PIEZOELECTRIC-DRIVEN GRAPHENE-BASED SELF-CHARGEABLE SUPERCAPACITOR FOR WEARABLE DEVICES

Abstract

Piezoelectric generators can produce electrical energy from mechanical energy. Any random mechanical stress or pressure put on a piezoelectric device leads to the generation of a potential difference. This kind of electrical energy can help in powering small low-powered devices like Radio Frequency Identification (RFID) tags, small sized sensors in Internet of Things devices, wearable devices etc. Traditionally, devices such as these and other handheld and personal devices are powered by Lithium-ion cells. These kind of heavy Li-ion batteries are expensive to manufacture, have negative environmental consequences, have long charging times and self-discharge over time.Supercapacitors are a promising next-generation energy storage device, which have very high power density, fast charge and discharge rates and long lifespan. Supercapacitors have a long lifespan of 1 million charge cycles compared to Li-ion batteries which have a lifecycle of 500-1000 charge cycles only. Hence, supercapacitors have become a promising power storage solution which can be used in next-gen low powered wearable devices. Wearable devices have received a lot of attention in recent days due to its flexibility, portability, ease of use and usage in medical monitoring devices. So, combining piezoelectric generators and supercapacitors, we can make an efficient and reliable power source for low power devices.

Keywords: Piezoelectric effect, supercapacitors, charging, power, wearable electronics

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I. INTRODUCTION

Low powered wearable electronic devices have garnered a lot of attention because of their versatile advantages such as being lightweight, flexibility and ease of being carried around. This has led to the emergence of various devices such as wearable healthcare monitoring devices, touch screen displays, smart skin, smart tongue etc. which are transforming the modern lifestyle. However, traditionally, these devices are equipped with heavy Lithium Ion batteries which need to be charged often and take up quite some time to completely charge. It makes the device non-functional for a specific period of time, which may be life threatening in some cases where the device is used for health monitoring purposes. Also, places where electricity is not available, the device would be of no use. So deeming all these issues, there is an emergence of reliable and efficient device that can harvest and stockpile energy.

For generation of the required electricity, a crucial technology is the usage of piezoelectricity. Piezoelectric devices are able to convert mechanical energy into electrical chemical energy. Mechanical pressure on a piezoelectric device changes the orientation and distance between bonds in the molecule of the piezoelectric material. This, in turn, leads to the generation of potential difference across the material and electrical energy is generated. We will discuss about piezoelectricity in detail in the coming sections.

Now comes the question of storage of this electric current. The overall power output of piezoelectric devices are less compared to other sources of electricity. So, to store this low powered current, we would require such a device characterized with soaring charging and discharge rate. The charging rates of regular use batteries such as Lead acid, Nickel Cadmium or Lithium ion is very low and charging them with piezoelectricity won't be a feasible option. So, to counter this problem, we would need an energy storage device exemplified by comparatively high rate of charging. This can be done using a Supercapacitor. A super capacitor is a semiconductor device, similar to a capacitor, but contains electrolyte instead of a dielectric medium. It can be charged completely in a matter of a few seconds to a few minutes. It also has a massive lifecycle of around 1 million charge cycles as opposed to 500-1000 of a lithium ion battery. The only downside of a supercapacitor is that it has a low energy density due to the combination of low operating voltage and small specific capacitance. Researchers are continuously exploring different materials and structures which will increase the energy storage capacity of the supercapacitor. We will discuss about structure, working and all other aspects of supercapacitors in the coming sections.

II. PIEZOELECTRIC EFFECT

The Piezoelectric Effect is a property found in some materials that enables them to convert mechanical energy into electrical energy. These materials can produce an electric current when mechanical stress or pressure is applied to it. It is reversible process i.e. when these materials are subjected to electric fields; they change their shape and gets deformed. The term piezoelectric is derived from the Greek words “Piezein” which means “to press or squeeze” and “electron” meaning “electrostatic charges in amber”.

1. **Properties of Piezoelectric Materials:** The piezoelectric materials have specific properties which make them useful for broad range of applications. To optimize their performance and to make them efficient, we need to understand their properties.

    - **Piezoelectric Coefficients:** These are parameters which define the strength of piezoelectric effect in a particular material and orientations. The value of piezoelectric coefficients change with the change in crystallographic direction of the materials.
    - **Anisotropy:** Piezoelectric material is anisotropic which allows them to experience varying sensitivity and response in the direction of applied pressure or electric field.
    - **Long-term Stability:** Piezoelectric materials exhibit piezoelectric effect for a long time which makes it very useful for application in systems that require reliable and efficient power supply in the long run.
    - **Polarization:** Piezoelectric materials possess electric dipole moment which always exists. This is due to the irregular arrangement of the positive and negative charges. This polarization is very important for maintaining the direct piezoelectric effect.
    - **Broad Frequency Range:** Piezoelectric materials can operate in a broad range of frequencies. This property makes it useful for devices working with varied frequencies such as SONAR, ultrasonic imaging etc.

2. **Mechanism and Working**

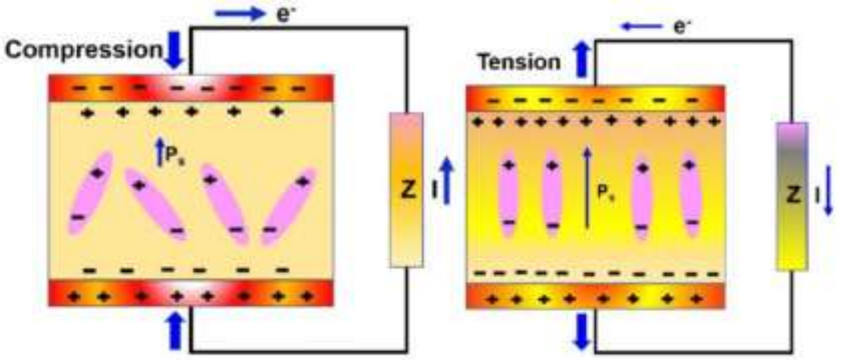


Figure 1: Effects of pressure and electric current on a piezoelectric material

The existence of electric dipole moments within solids is directly related to the piezoelectric phenomenon. These dipole moments can either be directly carried by chemical groups, as is the case in compounds like cane sugar, or they can be generated in ions at crystal lattice locations with an asymmetric charge distribution. Summing up the dipole moments per unit volume of the crystallographic unit cell yields the polarisation or dipole density (measured in C•m/m3) for crystals. The polarisation (P) becomes a vector field since each dipole is represented as a vector. Nearby dipoles have a tendency to align, forming areas known as Weiss domains. Although these domains generally have random orientations, they can be aligned through a process called poling (distinct from magnetic poling). Poling involves applying a strong electric field across the material, typically at elevated temperatures. It's an important factor to note that it is not possible to effectively pole all piezoelectric substances.

When mechanical stress is applied, the polarisation (P) changes, which has a significant impact on the piezoelectric effect. This alteration may result from a restructuring of the environments that induce dipoles or from a reorientation of molecular dipole moments brought on by the external stress. Because of this, piezoelectricity can show up as a change in the strength and/or direction of polarisation, with it depending on: 1. the directionof P inside the crystal; 2. the symmetry of the crystal; and 3. the amount and direction of the applied mechanical stress. The variation in surface charge density on the crystal faces brought on by this change in polarisation alters the electric field in between these faces of crystal due to the variation in dipole density.

3. **Types of Piezoelectric Materials:** Piezoelectricity is shown by various kinds of materials. Such as:-
   - **Crystalline compounds**
     - Quartz
     - Rochelle Salt
     - Topaz
   - **Ceramics**
     - Lead zirconatetitanatea.k.a PZT
     - Zinc Oxide (ZnO)
     - Potassium niobate (KNbO3)
   - **Semiconductors**
     - GaN
     - InN
     - AlN
   - **Polymers such as PVDF**

Figure 2: Quartz

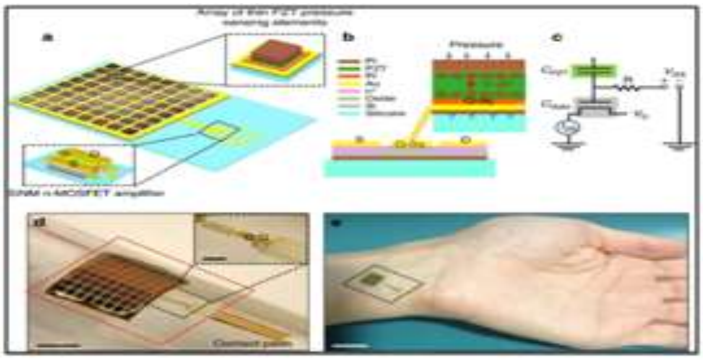


Figure 3: PZT used in wearable

4. Applications

- **Power Source:** Researchers in DARPA are working on what they call “Energy harvesting”, where they plan to power devices needed during war with piezoelectric generators equipped in soldier’s boots.
- **Frequency Standard:** Crystal oscillators made of quartz which utilizes piezoelectricity to create regularly timed electrical pulses is used by Quartz Clocks.
- **Surgery:** Piezo-surgery aims at cutting a specific tissue without affecting the surrounding soft tissue. This is done by causing micro-vibrations in the piezoelectric materials.
- **Antenna:** Cambridge university researchers, who are working on piezoelectric materials, discovered these materials act as efficient radiators, at a specific frequency.
- **Other Potential Applications:**
  - Tyre Company “Goodyear” has been planning on developing a tyre which would generate electricity as the car moves. This would be done by using piezoelectric generators inside the tyres.
  - There have been numerous attempts made to generate electricity from the kinetic energy of walking pedestrians. This would require piezoelectric tile placement in footpaths and sidewalks.

III. SUPERCAPACITOR

In this age of increasing rate of new technological advancementsalong withhigh demand for a small, easy-to-carry and more functionally efficient electronic devices. This necessitates the need of power supplies thatcan store huge amounts of energy and can run longer, and can also enable multiple loads by having high power capacity. But with current technology, all these demands cannot be fulfilled altogether.

Since a very long time, batteries have remained the most preferable means of energy storage due to their high energy density. But the only major problem with batteries is that they can take long times to charge and also to discharge which can lead to low power delivery. It is nearly impossible to overcome this power deficiency. New generation technologies such as Lithium-ion and Nickel-Cadmium are also not successful in delivering high power. Over-engineering the batteries are still not the right solution for the increasing the power efficiency, in turn it would eventually increase its weight, cost of manufacturing and size, and can also reduce the energy and life of the battery. This power deficit has increased with the increasing demands in Internet of Things (IoT). Though these devices are wireless, still they need multiple features in a very compact design and size. The necessarily small batteries are not efficient for the high demand of power in these IoT devices. So to overcome all this, supercapacitors are believed play an important role for the IoT and other devices which need high energy and power as they provide high energy and high power simultaneously, in a flat, compact and very portable package.

A supercapacitor is an electronic charge storing device developed in the 1970s-1980s, which has the capability to store electrical charge using the method of electrochemical and electrostatic processes. They have the unique capability to hold electrical charges of incredibly large amounts and they have high energy density. They are also known as Electrical Double-Layered Capacitors (EDLC) or ultracapacitors and with time they are becoming quite popular in the field of electric energy storage. They are known for their unique ability to charge and discharge quickly which makes them a feasible alternative to traditional batteries. We know that there are normal capacitors like Ceramic capacitors, Electrolytic capacitors and few more, which can store electric energy very quickly and also, discharge quickly but they are not in the same par as the supercapacitors.

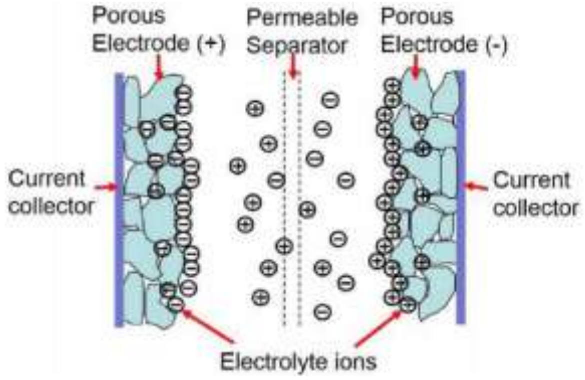


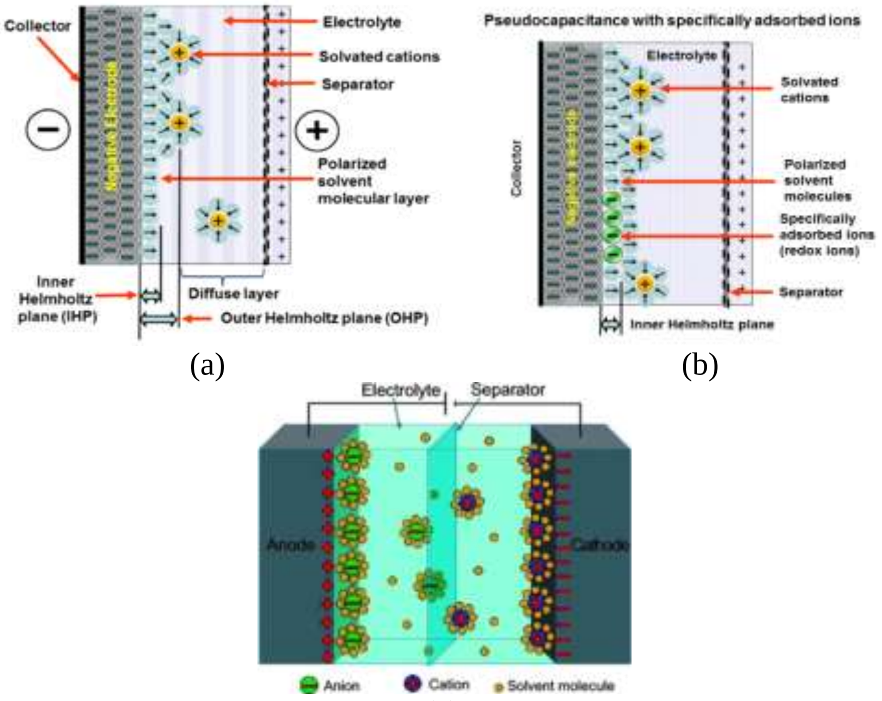
Figure 4: Schematic diagram of Supercapacitor

Based on their principle of storing electrical charge, supercapacitors can be divided into three different types which are different from traditional dielectric, they are as follows:

- **Electrostatic Double-layer Capacitor**-The constituent parts of these capacitors are two electrodes, a separator, and an electrolyte. A mixture of positive and negative ions in water is known as an electrolyte. The two electrodes are split in half by the separator. The electrostatic double-layer capacitance of the carbon electrodes or their derivatives used in these capacitors is substantially greater. Their charge separation is less than that of ordinary capacitors, ranging from 0.3 to 0.8 nm.

- **Pseudo-Capacitor:** Pseudo-capacitors are also known as Electrochemical pseudo-capacitors (EPCs). These devices often make use of current-conducting polymer metal rods as electrodes or metal-oxide electrodes with some amounts of metal oxide electrochemical pseudo-capacitance. These devices amass electrical energy by undergoing a transfer of electric charges between the electrode terminals and the electrolytic compound.

- **Hybrid Capacitor:** Hybrid capacitors are built by combining the double-layered capacitor and pseudo-capacitors (EPCs). For this type of supercapacitor, the electrode-material is chosen on the basis of specific properties required. Electrodes , placed side by side demonstrate electrochemical capacitance on one electrode and electrostatic capacitance on the other.



(a) (b)

(c)

Figure 5: Schematic diagram of (a) Electrostatic double-layer capacitor, (b) Pseudo capacitor, (c) Hybrid capacitor

Now, the double-layer capacitor is electrostatic in nature and use electrostatic charge storage, whereas the pseudo capacitor is electrochemical in nature and uses electrochemical method, and the hybrid capacitor is a mixture of both of the previous mentioned methods. Hence, the supercapacitors function as the combination of traditional capacitors and batteries. They have high energy capacities like traditional batteries and can deliver high amounts of power similar to capcacitors. With the proper utilization of these methods, we can successfully produce capacitors with capacitance as high as 15000 F.

To attain its high degree of energy density, supercapacitors use electrodes made of activated carbon with a very large surface area and a layer of electrolyte that is only a few molecules thick. Supercapacitors have a very high energy density because the energy that can be stored in a capacitor is proportionally related to the surface area of the electrodes and inversely related to the distance between the electrode and the electrolyte material. They can therefore store very large electrical charges.

A supercapacitor may be charged or drained much more quickly (milliseconds to seconds) than a battery since there is no chemical reaction necessary. Again, unlike a battery, a supercapacitor has a nearly infinite number of charge-discharge cycles since there are no chemical processes taking place.

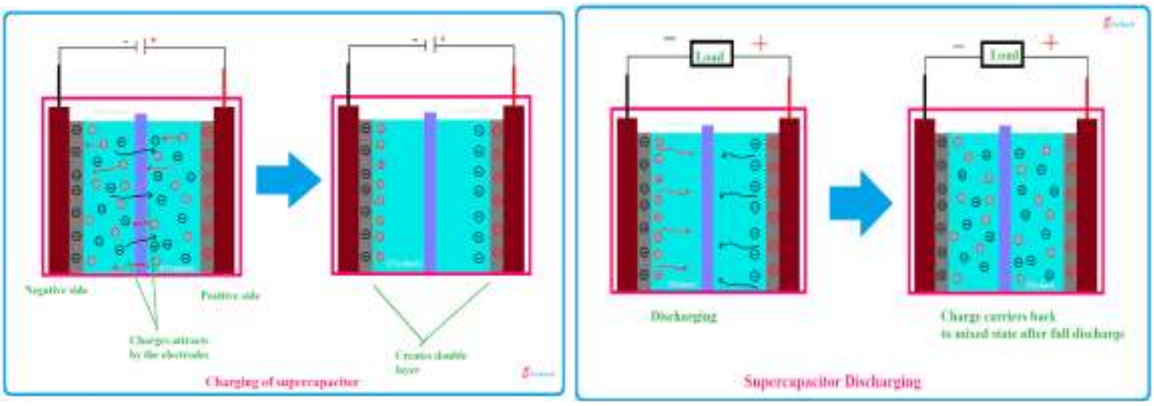
The Earth has a self-capacitance of around 710 Farads which makes up only a small fraction of the capacitance of a supercapacitor, which is 15 million times larger. A supercapacitor has a maximum charge voltage level between 2.5 to 2.7 volts, compared to the high maximum functioning charge voltage of a regular traaditional capacitor.

1. Characteristics

- Time elapsed to charge/discharge: Milliseconds to seconds.
- Optimal Operating Temperature: -40℃ to +80℃
- Operating Voltage: Aqueous electrolytes~1V; Organic electrolytes 2-3V.
- Capacitance lies between 1mF to over 10,000F.
- Operating life: 5,000 to 50,000 hours
- High power density, up to 300W/KG~5000W/KG
- Energy Density lies between 0.05Wh/kg to 10Wh/kg
- Green power supply as there is pollution in the composition of raw materials.
- It has extremely low internal resistance and heating levels.
- Convenient detection, with direct readout of remaining charge.
- Simple charging and discharging, no need for rechargeable batteries, high safety factor, long-term use and maintenance free.

2. Working Principle

- Static electricity is stored in capacitors as electrostatic energy. Positively and negatively charged ions are present in the electrolytic solution between the two plates of the supercapacitor. When a potential difference is applied across the plates, the plates develop positive and negative charges respectively.
- Due to this, the plate which is positively charged attracts the negative ions from the electrolyte, while the negatively charged plate attracts the negative ions from the electrolytic solution. A thin coating of ions is formed on the inner surface of both the plates. Hence, an electrostatic double-layer is generated which is similar to connecting two capacitors in a series connection.
- Due to the small distance between the plates in both the capacitors, their capacitance value is quite high.
- The electrodes cannot attract the ions when a load is connected to the supercapacitor and the ions start distributing and mixing in the solution and reaches a mixed state. This process is the discharging of supercapacitor.



(a) (b)

Figure 6: (a) Charging of Supercapacitor (b) Discharging of Supercapacitor

3. Advantages

The supercapacitor has many advantages like:

- It offers higher energy and power density compared to other capacitors.
- It has very high charging and discharging rates.
- It is cost efficient.
- It offers high capacitance.
- They can get charged very quickly.
- They show reliable and efficient performance.
- It improves safety, no corrosive electrolyte and low toxicity of materials.
- It can be installed in a short area as it is very small in size.
- It provides peak power and backup power.

4. Disadvantages

The disadvantages of supercapacitors are:

- Their rate of discharge is high compared to a battery and they also discharge very often.
- To generate high output voltage, it is necessary to connect them in a series fashion, as low voltages exist within individual cells.
- It can only work with DC current and won’t work with current with high frequencies.
- They have the highest dielectric absorption among any type of capacitors.
- Price of supercapacitors is higher than Li-ion batteries for the same capacity.
- It is very difficult to make very high voltage supercapacitors at the present time.
- As their internal resistance is very low, they discharge almost instantly when shorted.

5. Applications

Supercapacitors are used in:

- Electric cars
- Wind turbines
- Photographic flash
- Static memories
- Regenerative breaking in the automotive industry
- Flywheel in machines
- MP3 players
- Industrial electric motors
- Tools- Supercapacitor-based cordless electric screwdrivers have a runtime that is half that of models with comparable battery capacity, but they can be fully charged in under 90 seconds.
- Voltage stabilizers- By serving as dampers, supercapacitors can control voltage variations for power lines.
- Power buffer for grid.
- Power buffer for low-power equipment.
- Micro grids

- Energy harvesting- For systems that capture energy, supercapacitors make good temporary energy storage options.
- Incorporation into batters- A combination rechargeable lead-acid battery and supercapacitor make up the Ultra Battery.
- Medical field- To shock the heart back into sinus rhythm, defibrillators use supercapacitors, which have a 500 Joule energy output.

IV. PIEZOELECTRIC-DRIVEN SELF-CHARGING SUPERCAPACITOR

A Self-Charging Piezoelectric Supercapacitor power cell (SCPSC) can be fabricated by using Polyvinyl Difluoride (PVDF)-ZnO as the piezoelectric material and additionally as the separator, Polyvinyl Alcohol Phosphoric acid (PVA-H_3PO_4) as the electrolyte gel and electro-chemically active Manganese oxide (MnO) as the positive electrodes and negative electrodes. Due to low cost, environmental friendliness and high specific capacitance (∼1400 $F.g^{-1}$) of MnO, it is chosen as the electrode material.

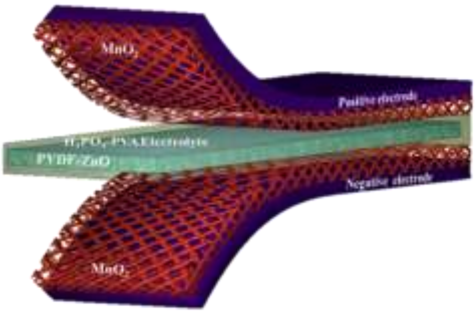


Figure 7: Schematic diagram of the fabricated SCSPC.

The electrochemical oxidation and reduction reaction—also known as the faradic reaction—is the basis for the SCSPC's functioning mechanism. At the beginning, the device is at the discharge state, in which there is no electrochemical reaction due to the electrochemical equilibrium between the electrolyte and electrodes (active material). At this stage, there is no external deformation applied to the device. When a compressive stress is applied on the device, the PVDF layer undergoes polarization due to piezoelectric effect.An electrical potential difference is created throughout the PVDF-ZnO layer as a result of the polarization of ions. This potential difference drives the ions in the electrolyte(PVA-H_3PO_4) towards the electrodes which leads to an ionic imbalance at the electrolyte and positive electrodes and negative electrodes. Thus, oxidation and reduction reactions take place at the electrode surfaces to achieve chemical equilibrium. This is how the reaction can be expressed in the following manner-

$$\mathbf{MnO_2 + H^+ + e^- \Leftrightarrow MnOOH}$$

To maintain the neutrality of the charge and the ongoing charging process, the released electrons are transferred to the negative electrode. The charging cycle is repeated as long as the mechanical force is exerted, which results in the transformation of mechanical energy into electrical energy.

With the help of Nernst Equation, we can show explain the relation between electrode potentials and the H^+ ion concentrations. When external stress is applied, H^+ ions migrate from the positive to the negative electrode. Consequently, the concentration of H^+ ions on the oxidative electrode decreases and simultaneouslyincreases on the reductive electrode. The negative electrode is at a higher potential than the positive electrode, and hence the device starts self-charging due to the gradient of H^+ ions.

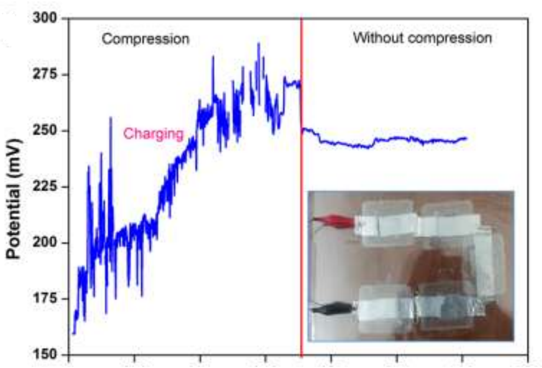


Figure 8: Self-charging performance of serially connected SCSPC

1. Schematic Diagram of the Working Mechanism

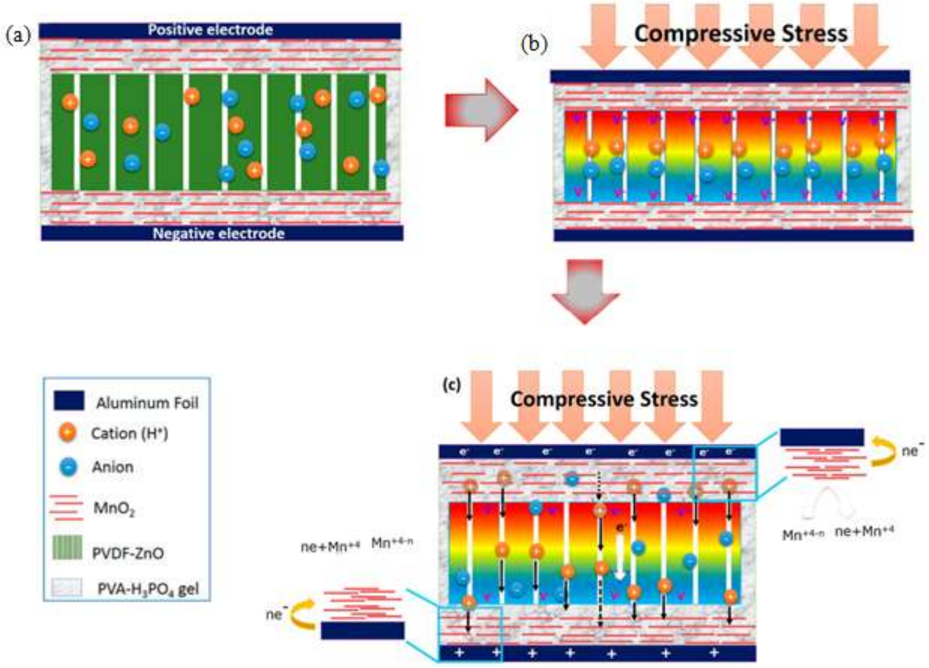


Figure 9: Working mechanism of the SCSPC driven by mechanical deformation. (a) Fabricated SCSPC at the discharge condition. (b) Mechanical deformation is applied on the top of the device; it creates a piezoelectric field (potential) in the PVDFZnO separator film. (c) Under the piezoelectric field, the H^+ ions will migrate through the PVDFZnO separator in the electrolyte to the negative electrode, leading to the corresponding charging reactions

2. **Results and Conclusion:** A PVDF-ZnO separator (piezoelectric generator) and MnO2 nanowires employed as the positive and negative electrodes may be successfully constructed into a piezoelectric-driven self-charging supercapacitor power cell, which is used to simultaneously harvest and store the generated energy.

   The SCSPC based on aluminum foil can generate around 110 mV for 300 seconds while the cloth-based one can generate around 45 mV for 300 seconds on being subjected to external stress.

   The creation of next-generation self-powered sustainable power sources for wearable and flexible electronic devices is made possible by the SCSPCs, a new and promising area in supercapacitor research.

V. GRAPHENE BASED SUPERCAPACITOR

Graphene is a very thin layer of pure carbon that is linked and packed closely together in a hexagonal honeycomb structure. It possesses a wide range of interesting qualities, like being the thinnest substance ever discovered by humans at just one atom's thickness and being extraordinarily powerful (i.e., nearly 200 times stronger than steel). Additionally, graphene has a remarkable ability to absorb light while also being a great conductor of heat and electricity. Carbon is abundant in nature and is a component of all living things, thus it is even environmentally benign and sustainable. It is a versatile substance that may be combined with other substances, such as metals and gases, to create a variety of materials with superior qualities.

Due to its property of high relative surface area, graphene is frequently recommended as a replacement for the activated carbon found in supercapacitors because it is even more substantial than that of activated carbon. A capacitor's surface area is one of the factors that prevent it from having a high capacitance since a larger surface area allows for better electrostatic charge storage. Additionally, supercapacitors made of graphene will be light-weight in nature and have greater elasticity and mechanical characteristics.

A graphene-based supercapacitor can charge and discharge in seconds and sustain all of this across tens of thousands of charging cycles, allowing it to store almost as much energy as a lithium-ion battery. One approach to accomplishing this is to use a highly porous variety of graphene with a sizable internal surface area, which is created by pressing and drying graphene powder into a coin-shaped cell. The efficiency of supercapacitors is the most important factor to bear in mind. In the past, scientists were able to create supercapacitors that have the capability to store 150 Farads per gram, but many have suggested that the theoretical upper limit for graphene-based supercapacitor is 550 Farad per gram. This is particularly even more impressive when compared against current technology: a commercially available capacitor can store 1 Farad of electrostatic energy at 100 volts and would be about 220 millimeters of height and weigh about 2 kilograms. Though in terms of dimensions relative to energy store values, current supercapacitor technology is same as that of a graphene-based supercapacitor.

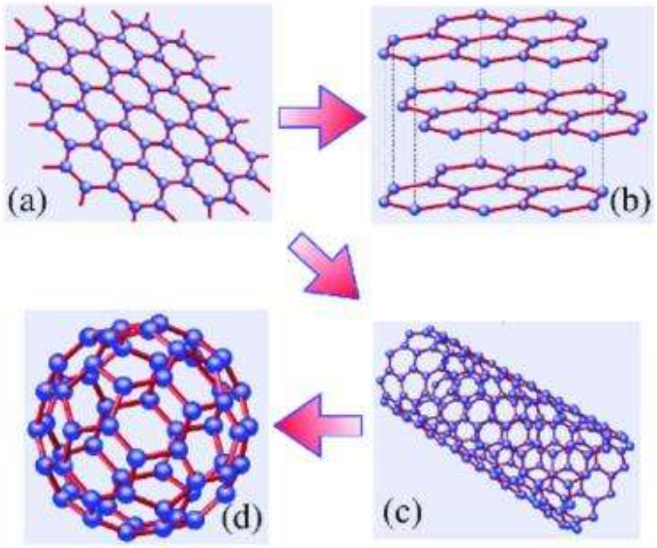


Figure 10: Schematic diagram of graphene

1. Supercapacitor Electrode Materials Based on Grapheme

Graphene can be put together to form a variety of structures, including -

- free-standing particles or dots
- one dimensional fibers or yarns
- two-dimensional films
- three-dimensional foams and composites

According to their macro structural complexity, recent investigations have focused on graphene-based electrode materials, i.e.

- zero-dimensional (0-D) (example- free standing graphene dots and particles),
- one-dimensional (1-D) (example- fibre-type and yarn-type structures),
- two-dimensional (2-D) (example- graphene-based films and graphenes),
- three-dimensional (3-D) (example- graphene composites and graphene foams).

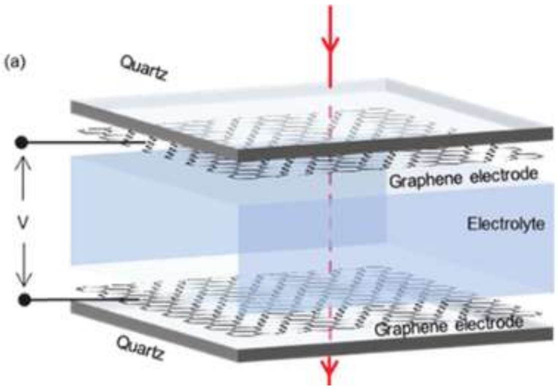


Figure 11: Schematic drawing of a parallel plate graphenesupercapacitor formed by two large area graphene electrodes and electrolyte medium in between.

- **Graphene Dots and Particles as Supercapacitor Electrodes:** Making graphene dots and particles involves chemically converting graphite into graphene oxide (GO), which is then reduced in a controlled manner using a reduction agent like hydrazine hydrate. The reduced Graphene Oxide (rGO), which is subsequently treated in water or an aqueous environment, becomes hydrophobic by the subsequent reduction and the resulting graphene particles quickly collect. The amphiphilic nature of graphene oxide (GO), in contrast, has hydrophilic edges that are negatively charged and a hydrophobic basal plane. Due to this distinctive quality, graphene oxide (GO) only interacts with specific surfactants, which are able to regulate the amphiphilicity of graphene oxide (GO) and regulate the production of rGO.

  Because of their enormous surface area and superior electrical conductivity, graphene powder-based supercapacitor electrodes often exhibit a high power density, but they also transfer charge very quickly. A moderate capacitance value of 200 F/g normally serves as their upper limit. This means that the device's energy density and overall performance are still inadequate. In electrostatic double-layer capacitors (EDLCs), carbon-based materials like graphene serve as the primary electrode materials. Creating hybrid electrodes that include metal oxides, metal hydroxides, or conductive polymers with graphene network is one method for efficiently coordinating the EDLC and pseudocapacitance. In contrast to pseudocapacitance electrodes, which are comprised of Metal oxides, Hydroxides, or conductive Polymers, hybrid electrodes, which are constructed of graphene, will serve as a conductive channel in which charge transfer occurs. As a result, the overall conductivity will improve.

  Though the process of chemical reduction for producing graphene is an effective and affordable way to make graphene on an extremely huge scale, the substances that are obtained typically show a moderate conductivity for electricity and usually do not have micro pores, and these are crucial for electrochemical energy storage.

- **1-D Graphene-Based Supercapacitor Electrodes:** Owing to the combined advantagesof low volume, excellent flexibility, and weave-ability, graphene-based yarns and fibers have a significant capability for practical use. These fibers and yarns may find use in the forthcoming generations of supercapacitors for wearable, portable, and electrical vehicle applications. There are numerous yarn and fiber shapes that can be created from carbon-based materials such as carbon fibers, CNTs, graphene, and mesoporous carbon. Additionally, they can be mixed with specific electrical active materials such conducting polymers, metal oxides, and hydroxides that exhibit faradaic pseudocapacitance.

- **2-D Graphene Film-based Supercapacitor Electrodes:** Due to its distinct structural and distinctive features, graphene is regarded as one of the most intriguing material for the upcoming-generation malleable thin-film supercapacitors-

- Having a vast surface area allows the two-dimensional structure to serve as an extended electrolyte transport platform.
- Because graphene sheets have high levels of conductivity and a low diffusion resistance, there is a gain in power and energy density.
- Graphene sheets can be effectively built into free-standing films that have high mechanical stability thanks to their exceptional mechanical properties.

  Due to its advantageous traits, including as light weight, structural flexibility, tuneable thickness, and electrical properties—which are the main requirements for malleablesupercapacitors—graphene papers have drawn a lot of attention among the graphene-based 2-D films.

- **3-D Graphene Film-based Supercapacitor Electrodes:** The diminution of graphene accumulation, which is otherwise constrained by ion access to the overall 2-D structure, can be favored by graphene-based nanocomposite films that include nanoparticles into 2-D graphene sheets. The development of 3D networked graphene-based macrostructures, such as aerogels, graphene foams, and sponges, was undertaken to address these and other significant difficulties. These 3-D-based materials, which have huge surface areas, fast ion or electron transfer channels, and micro, meso, and macro-interconnected pores, are widely desired for boosting power and energy density and enhancing the overall performance of supercapacitance.

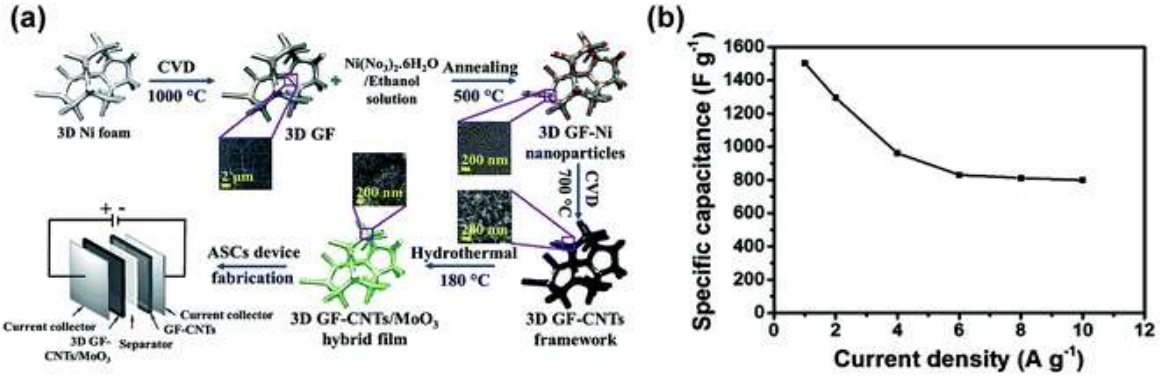


Figure 12: (a) schematic diagram illustrating all steps involved in the synthesis of 3D GF/CNTs/MoO3 hybrid film-based electrode and the asymmetric supercapacitor device and (b) specific capacitance vs. current density obtained with this supercapacitor.

In electrochemical energy storage devices like supercapacitors, graphene-based materials in diverse forms of 0-D, 1-D, 2-D, and 3-D have shown to be ideal choices for electrode materials. Significant progress has been made in the previous few years in the areas of structural design, material production, evaluation of performance, and electrochemical process comprehension. The quality and production volume of the electrode materials must be raised for wide-scale practical application. The chemical disintegration of graphite into graphene oxide (GO) and successive reduction of GO into rGO are the most efficient and affordable methods for creating graphene-based products.

The slurry casting approach, in which it is seen that for the purpose of connecting electrode material with current collectors, the effective material powders were combined with a polymer binder and conductive additives, was typically utilized to construct supercapacitors with free-standing graphene particles. However, thevolumetric and gravimetric capacitance of electrodes are both decreased by these polymers and the conductive additions, which normally contribute little to the overall capacitance.

2. Fabrication of Graphene Based Piezo-Electrolyte, Electrodes and Supercapacitor

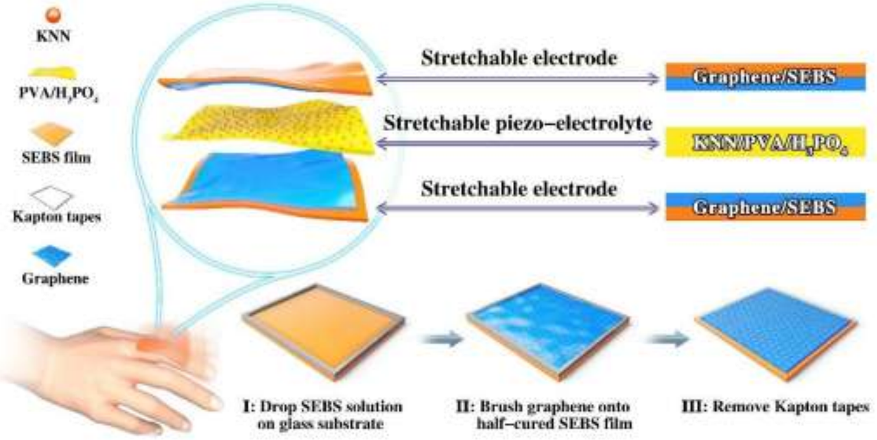


Figure 3: Schematic representation of the stretchable Self-charging SC consisting of stretchable graphene electrodes and KNN/PVA/H3PO4 electrolyte, and the fabrication process of the stretchable graphene electrodes.

The elastic SEBS substrates were coated with graphene powders to create stretchable graphene electrodes. First, 200 mg-ml-1 of commercial SEBS particles were dissolved in toluene with constant stirring at 90 °C. It was then coated gently on the stretchable graphene surface with a slight pressure until the film was fully applied, which led to the graphene sheet being inserted halfway through the SEBS film. The resulting solution containing SEBS was then poured onto a cleaned glass substrate that had patterns for making stretchable films using tape. In this way, the stretchable graphene film was developed.

The stretchy KNN/PVA/H3PO4, piezo-electrolyte film was made by first dissolving 10 g of PVA in 100 mL of deionized water for 3 hours at 95 °C. Then, 5 g of self-made KNN piezoelectric particles and 10 g of concentrated HPO4 (99+% crystallised, Aladdin) were added. To create a uniform grey solution, the mixture was agitated for an additional two hours in the same environment. Now, this solution was poured on the glass substrate with the patterns that we got from the last step. The resulting film was separated from the substrate. Then, after drying for over a day, a stretchy film of piezo-electrolyte was made. Before tests, the film was poled by putting a DC field of 10kV across it for 24 hours.

Two strectablegraphene/SEBS films were used to provide the working electrodes for the stretchable SCSC devices, and a stretchable KNN/PVA/H3PO4 piezo-electrolyte film served as both the piezoelectric separator and the electrolyte. Both the stretchable films were cut into the same size and placed together to form the SCSC device. After that, the two graphene/SEBS electrodes were sandwiched with the KNN/PVA/H3PO4 piezo-electrolyte. Transparent adhesive tapes were utilised to seal the elastic SCSC device used for palm patting, while elastomeric SEBS film was employed to seal the device used for repetitive stretching.

VI. CONCLUSION

To summarize everything, we successfully fabricated a stretchable and self-chargeable supercapacitor driven by piezoelectricity by simply using a stretchable piezo-electric film between two stretchable electrodes. The stretchy supercapacitorshows great efficiency of energy collection, conversion, and self-charging under continuous palm pressure and repetitive stretching due to the high elastoplasticity and piezoelectricity of graphene.The system also has the ability to power LED lights and electronic calculators continuously, highlighting the intriguing uses for integrating and powering stretchy electronics. Additionally, it paves the door for the creation of extremely flexible and self-charging energy devices employing comparable electrodes and piezo-film on a global scale

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