-\frac{t}{\tau}}) + T_1$$

Where, t is the time elapsed from the onset of operation.

Generally, sensor response time = 5 * τ.

7.2. RESISTANCE TEMPERATURE DETECTORS

An RTD is a passive transducer, meaning it requires an external energy source to convert one kind of signal to another. It works on the principle that the resistance of a metal changes with changes in temperature. Generally metals with high temperature coefficients are used.

$$R = R_{ref} [1 + \alpha (T - T_{ref})]$$

Here, R is the resistance at temperature T

α is the temperature coefficient

R_{ref} is the reference resistance at reference temperature T_{ref}

Clearly, the relationship between resistance and temperature is linear, making calibration of the device very easy. The material used is often platinum because of:

a. High sensitivity
b. Repeatability
c. High stability

However, it is very expensive and the next most commonly used material and an alternative to platinum is nickel.

The device consists of the metal wire that is coiled in order to make sure that the overall device has a small size. In most cases, this setup is encased in a protective sheath. This increases the response time but is a necessity, especially for use in hostile environmental conditions. RTDs have among the highest accuracy among thermal sensors. However, it cannot be used for higher currents because high currents lead to heat dissipation, adding to the temperature rise. This affects the reading.

7.3. THERMISTORS

Thermistors are also based on the principle that the resistance of certain materials change with temperature in a certain manner. Often, the materials that are used to make thermistors are semiconductors or mixtures of certain metal oxides. These materials show a high temperature coefficient of resistance, that is, the resistance changes a lot with small changes in temperature.

However, the temperature-resistance relationships are often non-linear and very complex. This makes the calibration process very important and difficult. Based on the temperature coefficient, they are of two main types:

a. **NTC (Negative Temperature Coefficient):** The resistance decreases with increment in temperature in this case. They are often made of semiconducting materials. Semiconductors are insulators at absolute zero temperature. The electron band structure consists of a completely filled valence band and a conduction band, which are separated by the band gap. As temperature increases, more and more electrons have the energy to jump from the valence band to the conduction band, that is, they become freely moving. This results in an increase in the conductivity of the substance and thus, a decrease in resistance.
b. **PTC (Positive Temperature Coefficient):** The resistance increases with increase in temperature in this case. Metals exhibit this characteristic. PTCs are often made using doped polycrystalline ceramics like barium titanate.

7.4. THERMOCOUPLES

The thermocouple is based on the Seebeck effect/ Peltier effect/ thermoelectric effect. Unlike the previous two examples, the output signal or response of a thermocouple is a potential difference. The construction consists of two dissimilar conductors. When these two are maintained at different temperatures, an EMF is developed. This EMF is read and used to obtain the differential temperature (temperature difference between the two junctions of the thermocouple).

One of the ends of the thermocouple is kept in a cold junction. Previously, an ice bath was used for this purpose. This is because a thermocouple junction does not generate any thermocouple when it is maintained at 0℃. Nowadays, a cold junction compensation is used. This consists of a circuit to simulate the required conditions to obtain a reference temperature with respect to which the temperature of the required object/material can be measured.

Thermocouples are self powered and have a low response time. However, they are still not preferred over the other options because:

a. It offers lower accuracy
b. It measures the differential temperature with respect to a reference known as the "cold junction"

Based on the material used to make the thermocouple, the operation range and sensitivity, there are various types of sensors, designated as: E, J, K, M, N, T, etc. For example: J type thermocouple has the following specifications:

a. Made of: Iron-constantan combination
b. Range of operation: -40℉ to +1380℉
c. Sensitivity: 27.8 μV/℉

7.5. CHOICE OF A THERMAL SENSOR

The choice of a device depends on the application and the decision is taken by weighing the pros and cons of the available options (cost, sensitivity, response time, time constant, operating temperature range, etc). The main advantages and disadvantages of the various devices discussed previously are as follows:

Advantages:

a. **RTD:** Platinum is highly stable and can be used for very high temperature applications, highly precise, sensitive and repeatable
b. **Thermocouple:** self powered, cheap, large operating temperature range
c. **Thermistor:** highly sensitive, low cost and easy to replace, fast response

Disadvantages:

a. **RTD:** expensive, larger response time

b. **Thermocouple:** non-linear relationship voltage and temperature (thus, calibration is important and difficult), measures differential temperature with respect to a reference and not absolute temperature (a cold junction is required)
c. **Thermistor:** non-linear relationship between resistance and temperature (thus, calibration is important and difficult)

8. PIEZOELECTRIC SENSORS

Piezoelectric transducers measure changes in pressure, strain or force, based on the electrical potential developed in the piezoelectric crystal when a mechanical stress is applied. Actuators are transducers that convert electrical energy to mechanical stress by virtue of the inverse piezoelectric phenomenon.

Piezoelectric sensors find various applications:

a. Vibration analysis
b. Generation of a high voltage
c. Measurement of acceleration/force

In addition to this, the fact that piezoelectric materials can convert the work done on them to electrical energy can be used in electricity generation applications, as an alternative to the commonly available non-renewable sources of energy. They are also more reliable than other renewable sources of energy like wind energy, which is highly dependent on the climate, location and other similar factors.

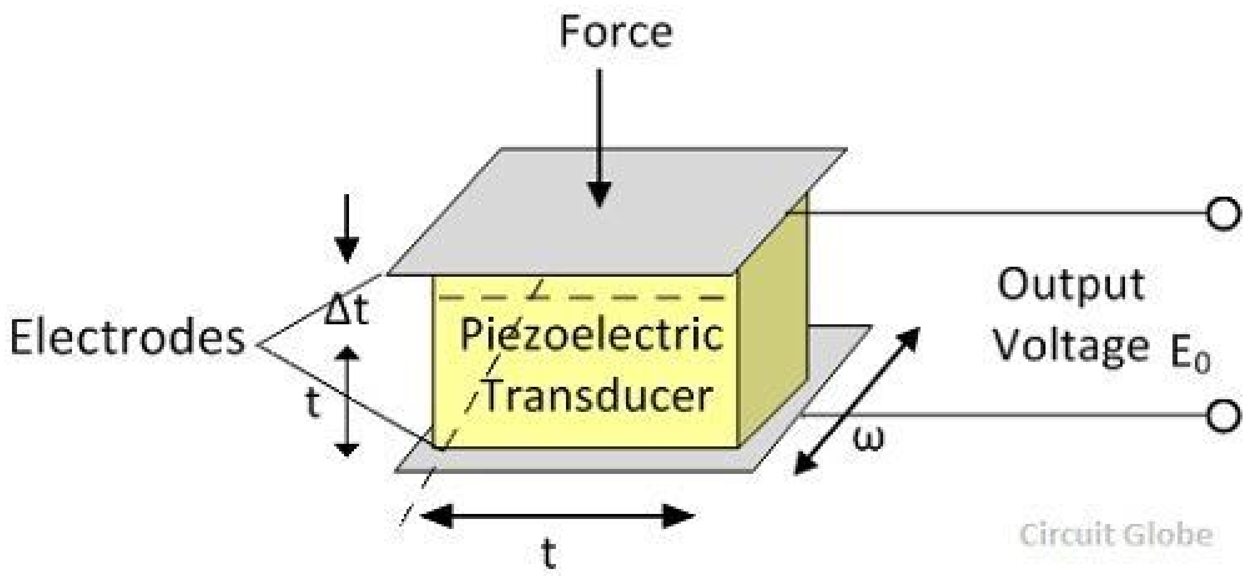

Figure 23: Basic configuration of a piezoelectric transducer

Piezoelectric transducers are capable of measuring the changes in pressure, strain or force by converting the work done on the material to electrical charges, and consequently, an electric current. This is what is most commonly used in piezoelectric sensors. Piezoelectric actuators convert the electrical energy into mechanical displacement or stress. Both these are a consequence of the properties of piezoelectric materials (piezoelectric phenomenon and inverse piezoelectric phenomenon).

8.1. PIEZOELECTRIC PHENOMENON

Piezoelectricity is a phenomenon due to which when a mechanical stress is applied on an object, an electric potential develops across it. Piezoelectric crystals lack symmetry in the unit cells, that is, the atoms or ions are not symmetrically arranged in the unit cell. However, they are electrically neutral. Meaning, they have equal amounts of opposite charges in the unit cell. When the piezoelectric crystal is compressed or stretched, the structure gets deformed as atoms/ions are pushed closer together or apart. This consequently disturbs the balance of charges and a net charge appears. This occurs throughout the crystal and thus, a net positive and negative charge appears on the opposite, outer faces of the crystal. This results in the electric potential noticed.

"Unique distribution of charges in the piezoelectric crystal gives rise to a net dipole moment when the material is deformed."

8.2. INVERSE PIEZOELECTRIC PHENOMENON

The inverse of the piezoelectric phenomenon is referred to as the inverse piezoelectric effect. When voltage is applied across a piezoelectric crystal, the atoms/ions experience electrical pressure and so they move in order to rebalance themselves. As a result, the crystal gets deformed.

An application of this phenomenon is actuators. Actuators are used to obtain motion by converting a type of motion or energy to that which is required. Piezoelectric actuators make use of inverse piezoelectric effect to achieve this.

8.3. OPERATIONAL MODES

The manner in which a piezoelectric material is cut defines one of the three main operational modes: transverse, longitudinal and shear.

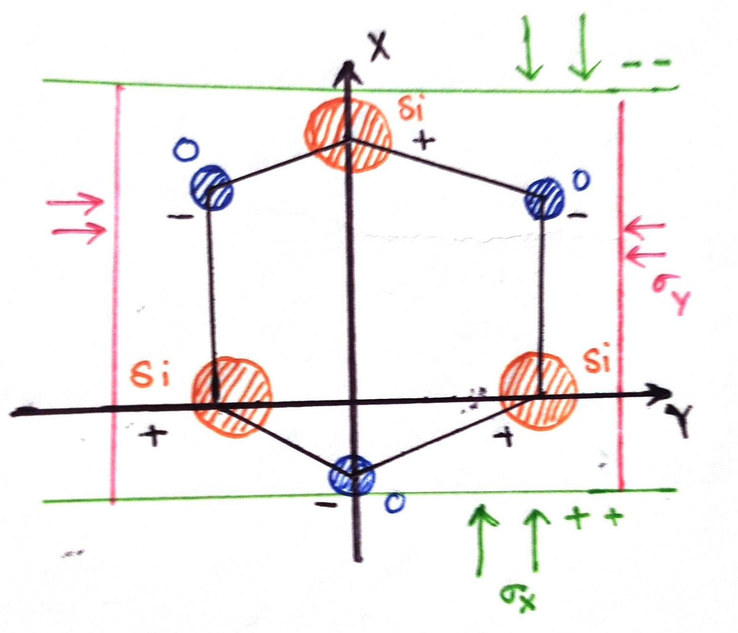

Figure 24: Operational modes of an SiO2 crystal

a. **Longitudinal Effect:** In the above crystal, when a force is applied along the x-axis, charges develop across A and B. This is known as the longitudinal effect.

$$Q_x = d_{xx}F_x n$$

Here,

d_{xx} = piezoelectric coefficient for a charge in x direction, released by forces along the x direction

F_x = force applied in x direction

n = number of stacked elements

In this case, the piezoelectric effect is independent of the piezoelectric element size and shape and thus, the charge output is enhanced by placing multiple elements mechanically in series (electrically parallel).

b. **Transverse Effect:** In a crystal, when force is applied along the y-axis, A and B, that are collecting charges along the x-axis, develop charges opposite to that in the previous case. This is known as the transverse effect.

$$Q_x = d_{xy}F_y b/a$$

Here,

a = dimension in line with y-axis (neutral axis)

b = dimension in line with the x-axis (charge generating axis)

d = piezoelectric coefficient

F_y = force applied in y direction

Clearly, it is possible to fine tune the sensitivity based on the force that has been applied and the dimensions of the element.

c. **Shear Effect:** In this case, the magnitude of charges produced is directly proportional to the force applied in a direction perpendicular to it. This effect too is independent of element shape and size.

$$Q_x = d_{xx} F_x n$$

Here,

d_{xx} = piezoelectric coefficient for a charge in x direction, released by forces along the x direction

F_x = force applied in x direction

n = number of stacked elements

8.4. PERFORMANCE PARAMETERS

Let's assume the following axes:

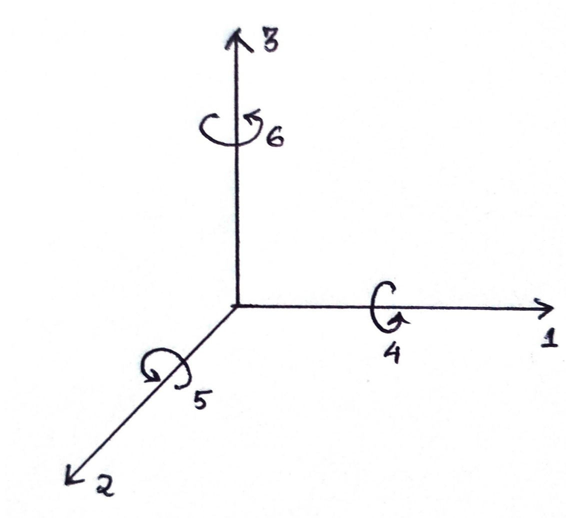

Figure 25: Axes for calculation of piezoelectric constants

a. **Piezoelectric constants:** There are two families of constants used to describe piezoelectric effect: "g" and "d". These are referred to as parameters of piezoelectric crystals.

   Let, i = direction of electric effect

   j = direction of mechanical effect

   The two parameters are defined as g_{ij} and d_{ij}.

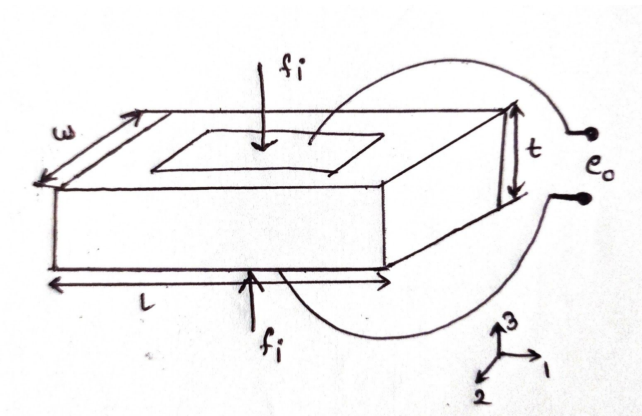

Figure 26: Dimensions of a piezoelectric crystal

g_{33} = (field produced in direction 3)/(stress applied in direction 3)

= (e_o/t)/(f_i/wl)

Where, t = thickness of the crystal

l = length of the crystal

w = width of the crystal

f_i = force exerted

e_o = potential developed across the crystal

d_{33} = (charge generated in direction 3)/(force applied in direction 3)

= Q/f_i

Where, f_i = force exerted

Q = charge generated

b. **Polarisation:** Clearly, due to deformation, charges are produced and polarisation of the crystal takes place. This can be quantified as follows:

$$P = [d]\ \sigma$$

Where,

P = polarisation

[d] = sensitivity matrix

σ = stress

c. **Flexibility:** Flexibility depends highly on the material being used. Most ceramic crystals like PZT are hard, brittle and rigid. On the other hand, piezoelectric polymers like PVDF are flexible and easy to shape. Wearable sensor applications require high flexibility.

d. **Charge sensitivity:** Charge sensitivity is indicative of the amount of charges that are produced by small changes in the mechanical strain or force applied. For greater readability and overall sensitivity of the sensor, we need high charge sensitivity.

e. **Response time:** Response time is the time required to reach about 99% of the final, steady state response of the sensor from the onset of operation. Generally, a low response time is highly preferred. Piezoelectric materials usually tend to have a low response time.

f. **Sensitivity:** Sensitivity refers to the change in the response change due to small changes in the input signal. Usually, high sensitivity is preferred as it allows one to detect the smallest of changes and differentiate between two or more very close signals. Generally, piezoelectric materials possess high sensitivity.

8.5. PIEZOELECTRIC MATERIALS

Piezoelectric materials exhibit both, piezoelectric phenomenon and inverse piezoelectric phenomenon. These materials can be classified into the following types:

a. **Naturally occuring crystals:** quartz, sucrose, topaz
b. **Man-made crystals:** gallium orthophosphate, langasite (both are analogues of quartz)
c. **Piezoelectric ceramics:** barium titanate, lead titanate, lead zirconate titanate (PZT)
d. **Lead free piezoceramics:** sodium potassium niobate, bismuth ferrite
e. **Biological piezoelectric materials:** silk, collagen, wood, tendon
f. **Piezoelectric polymers:** polyvinylidene difluoride (PVDF)

Piezoelectric polymers exhibit piezoelectricity that is several times larger than that of natural occurring quartz. Biological piezoelectric materials are not preferred because they are highly perishable and temperature sensitive.

8.6. CHOICE OF MATERIAL OF CONSTRUCTION FOR SENSOR AND ITS PREPARATION

The most commonly used piezoelectric materials can be categorized as follows:

a. **Natural:** Quartz, rochelle salt, tourmaline
b. **Synthetic:** Lithium sulphate, ammonium dihydrogen phosphate
c. **Polarised ferroelectric crystals:** Barium titanate, lead zirconate titanate

Generally, naturally occurring piezoelectric materials are not preferred for use. The reasons are as follows:

a. They are pretty expensive and not suitable for commercialisation
b. Low piezoelectric constant/sensitivity compared to the artificially prepared piezoelectric material

However, if carefully handled, these materials possess unlimited long term stability. However, since we are concerned about wearable sensors, we need materials whose performance does not decrease drastically with repeated bending/stretching.

Piezoelectric ceramics (like, PZT ceramic) are certainly better options and the reasons behind it are as follows:

a. They possess piezoelectric constants/sensitivity roughly two orders of magnitude greater than natural single crystal materials
b. They are produced by an inexpensive sintering process

However, as a consequence of the fact that their piezoelectric effect is “trained”, their sensitivity degrades over time. This degradation is temperature dependent too. This makes such materials unreliable in various applications.

Most piezoelectric crystals can be classified into two main types:

a. **Monocrystals:** They possess a symmetric arrangement of dipoles- polar axes of all the dipoles lie in one particular direction.
b. **Polycrystals:** They have an asymmetric arrangement of dipoles- the dipoles are arranged in multiple directions. Polycrystals have to be heated in the presence of a strong electric field in order to align the dipoles in one direction. Ceramics are polycrystalline and thus, have to be made piezoelectric by a special polarising process.

This goes for ferroelectric crystals too. They are artificially polarised by applying a strong electric field to the material and parallely heating the material to a temperature above its Curie Point. It is then slowly cooled. When the electric field is finally removed, the material possesses a remnant polarisation which allows it exhibit piezoelectric effect.

The use of piezoelectric polymers is highly favourable because of:

a. Reasonable piezoelectricity
b. High mechanical flexibility
c. High sensitivity to voltage change
d. Low impedance
e. Does not need to undergo the polarisation process mentioned previously

Piezoelectric polymers are of two types:

a. Amorphous

b. Semi-crystalline

The difference exists in the piezoelectric generation mechanism.

8.6.1. ELECTROSPUN PAN NANOFIBER VS ELECTROSPUN PVDF NANOFIBER

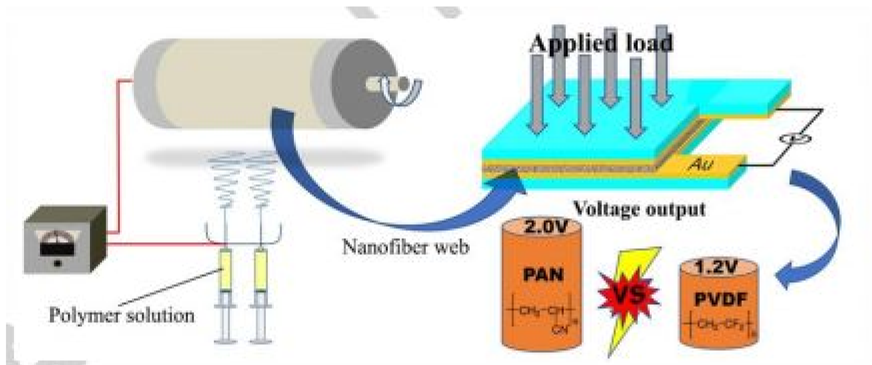

Figure 27: Electrospinning of PAN and PVDF nanofibers

Among the most commonly used piezoelectric materials is PVDF (polyvinylidene fluoride), a semi crystalline polymer material. Its high piezoelectric coefficient and favourable mechanical properties make it a great choice in various applications. It and its copolymers are currently ranked among the materials with the highest piezoelectric activity. PVDF possesses strong piezoelectricity in its "stretched and polarised" forms and thus, processing the polymer into fibrous membranes through electrospinning greatly improves its piezoelectric effect. The process involves large -ratio stretching and high-voltage poling at an elevated temperature. The structure of PVDF (β phase crystalline structure) is responsible for the piezoelectricity. Its dipole moment is around 2.1 Db. Electrospinning helps form a high β phase PVDF within the fibers. In comparison with PVDF dense films, electrospun PVDF nanofiber membranes can have up to 4 times higher piezoelectric outputs.

A recent development in this field is the discovery of the unexpectedly high piezoelectricity of electrospun polyacrylonitrile nanofiber membranes. PAN is an amorphous vinyl-type polymer.

In spite of the existence of the cyano group in each repeat unit which can generate a large dipole moment, it was generally established in the scientific community that PAN has low piezoelectricity. It was seen that incorporating charge carriers increasing the number of cyano groups in PAN was capable of improving the piezoelectricity to only a very small extent. For these reasons, it was not used in piezoelectric sensors.

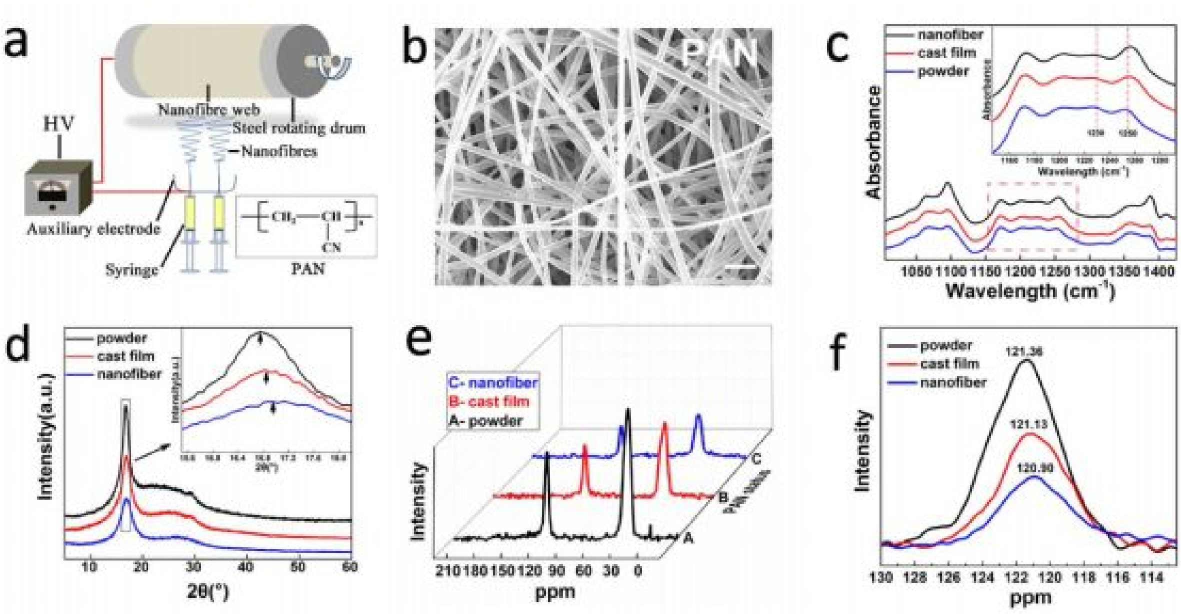

Figure 28: Electrospun PAN nanofiber. (a) Schematic illustration of electrospinning apparatus and PAN chemical structure, (b) SEM image of as-spun PAN nanofibers (solution concentration 12%; applied voltage 23 kV; spinning distance 15 cm; flow rate of polymer solution 0.5 ml/h; roller line speed 100 mm/s; scale bar 2 μm), (c) FTIR spectra of PAN powder, PAN cast film and electrospun PAN nanofiber membrane (roller speed 100 mm/s), (d) XRD patterns of PAN powder, PAN cast film and electrospun PAN nanofiber membrane (roller speed 100 mm/s), (e) solid-state 13C-NMR spectra of different types of PAN, (f) solid nuclear magnetic resonance peaks of C-N triple bond for different PAN samples

PAN, in the solid state, has two main conformations:

a. Planar zigzag conformation (“saw-tooth”)
b. 3’-helical conformation

The sawtooth conformation has an all-transform (TTTT) structure with a dipole moment of about 3.5 Db (clearly, this is greater than the value for β phase PVDF).

"PAN after being electrospun into a nanofiber membrane can have a piezoelectricity even stronger than PVD."

Apart from this, there are other reasons why PAN could replace PVDF as the material for piezoelectric sensors:

a. It has a much smaller dielectric loss
b. It has higher thermal stability
c. It is available at a lower price point

8.7. PIEZOELECTRIC WEARABLE SENSORS

Currently, the most common applications of piezoelectric wearable sensors use PZT, ZnO nanowires or PVDF. The various applications are as follows:

a. Skin-mounted sensors for tactile sensation
b. Finger bending motion detection
c. Measurement of the arterial pulse pressure waveform
d. Detection of body movements
e. Biomechanics characterisation

The use of piezoelectric materials in wearable sensors have various advantages:

a. They possess high sensitivity and have a fast response time (thus, can detect very small changes in force, pressure or strain, dynamically)
b. Piezoelectric mechanical sensors have the potential to achieve self-powered detection in wearable applications

There are, however, some disadvantages and the most important one among them is the fact that the material is capable of leaking charge. This makes it difficult, if not impossible, to detect stationary or low frequency mechanical stimuli.

Previously, the Rogers Group has introduced a tattoo-like piezoelectric pressure sensor capable of monitoring vital signs. For a thickness of about 25 μm, it has a sensitivity of 0.005 Pa and a mechanical response time of around 0.1 ms. It was later developed into a biomechanics characterisation tool that can be used to detect soft tissue viscoelasticity. The device is capable of remaining conformably in contact with textured skin or organ surfaces and conducts measurements under quasi-static and dynamic conditions.

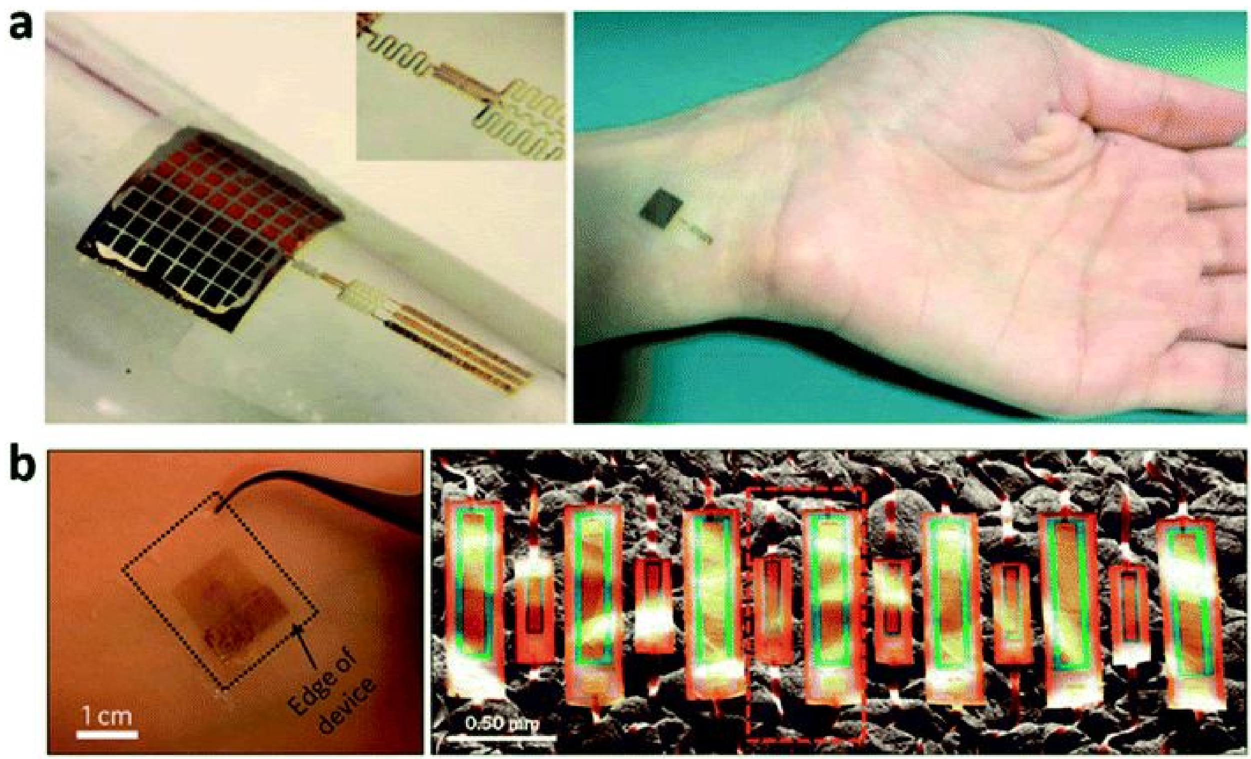

Figure 29: Wearable piezoelectric pressure sensor. (a) Picture of the sensor wrapped on a cylindrical glass support and laminated on a wrist. (b) Picture of the device fully laminated on the skin and its SEM image on an artificial skin sample for tissue viscoelasticity measurement.

8.8. APPLICATIONS OF PIEZOELECTRIC SENSORS AND HARVESTERS

Piezoelectric materials are very versatile and hence, find application in a wide variety of avenues. They can be used in sensors, harvesters or actuators, based on what phenomenon is being used dominantly. In fact, piezoelectric harvesters are the most popular choice for energy harvesters for wearable sensors. In terms of wearable sensors, it is possible to come up with designs that can broadly classified under two categories:

a. Embedded sensors
b. Skin-conforming sensors

The embedded sensors may have nanofibers woven into the fabric material or may have small devices embedded in the structure of various wearables like shoes, glasses, watches and clothes. The properties of the material that are required for such applications slightly differ.

8.8.1. ENERGY GENERATION FROM ROADS IN CALIFORNIA

The vibrational energy of the roads and walkways due to traffic and footfall can be harvested using piezoelectric devices. The electrical energy produced is predictable, based on traffic patterns, and locally storable.

The devices consisting of a piezoelectric crystal (PZT is the mostly common choice) can be placed about 5 cm below the asphalt surface. Due to the vehicles and people walking by, the material distorts, producing electric current.

Figure 30: Installation of the piezoelectric roads in California

Before the government of California, this was tested out by:

a. East Japan Railway Company (under the pedestrian gates of the subway station)
b. Under roads in Israel by Innowatech: when the devices were placed along a 1 km stretch of road, an average of 400 kW of power was generated. This can easily power about 162 US homes.

8.8.1.1. CALCULATIONS

PZT is the most commonly used piezoelectric material for such applications.

Assumptions:

a. While other factors may and do cause vibrations, for the purpose of understanding the efficacy of piezoelectric roads we assume that the vibrations in the road are solely caused by the traffic.

b. We also assume that all the “vibration events” are independent of each other. This requires that the vibrations due to a passing vehicle are sufficiently damped before the next one passess, so that we can treat each as independent events.

The following calculations are drawn for a 1 km stretch of road:

Total energy harvested by piezoelectric devices along 1 km stretch of road = (Maximum number of cars that pass) * (Vibrational energy transferred by each car to the road)

We know:
(Energy lost by cars as vibration to the road) < (Energy that a car puts into mechanical car over the stretch of road)

Now, we will make an overestimation to get an upper limit value:

Vibrational energy transferred to the road = The energy consumed by each car and put to mechanical work in the stretch of the road

We know:
Energy expended by a car = (Gasoline used) * (Energy density of gasoline) * (Thermal efficiency)

We get:
Energy expended = [(1 km * 0.621 mi/km) * (2.8 kg/gal * 4.43*10^(-7) J/kg) * 0.4]/(0.2 mi/gal)

= 1.54 MJ

Now, we also know that some of the mechanical energy is lost in various forms: friction, for use inside the vehicle, etc. In order to account for these additional losses, let's take thermal efficiency as 5%. We get:

Energy transferred as vibrations to the road = 0.19 MJ

Now this value is for a single car. Let's assume that for the period under consideration, a single "vibration event" takes place:

Total energy transferred to the road = (1 * 1.19) MJ = 0.19 MJ

Now, let's take a conversion efficiency of 3.9%.

Total energy harvested = [(3.9/100)*0.19] MJ = 7.41 * (10^-3) MJ

For an efficiency value of 13.9%, the value comes out to be 2.64 * (10^-2) MJ.

These values are not as high as we would like them to be. In fact, in reality, the values would be much lower because of other kinds of losses.

8.8.2. SHOE EMBEDDED PIEZOELECTRIC HARVESTER

Harvesting mechanical energy from human motion has been gaining a lot of attention in recent times and this is primarily due to the clean and sustainable nature of the energy obtained. This energy can be used to power a variety of devices, especially wearable sensors that make use of passive transducers, that is, require an external energy supply. This includes applications like health monitoring, activity recognition and gait analysis among others.

8.8.2.1. CHOICE OF HARVESTER FOR WEARABLE APPLICATIONS

Wearable sensors today are very small in size and the main aim of research being conducted in the field today is to make them even smaller and widely usable. Thus, they required compact, independent power supplies. The most commonly available alternative is electrochemical batteries, which unfortunately:

a. Very limited storage capacity
b. Pose potential environmental and health risks
c. Leak charges
d. Not very portable

Piezoelectric harvesters are envisioned to harness parasitic energy that is expended during human motion involved in a person' day to day activities and storage them for use in powering wearable sensors. Parasitic energy is essentially the mechanical energy that is dissipated during human motion, for example walking. Piezoelectric material based harvesters solve most of the problems associated with the use of batteries discussed above. In addition, the energy generated is renewable and clean.

In order to generate electricity from walking, the harvester may be integrated in a shoe. Apart from the main receptor based design, an additional circuit is required to carry out additional tasks like AC to DC interconversion, energy storage, etc. This section is known as the power management circuit. It is discussed in detail in a later section.

The design of two possible shoe embedded harvester design prototypes have been presented.

8.8.2.2. CHOICE OF MATERIAL OF CONSTRUCTION

Over the years, various kinds of harvesters have been studied:

a. Electromagnetic harvesters
b. Electrostatic harvesters
c. Thermoelectric harvesters
d. Nano-triboelectric harvesters
e. Piezoelectric harvesters

Among these possibilities, nano-triboelectric or piezoelectric harvesters are generally preferred. This is because of their capacity to convert mechanical energy to electrical energy directly. In addition, they are also more compact and have a simpler design. However, the materials of construction for nano-triboelectric harvesters are not easily accessible and so, the best option is a piezoelectric harvester.

PZT and PVDF are the most commonly used materials of construction in piezoelectric harvesters. Both have very high piezoelectric performance. Human motion has high amplitude and low frequency. The material of construction should suit such requirements.

PZT has the following characteristics:

a. Rigid
b. Brittle
c. Heavy

PVDF on the other hand possesses the following characteristics:

a. Flexible
b. Good stability
c. Ease of handling and shaping

Clearly, PVDF is the better choice.

8.8.2.3. HARVESTER DESIGN

A specially designed sandwich structure is utilized for the purpose of making a shoe embedded piezoelectricity based harvester. This structure is beneficial because of the following reasons:

a. Thin geometrical form
b. High performance
c. Excellent durability

Two prototypes have been presented here:

a. The first is made of a multi-layer PVDF film with a rigid engineering plastics structure, that is placed under the heel and generates more power.
b. The second is designed as an insole with a silicon rubber structure with two multilayer PVDF films that makes the prototype more comfortable.

An additional circuitry is required to transport the energy generated in the harvester to the wearable sensor, AC to DC interconversion, energy storage, etc. The circuit used in both the designs is given below.

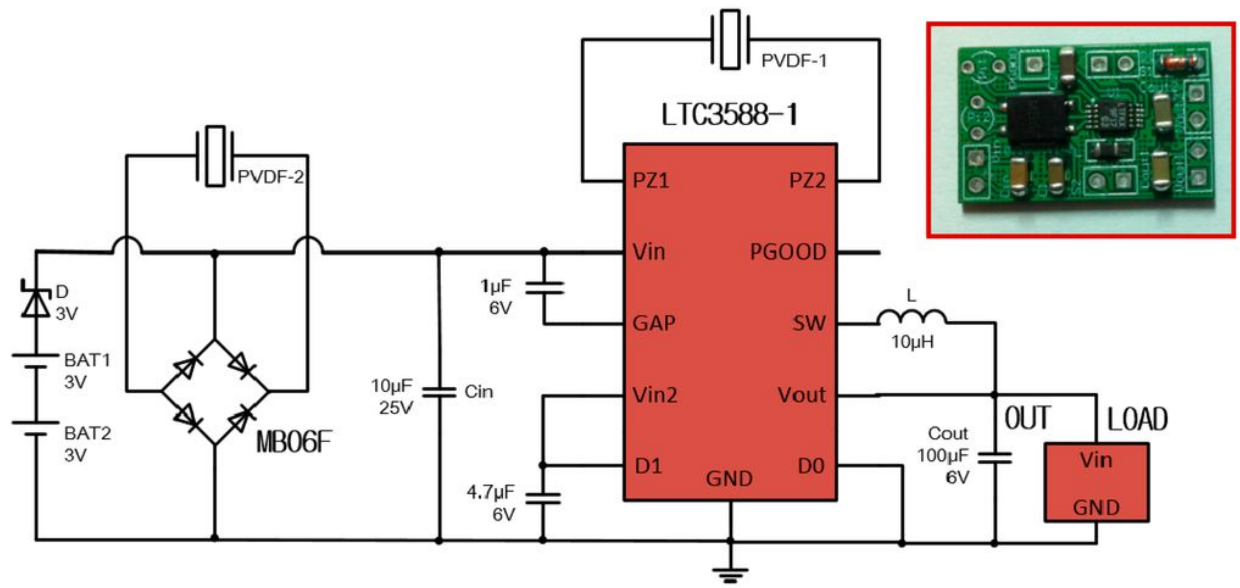

Figure 31: Additional circuitry employed in the two designs

The piezoelectric material used is a multilayer PVDF film that is composed of a stack of 8 PVDF layers in parallel, which results in a high power output. The essential properties of the PVDF multilayer film are as follows:

Material Property	Symbol	Value
Relative permittivity	ε_r	9.5 ± 1
Piezoelectric constant	d_{31}	17×10^{-12} C/N
Elastic modulus	Y	2500 MPa
PVDF layer thickness	h	30 μm
Yield strength	σ_s	45~55 MPa

Figure 32: Properties of PVDF

8.8.2.4. SANDWICH STRUCTURE

The PVDF multilayer film is sandwiched between two wavy surfaces with grooves characterised by the angle α. The multilayer film is fixed on to the lower plate whereas the upper plate is movable.

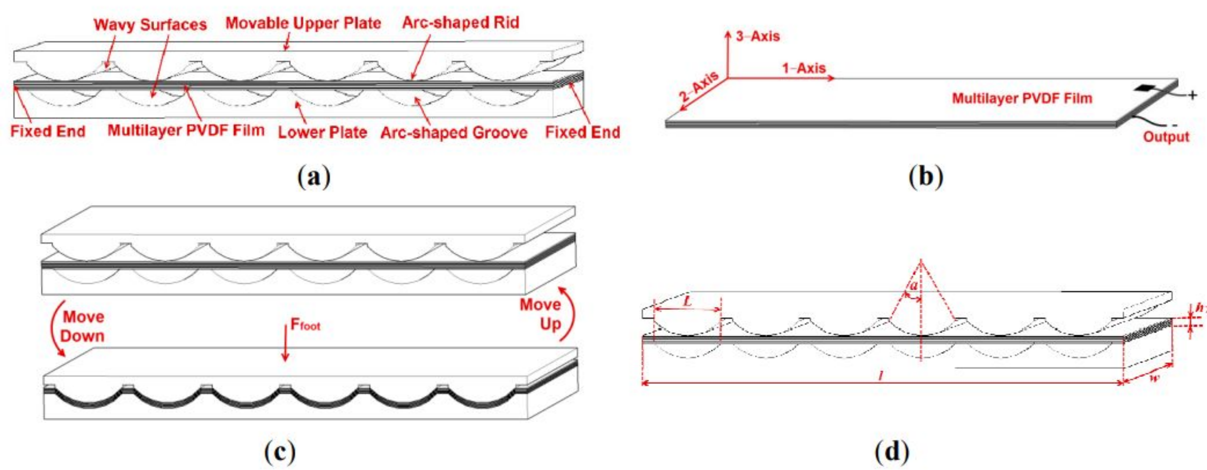

Figure 33: The main harvester design and design parameters

While stepping, a compressive force is exerted on the upper plate along the negative 3 direction. This causes it to move down and compress the PVDF film, which consequently stretches along axis 1. Piezoelectric field is generated inside every PVDF layer and this drives free electrons in the external circuit. When the force is lifted due to the lifting up of the foot, the PVDF film is relaxed. The piezo-potential diminishes and this results in a release of the accumulated charges. Thus, an AC output is obtained. The additional circuitry has the setup required to convert this to DC as most wearable sensors use DC current.

The main design parameters are as follows:

Parameter Name	Descriptions
l	PVDF layer length (along 1-axis)
w	PVDF layer width (along 2-axis)
h	PVDF layer thickness
A_1 (= wh)	Cross-sectional area of one PVDF layer
A_3 (= wl)	3-axis surface area of one PVDF layer
N	The number of PVDF layers
L	Chord length of an arc-shaped groove/ rib
2α	Intersection angle of an arc-shaped groove/rib
n (=INT(l/L))	Number of arc-shaped grooves/ribs

Figure 34: Main design parameters

We can now evaluate the different values. When the upper plate moves down to the lowest position, the tension of the PVDF multilayer film (F1) and the resistive force against the upper plate due to the PVDF film (F3) reach the maximum value. These forces can be visualised using the following image:

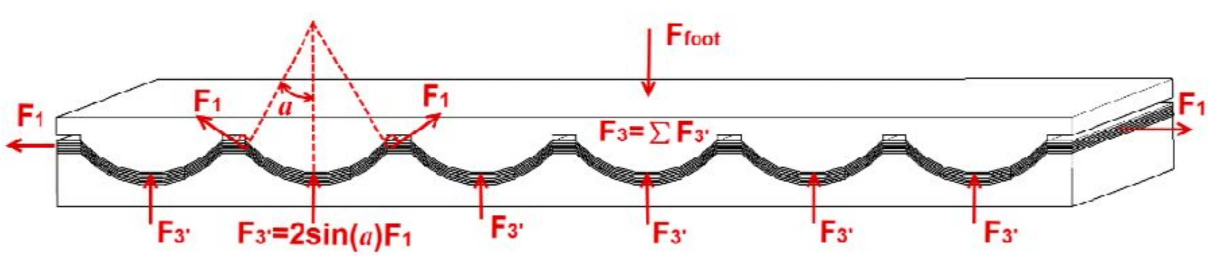

Figure 35: Forces acting on the sandwich structure

Assuming that the friction between the PVDF film and the two wavy surfaces are negligible, it is possible to evaluate the values of F1, F3, ε1 (normal stress) and σ1 (normal strain) using the following expressions:

$$F_1 = NA_1\sigma_1$$

$$\sigma_1 = \varepsilon_1 Y$$

$$\varepsilon_1 = \left[\frac{\alpha L}{\sin\alpha}\mathrm{INT}(l/L) - l\right]\Big/ l \approx \left[\frac{\alpha L}{\sin\alpha}(l/L) - l\right]\Big/ l = \left(\frac{\alpha}{\sin\alpha} - 1\right)$$

$$F_3 = \mathrm{INT}(l/L)\cdot 2F_1\sin\alpha \approx (l/L)\cdot 2F_1(1-\cos\alpha) = 2\frac{Nwhl}{L}(\alpha - \sin\alpha)Y$$

Figure 36: Formulae for F1, F3, ε1 and σ1

Using these expressions and the design specifications of the individual designs, it is possible to evaluate the limiting values of the different parameters.

8.8.2.5. FABRICATION OF PROTOTYPE 1

This design aims to exploit the high pressure that is exerted in a heel strike. The peak force of a heel strike is about 400 N. So, it is required for the resistive force, that is, F3 to be less than or equal to this value. The elastic region of the PVDF film is about 0-2%. This is the required ε1 value. From the equations discussed previously, the maximum value of α, which is an important design parameter, is evaluated to be about 19.7°. In accordance with the normal heel size, the length l is taken as 80 mm and width w as 50 mm.

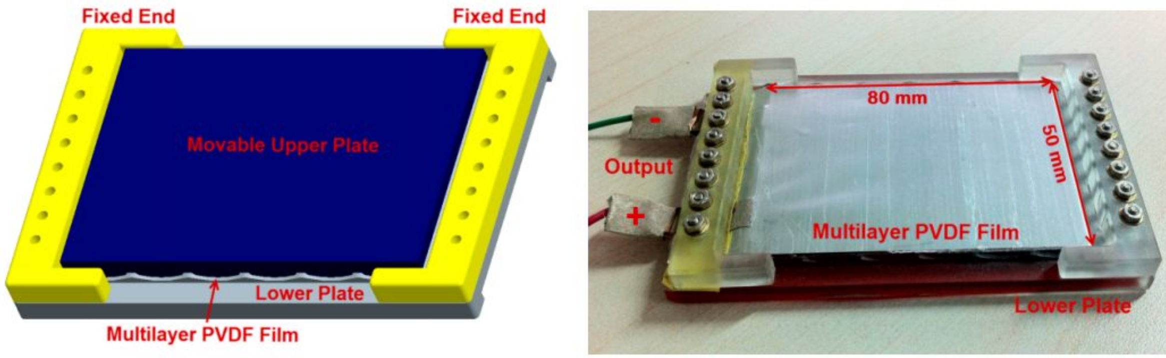

Figure 37: Prototype 1 schematic and end result

A total of 8 layers are used in the multilayer PVDF film which is bolted to the lower plate. Both the plates are made of engineering plastic which has a far superior stiffness compared to PVDF. Taking the entire sandwich structure into account, the total thickness has a limiting value of 3 mm. The optimisation process gives the following sets of values:

$$\begin{cases} 1 \le N \le 8 \\ 15° \le \alpha \le 20° \\ 5\ \text{mm} \le L \le 20\ \text{mm} \end{cases}$$

Figure : Results of optimisation of the prototype 1 design

8.8.2.6. FABRICATION OF PROTOTYPE 2

This prototype is designed with comfort in mind and has an insole shape. The entire structure can be divided into 3 individual parts as given below:

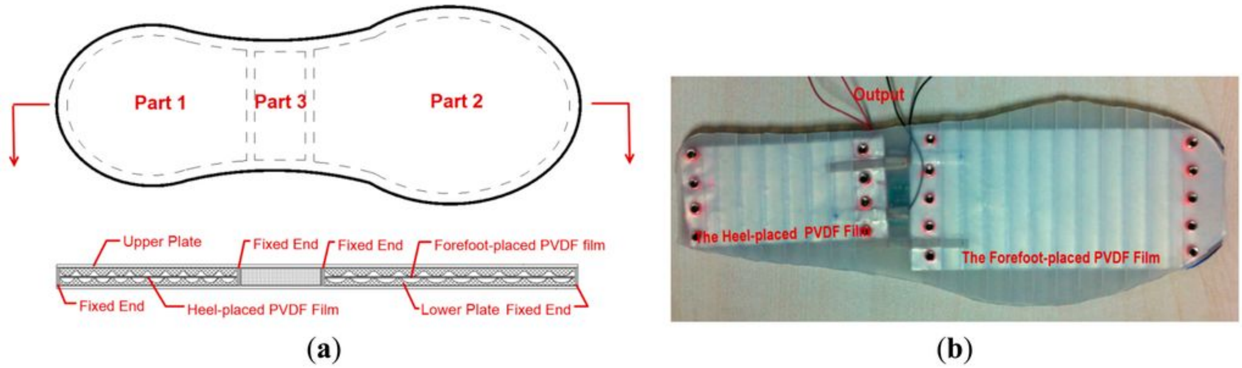

Figure 38: Prototype 2 schematic and end result

Part 1 and Part 2 consist of the sandwich design described earlier with 8 PVDF film layers each to harvest energy. Of these, part 1 harvests from the heel strike similar to the prototype 1 and part 2 harvests energy from the bending of the show. Part 3 is placed under the foot arch. The pressure here is low and so, the additional circuitry described earlier is accommodated in this part.

The two plates are made of silicone rubber by the injection modelling process. The stiffness of this material is much less than engineering plastic used in prototype 1. Therefore, the film deformation is less than the maximum value of $\varepsilon 1$ obtained from the equations discussed. In order to counter the influence of the flexible material, the design characteristic α is increased to 27.7°. This results in a maximum value of $\varepsilon 1$ as 4 %.

8.8.2.7. CONCLUSIONS FROM THE EXPERIMENTS

In comparison with the previously reported designs of shoe-embedded piezoelectric based harvesters, the designs discussed here have the following advantages:

a. Thin geometrical form (and thus, more comfort)
b. High performance
c. Excellent durability

The prototype 1 generates more power but the prototype 2 is much more comfortable. The deformation of the PVDF multilayer film is kept elastic. The maximum deformation is near the elastic limit. There is a tradeoff between performance and durability.

The specific design of the surfaces allow the PVDF multilayer to generate a large longitudinal deformation, thereby reducing the harvester thickness. This enhances the performance and allows one to embedded the harvester design in the limited space of a shoe.

8.8.2.8. RECOMMENDATIONS FOR FUTURE DESIGNS

Design components of the two prototypes may be combined to obtain a better harvester. The following changes can be made:

a. The grooves on the two plates can be made of a harder material, for example, polyurethane. This will improve the PVDF film deformation thereby enhancing the energy produced.
b. Other parts of the design can be made of more flexible materials to add to the comfort level. This will also help in the commercialisation of the product.
c. Increasing the number of PVDF layers will improve the performance. However, a thicker design will add to the discomfort. So, the thickness needs to be optimised.

8.8.3. WEARABLE HUMAN MACHINE INTERFACE (IOT DEVICES) AND HEALTH MONITORING

Muscle motion or motion on the skin is caused due to various reasons- blood flow through arteries, surface electromyography signals, etc. These motions can lead to stretching/compression/bending/movement in ultra-thin piezoelectric sensors that are laminated onto the surface of the skin and conform to it. The conformal contact between the PVDF sensor and the surface of the skin takes place through Van der Waals forces.

8.8.3.1. WORKING PRINCIPLE

Epidermal electronic devices that adhere to the surface of the skin are often used for various clinical purposes including diagnosis of diseases, studies of muscle pain and control of prosthetic devices. Various electrophysiological signals corresponding to various kinds of human action are found at all times. It is possible to use a PVDF sensor with ultra-thin stretchable substrate that is capable of conforming to the skin because of Van derWaals forces to measure these signals. The signals can then be analysed or put to other kinds of use like training a machine learning model and using it to command and control robots. One of the numerous electrophysiological signals is the sEMG (surface electromyography) signal. This can be measured very accurately from muscle motion which can be detected on the basis of the stretching/bending of a PVDF thin film. The main characteristics required to accomplish this are as follows:

a. Ultra thin for less resistance to movement
b. Modulus of elasticity very close to that of the skin to allow conformation to the skin
c. Lightweight for portability and ability to wear without much discomfort
d. High stretchability so that the performance does not degrade drastically with the excessive stretching

The accuracy of detecting and measurement of the sEMG signals depends highly on the material selection and the structure of the sensor. As PVDF fulfils all the material requirements mentioned before, it is chosen as the material of construction.

The main reason why the layout of the sensor is important is because the amount of electrical noise recorded depends on it. This highly impacts the measurement of the sEMG signals. Post processing techniques to deal with the noise and precautionary measures to be taken has already been discussed in the “wearable sensors” section.

The Internet of Things (IoT) is a network of objects referred to as "things" that have various technologies like sensors and other softwares embedded in them, which allows the sharing and exchange of data over the internet. It allows the sharing of the information or signals obtained between devices that allows fast analysis. This can enhance the speed of diagnosis of diseases. Early diagnosis is a boon in many terminal and chronic disorders or illnesses.

8.8.3.2. APPLICATIONS

There are two main possible applications of this kind of sensors:

a. **Controlling robots**: The PVDF sensors are laminated onto the wrists of both the hands. Motion results in signals. These signals corresponding to specific kinds of motion are classified. This classification can be done using machine learning models.

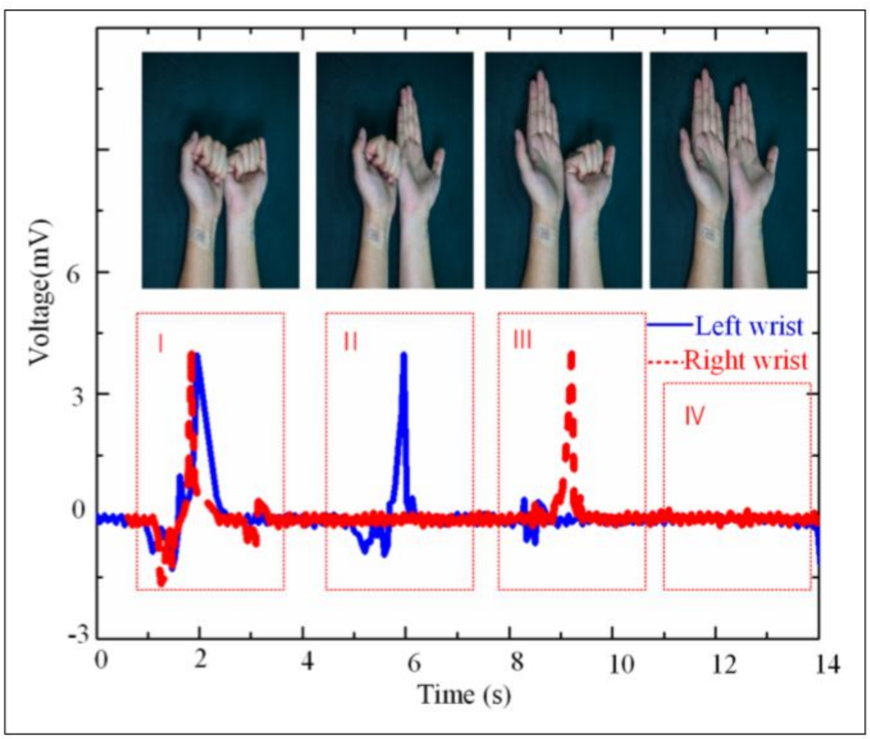

Figure 39: Classification of signals obtained from PVDF sensor

The signals are communicated to the robotic device through a wireless transmitter. Each classified signal corresponds to a simple command that causes motion in the robot that receives them. The motion corresponding to the signals classified in the previous picture is given below:

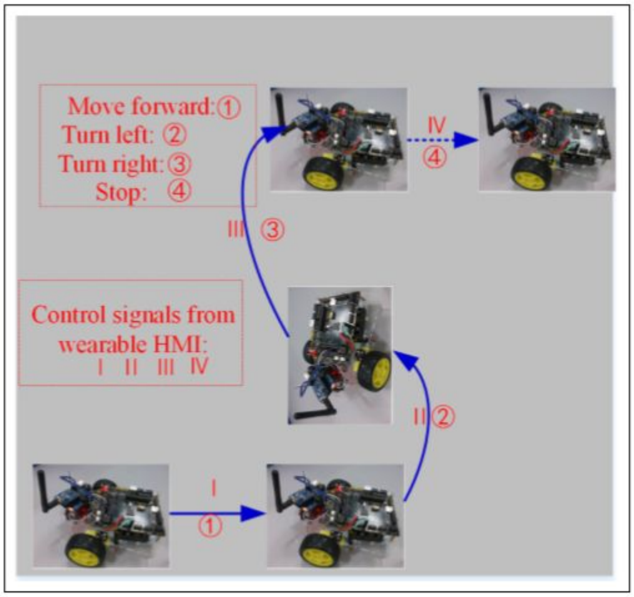

Figure 40: Controlling the robot using the PVDF sensor signals

b. **Health monitoring:** Arterial pulse is caused due to the heart beat that results in the pumping of blood. Due to the pulse, there is a specific kind of motion in the skin that is directly above. This motions causes stretching/bending in a piezoelectric sensor laminated onto the skin. Sensor signals are thus obtained and can be analysed to detect any anomalies. The construction of the sensor and its use has been discussed in details in the following section.

8.8.4. ELECTROSPUN NANOFIBER MAT AND ELASTOMERIC SUBSTRATES (HEALTH MONITORING APPLICATION)

The main idea is to prepare ultra thin small mats made of piezoelectric polymer based material that is capable of conforming to the skin. It must be capable of detecting very small displacements in the skin caused by various sources including but not limited to pulse (leading to blood flow through an artery). Design requirements include high flexibility and resilience of the materials of construction; and durability and long term stability of the device. Its performance should also not decrease drastically due to repeated stretching and folding. Skin attachable film/sheet type mechanical sensors can be used in various medical monitoring devices, electronic skin and other wearable applications.

8.8.4.1. CHOICE OF MATERIAL OF CONSTRUCTION

The most common choices of material of construction for related applications are as follows:

a. Inorganic: ZnO, PZT, BaTiO3, Pb(Zr,Ti)O3
b. Organic: PVDF-TrFE

On comparing the piezoelectric properties of all these materials, it is found that inorganic materials have far superior properties. However, there are other benefits of using polymer based materials:

a. Facile process
b. Cost effectiveness
c. High flexibility
d. Transformability
e. Stretchability
f. High durability
g. Large area processability

For the sensor discussed in this section, PVDF-TrFE is chosen. In addition, to make the structural components of the sensor, PDMS is used because of its:

a. Shape variability and ability to form very thin sheets
b. Flexibility
c. Ability to conform to the skin

8.8.4.2. PREPARATION OF ELECTROSPUN NANOFIBER MAT

The electrospinning is done using a 70/30 mol% PVDF-TrFE solution dissolved in a 60/40 volume ratio mixture of dimethylformamide and acetone. The solution was infused at a rate of 0.2 mL/min through a 25 gauge (that is, an inner diameter of 25 mm) metal needle under a potential difference of 15 kV between the needle and the collector surface separated by 20 cm. For optimisation, the following experiments were done:

a. Electrospinning using PVDF-TrFE solution of concentration 14, 18 and 22% (w/v)
b. Electrospinning time of 1, 5 and 10 minutes to study the relationship between the input deformation/displacement and the output signal

Finally FTIR spectrophotometer was used to carry out an IR spectroscopy study to confirm the dipolar crystalline structures of the electrospun nanofibers of piezoelectric material.

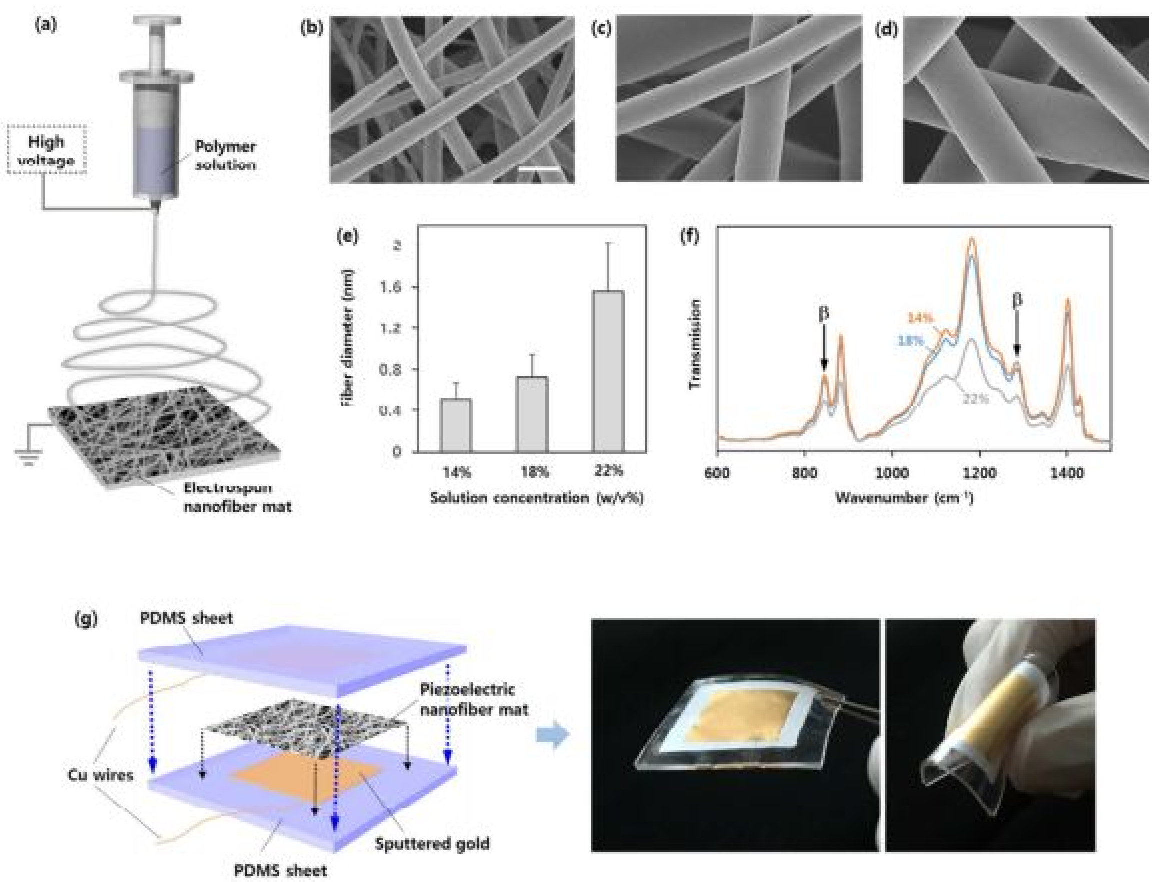

Figure 41: Electrospinning details and mat structure. (a) Schematic illustration of electrospinning. SEM images of electrospun fibers at different solution concentrations of (b) 14,

(c) 18, and (d) 22 w/v%. The scale bar in (b) is 1 μm, and the other images are at the same magnification. (e) Fiber diameter data and (f) FTIR spectra of electrospun mats. (g) Schematic illustration and photographs of a flexible piezoelectric sensor configuration.

8.8.4.3. CONSTRUCTION OF THE SENSOR

Once the nanofibers were prepared, they were used to make the mats. It is then sandwiched between a PVA-PDMS bilayer sheet and a PI-PDMS bilayer sheet sputtered with gold (electrode). The bilayer sheets are prepared by spin coating PDMS on a PVA or PI sheet. Both the top and the bottom layers are high elastomeric.

The procedure for application involves peeling off the PI sheet first. It is then applied on the skin by removing the PVA sheet by rubbing with water. This ensures conformation to the skin and a wet contact. Due to the very small thickness of the entire mat, it is capable of detecting the smallest of deformations on the surface of the skin and being lightweight, it is not uncomfortable and is very portable.

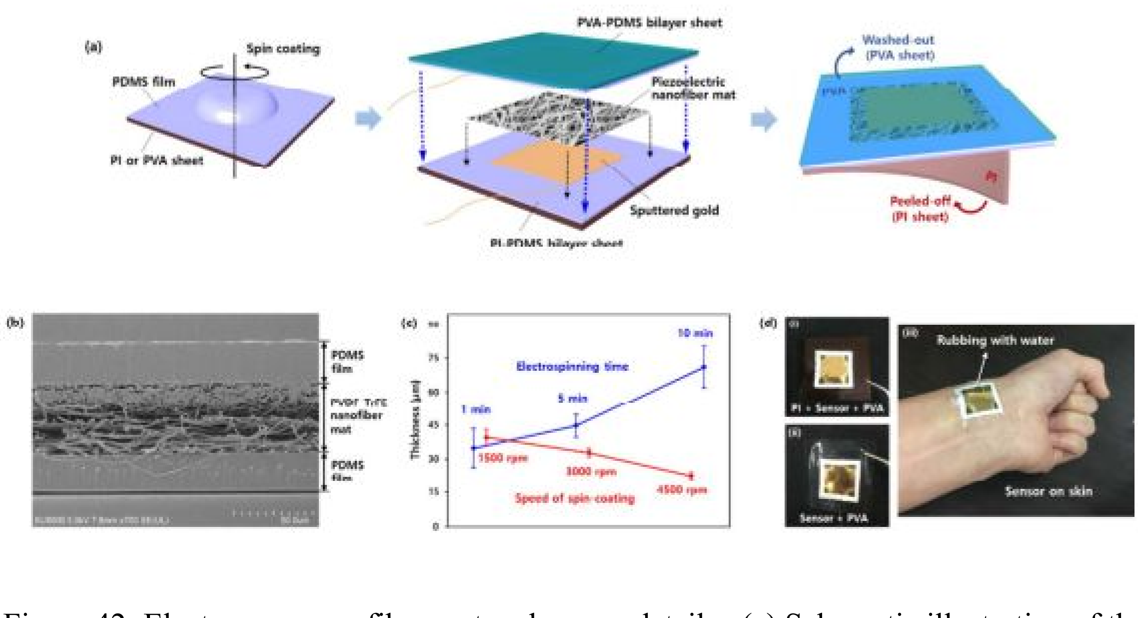

Figure 42: Electrospun nanofiber mat and sensor details. (a) Schematic illustration of the procedure for fabricating a thin sensor, including the spin-coating of PDMS on PI and PVA

sheets, sandwiching integration of the sensor components and removal of the PI and PVA sheets. (b) SEM image of the cross-section of the integrated sensor. (c) Feature thickness data of the electrospun mat and spin-coated PDMS film controlled by the spinning time and revolution speed, respectively. (d) Photographs of the integrated sensor (i) before and (ii) after detaching the PI sheet and of (iii) skin application and removal of the PVA sheet by rubbing with water.

8.8.4.4. SENSITIVITY AND DURABILITY OF THE SENSOR

The mats made of piezoelectric polymer based nanofibers were conjugated with Au-deposited elastomer sheets. This resulted in the sensor being:

a. Very highly sensitive
b. Extremely flexible
c. Highly durable

The highly polar PVDF-TrFE nanofibers are responsible for the high input-output linearity and the ability to detect the smallest of stimuli (deformations as small as 1 micrometer). The device was also found to be extremely durable and about a 1000 cycles of stretching/folding showed very little signal variation. The reason behind this durability is the highly flexible and resilient nature of the PDMS sheets as well as the non-woven polymeric nanofiber mat.

8.8.4.5. THICKNESS TUNING AND SKIN CONFORMATION PROPERTIES

PDMS can be easily shaped and can be made into sheets of a large range of thicknesses. It is also extremely flexible. These properties make PDMS the ideal choice for making the structural components of a wearable sensor.

The thickness of the entire sensor configuration can be varied by controlling the electrospinning time and making use of spin coated thin PDMS films. The sensor discussed here has a thickness of less than 100 micrometer. It easily attaches itself to the skin via Van der Waals forces of attraction. Due to the fact that it is capable of conforming to the skin at all times, it can detect skin displacements less than 10 micrometer. This is about the amount of displacement caused due to a heart pulse.

The stable applicability to the skin allows for the real time monitoring of highly resolved pulse waveforms.

8.8.4.6. APPLICATIONS IN HEALTH MONITORING

The heart undergoes cycles of systole and diastole. The pumping of the heart results in pulses, which helps the blood flow through every artery and then return to the heart through veins. Due to the flow of the blood through the arteries, the arteries momentarily expand along the diameter (called arterial distension) leading to a slight displacement in the skin of the order of 10 micrometer. The sensor, which is ultra thin and capable of conforming to the skin can detect this displacement.

Under different conditions, heart beat rates (that is, pulse rates) are different. For example, after a period of exercise, the heart is expected to beat faster. This results in output curves of much larger magnitude compared to those obtained when one is at rest. This setup thus allows real-time monitoring of the heart rate.

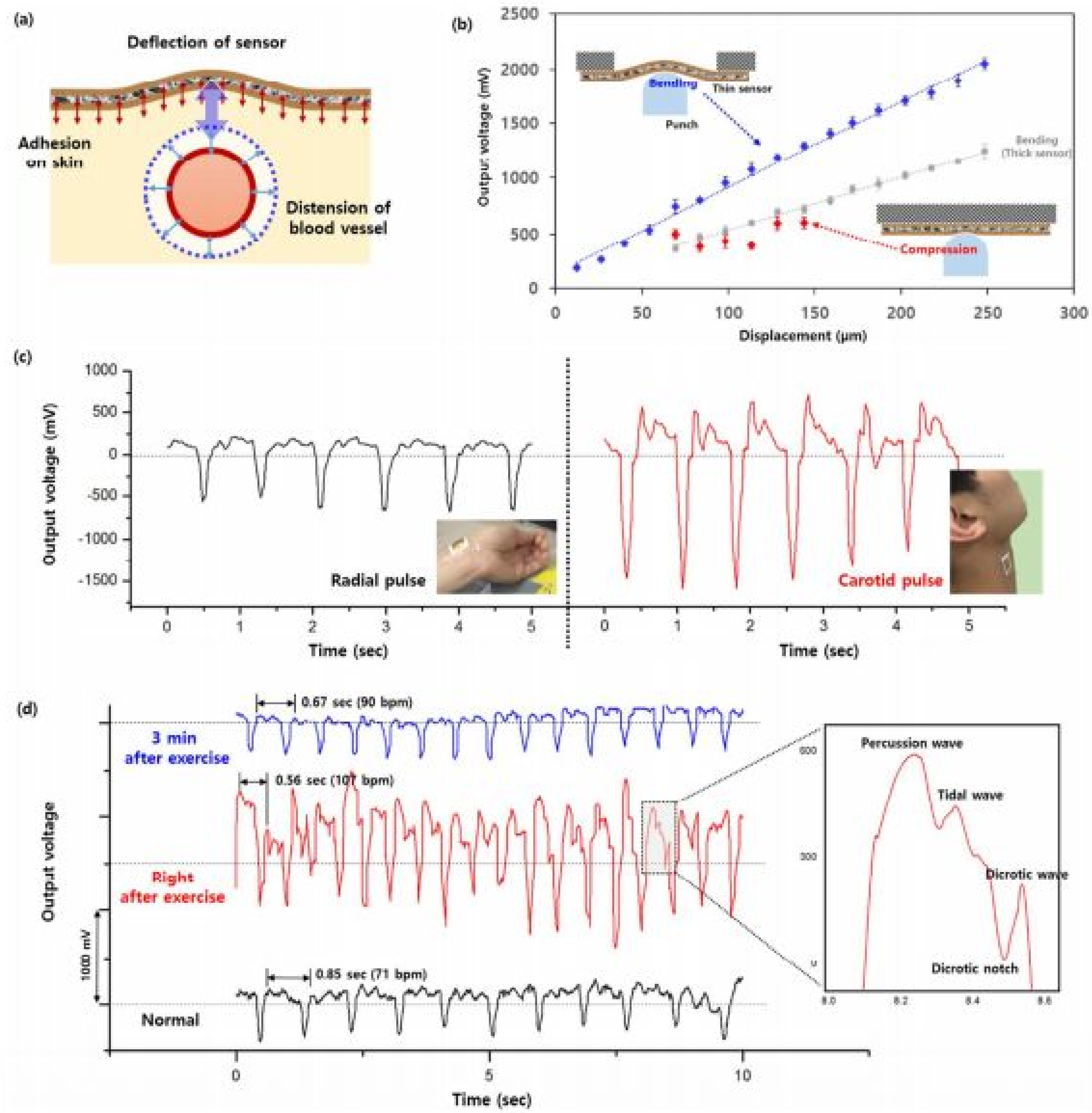

Figure 43: Use of the sensor in health monitoring. (a) Schematic illustration of the working mechanism of sensor–skin deflection by arterial distension. (b) Relationship of the sensor output distribution according to displacements under different forcing modes in bending and compression. The inset schematic images describe the forcing modes. Data shown as the mean ± standard deviation (n=10 of upper peaks versus each input). (c) Real-time sensor output waveforms measured from radial and carotid pulses (Movie 2 in the Supporting Information). (d) Real-time sensor output waveforms at three consecutive body conditions before and after exercise. The inset shows a multi-peak waveform of the pulse.

9. RECOMMENDATIONS AND CONCLUSIONS

Based on the study conducted, the following are the main conclusions (regarding piezoelectric material based devices):

1. **Types of effects and operational modes:** There are three modes of operation in regards to a piezoelectric crystal: transverse, longitudinal and shear. In the case of the longitudinal and shear effects, the number of stacked piezoelectric elements is proportional to the piezoelectric effect obtained, which in turn is directly proportional to the sensitivity.
2. **Performance parameters:** The main performance parameters include the piezoelectric constants, flexibility and charge sensitivity, all of which are properties of the piezoelectric material. Piezoelectric sensors are known to be highly sensitive and have low response times. The common issues faced during the design involves possible leakage of charge and low magnitude of signals (which can be improved using amplifiers).
3. **Choice of the material of construction:** Trained piezoelectric effect offers high sensitivity but the activity degrades with time. Natural piezoelectric materials tend to be better in this aspect. Piezoelectric ceramics have high piezoelectric constants and are comparatively inexpensive. However, they are rigid and brittle. Piezoelectric polymers, which are more flexible and easily shapeable, have extremely high piezoelectric effects which can be enhanced by electrospinning, especially in the cases of PVDF-TrFE and PAN. Of the two, PAN was recently established as the better piezoelectric material.
4. **Material for flexible electronics' construction purposes:** Materials like PDMS are flexible and comfortable when used in wearables. For devices that need to conform to the skin, materials that have Young's Modulus close to that of the skin like Ecoflex or PDMS are used. Piezoelectric crystals are avoided in such applications because of their rigid and brittle nature. Polymers are preferred because of their flexibility and ease of handling and shaping.

5. **Impedance:** Impedance is offered by every component of a circuit including the cable and the amplifier. Charge amplifiers are used to enhance the static sensitivity. Electrical impedance of the skin is reduced by using wet electrodes instead of dry ones. Impedance is approximated by modelling structures as equivalent series or parallel circuits composed of resistors, inductors, capacitors, etc. Mechanical impedance can be reduced by ensuring good conformation to the skin.
6. **Noise:** It is preferred to have a signal to noise ratio of 3:1. Noise can be avoided by taking preventative measures like insulating and shielding of electrical devices, using buffers, etc or by post processing techniques like digital signal processing algorithms and redundant sensors.
7. **Additional circuitry:** The main wearable sensor circuit is generally composed of the piezoelectric material and amplifier, connected by cables. In cases where passive transducers are used, an additional circuitry that includes an energy harvester or nanogenerator for energy supply is used. There are also components for energy storage, interconversion between AC and DC current and so on and so forth.
8. **Applications:** Piezoelectric materials find applications in harvesters that may be large scale (implemented in roads or pavements) or small scale (wearable harvesters like shoe embedded energy harvesters). Piezoelectric sensors are used for gait analysis, motion monitoring and other health monitoring applications. sEMG signals of the skin, which can be detected from muscle motion using piezoelectric sensors, can be used to build wearable human machine interfaces. These devices can be improved by the involvement of the Internet of Things. Ultra thin piezoelectric devices that are capable of conforming to the skin can be used to detect minor displacements in the skin due to arterial distension allowing us to monitor the heart rate real time.

Clearly, piezoelectric materials are a boon in terms of harvester, sensor and actuator making and with some design alterations, can be used in a much wider variety of applications in the future.

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GLOSSARY

1. **Actuators:** Actuators are used to obtain motion by converting a type of motion or energy to that which is required. Piezoelectric actuators make use of inverse piezoelectric effect to achieve this.

2. **Amplifier:** It is an optional component of a sensor that is used to amplify the output signal especially when it is too small to carry out any kind of analysis or is not within the standard ranges used by industries.

3. **Electrospinning:** It is a process that is used to make nanofibers of different thicknesses from a polymeric solution or melt. This process makes use of electric force that is greater than the surface tension of the solution being used to draw charged threads of polymers that are collected on a collector, which is often rotating.

4. **Harvesters:** Harvesters are devices that are used to harvest energy from various sources, that are more often than not, renewable. These may be small or large scale depending on the source from which the energy generation and collection takes place.

5. **Impedance:** It refers to the net resistance offered by any component in the sensor or any other electrical circuit, that results in a degradation of the signal obtained. Apart from the components used in the circuitry like capacitors and inductors, the material of the sensor itself offers some impedance which results in a loss of energy.

6. **IoT:** The Internet of Things is a network of objects referred to as “things” that have various technologies like sensors and other softwares embedded in them, which allows the sharing and exchange of data over the internet.

7. **Nanofibers:** It is a 1-dimensional nanostructure that is prepared using various methods like electrospinning. It looks like wires with the diameter in the nanoscale range (1-100 nm) and an undefined length.

8. **Noise:** It refers to the additional signals that are picked up by sensors and hamper the analysis process. It is important to develop methodologies to eliminate noise from the signal.

9. **PAN:** Poly(acrylonitrile) is a piezoelectric polymer.

10. **PDMS:** Polydimethylsiloxane is a commonly used silicone elastomer.

11. **Performance parameters:** There are specific characteristics or values that are evaluated for sensors to judge their working, use-cases and benefits of using them. Sensitivity, specificity, limit of detection, etc come under this category.

12. **Piezoelectric phenomenon:** Piezoelectricity is a phenomenon due to which when a mechanical stress is applied on an object, an electric potential develops across it. The reverse of this, referred to as the inverse piezoelectric phenomenon is also possible. Various piezoelectric materials are available today like quartz, PVDF, PZT, etc.

13. **PVDF-TrFE:** Poly(vinylidenefluoride-co-trifluoroethylene) is a piezoelectric polymer.

14. **Sensor:** It is a device, module, machine, or subsystem whose purpose is to detect events or changes in its environment and convert the signals into readable and interpretable form.

15. **Transducer:** It is a component of the sensor that helps in converting the signal obtained from the detector or recognition element into a signal that is readable. The output of transducers is often electrical signals because of how easy it is to analyse and process

them. Transducers are a necessity only when the output is not already in a readable form of signal.

ABBREVIATIONS USED

1. **ELISA:** Enzyme Linked ImmunoSorbent Assay
2. **CL:** Chemiluminescence
3. **HMI:** Human Machine Interface
4. **IoT:** Internet of Things
5. **MIP:** Molecularly Imprinted Polymer
6. **mAb:** Monoclonal Antibody
7. **pAb:** Polyclonal Antibody
8. **PAN:** Polyacrylonitrile
9. **PDMS:** Polydimethylsiloxane
10. **PVDF:** Polyvinylidenefluoride
11. **PVDF-TrFE:** Poly(vinylidenefluoride-co-trifluoroethylene)
12. **PZT:** Lead zirconate titanate
13. **SEM:** Scanning Electron Microscopy
14. **STM:** Scanning Tunneling Microscopy
15. **sEMG:** Surface Electromyography
16. **SPR:** Surface Plasmon Resonance
17. **SELEX:** Systemic Evolution of Ligands by Exponential Enrichment