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Piezoelectric Smart Material-Based Self-Charging Supercapacitor

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In order to meet the demand for an alternative source of energy, researchers are conducting a focused research-based study. This is due to the ongoing growth and breakthroughs in the development of self-charging (SC) supercapacitors. Numerous research-based studies have been published in the recent years, and numerous fabrication methods for piezoelectric material-based self-charging supercapacitors have been used (SCPSCs). Due to their efficiency in energy conversion, storing, and harvesting, SCPSCs are becoming more and more common. A wonderful method has been developed that combines two devices (energy storage and energy harvesting) into a single SC supercapacitor in order to meet the demands of the energy deficit. This is accomplished using the two separate independent units, a piezoelectric nanogenerator and a Li-ion battery. These two are employed in the process of electrically transforming mechanical energy into chemical energy and storing the same. This integrating technology has a wide range of applications in monitoring devices, SC devices (i.e., wearable electronics), and at the micro- and macroscale. The present study is a modest attempt to inform readers about recent developments in SCPSCs by reviewing these developments in SCPSCs, their mechanisms, the piezoelectric phenomena, and their fabrication techniques. In terms of design, fabrication, and materials employed, several difficulties, restrictions, and future research directions have also been outlined.

Keywords: Self-Charging (SC) Capacitors, Piezo-Materials, Piezoelectric Effect, Piezo-Separator

1 Introduction

The continuous exploration and demands for renewable, alternate, reliable, and environment-friendly energy sources for sustainable development have become prime importance and are in top priority with involved complicated challenges to meet the energy demands in recent decades[1]. The exponential growth in environment-related concerns is motivating research towards the quest for safe, clean, and versatile energy resources[2]. In this regard, energy harvesting and storage have become the prime concern for having fast and sustainable development in this field. By 2050, the world's energy requirements are estimated to be double as per the "World Energy Council website"[3]. The primary sustainable energy sources are intermittent; hence, the requirement for compatible and versatile energy harvesting and storing devices is evident in their significant applications in the electronics field[2,4]. It is a well-known fact that most of the energy resource depends upon climate condition. Hence, harvesting and storing eco-friendly and cost-efficient energy resources is the major challenge to meet today's energy demand. The design and development of such systems energized the researchers towards SC devices due to the quick exhaustion of fossil fuels. SC devices comprise two different processes as (i) the generation of energy, i.e., the energy harvesting, and (ii) the storage of generated energy, i.e., the energy storage[5].

Renewable energy resources such as solar energy[6], thermal energy[7], wind energy[8], hydropower[9], mechanical energy, i.e., the piezoelectric nanogenerators (NG)[10], etc., are termed as the energy harvesting systems. as shown in Fig. 1. Whereas the batteries, fuel cells, and supercapacitors are regarded as the energy storage systems and employed in fabricating the SC power systems. The hybridization of two different processes (such as energy generation and energy storage) was discovered by wang and

Fig. 1 — Schematic showing the classification of energy harvesting sources[8].

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coworkers[11] in the form of SC systems. Those mentioned above two distinct processes are done using two separate units, piezoelectric nanogenerator, and Li-ion battery. The first one is used to convert mechanical energy into electrical energy, and the other store these electric energies as chemical energy. The piezoelectricity-based devices instantly convert mechanical energy into electrical energy[12, 13].

Different devices exhibit different energy storage capabilities[14]. Many possible efforts have already been employed for hybrid energy power, chemical cells, fuel cells, etc. but, they are not fully efficient in solving energy storage problems and possess some limitations. However, at present most of the electrical energy is being stored in consumable batteries. Still, these possess many issues such as limited power-storage, limited lifespan, replacement difficulties, that affects the environment adversely[15]. Such limitations and unresolved issues forced the researchers to develop such a system that possesses high-performance self-charging capabilities having power cells with high energy conversion efficacy. However, the main concern of developing the SCPSCs is to enhance the efficiency at lower manufacturing costs for their market survival. The SCPSCs technology alone, requires complete understanding which itself is on developing stage. "There is a requirement for efficient electrodes and electrolytes that boost productivity at reduced costs." Capital expenditure includes cost-effective and high-quality raw materials, optimized manufacturing process and machining process and the usage of "nontoxic and environmentally friendly materials". Therefore, the piezo-based super capacitors possess slightly higher costs.

The development of supercapacitor serves the purpose efficiently, including high capacitance and significant potentials of storing large amount of electrical energy along with unique characteristics of rapid charging-discharging rate. The high-power density of supercapacitors made it possible to use as an alternate energy source to fulfill the energy requirement of present energy demands. Piezoelectric materials, electromagnetic and triboelectric, are such mechanical sources used to develop the SC capacitors. The supercapacitors involve the mechanical energy in vibrational form during human interactions, their activities, and environmental events and convert them into electrical energy[3,12]. Such nanogenerators have gained their popularity in the energy hybridization conversion (energy harvesting and storage) process.

The piezo-materials based SC capacitors have shown the most promising results and proved to be the most efficient energy source. Such SC devices use the piezoelectric effect. The energy hybridization (conversion and storage) is done in a single step. Generally, organic and inorganic materials are utilized in developing the SCPSCs[16,17]. In the subsequent sections, the term 'piezoelectric' has been used as 'piezo' for short and suitable use with other terms. The current work is a modest attempt to enlighten the readers about the mechanisms and behavior of such smart and attractive materials (piezoelectric) based devices, their efficacy, applications, and challenges with future research. Various progress in SCPSCs development can be estimated through the published documents as illustrated in Fig. 2.

2 Materials and Methods

2.1 Construction, Mechanism, and Operation

Supercapacitors have attracted the great attention of the scientific community due to their unmatched high performance, energy storage capability, high power density, low maintenance cost, and environment-friendly nature. The energy-storing supercapacitors behave as a charge carrier that conserves the charges by applying an external voltage and functions like a rechargeable battery. An ordinary capacitor is a simple charge storing device, where a dielectric material is placed in between the two parallel electrodes (plates). Whereas the supercapacitor has no such dielectric material and consists of the two plates (electrodes: cathode and anode), electrode separator, and an electrolyte solution. The two electrodes are separated by a thin

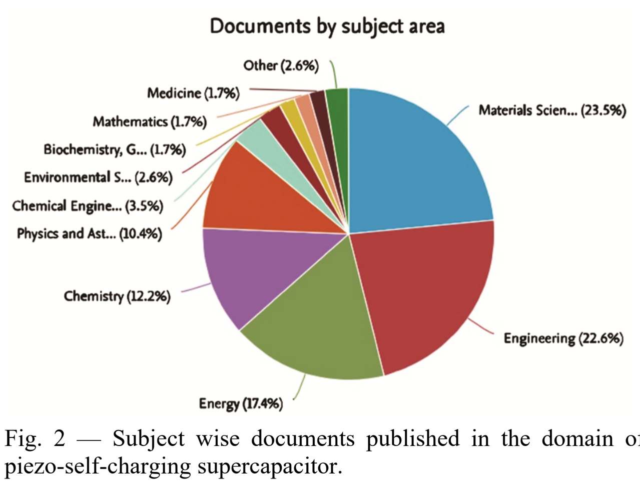

Fig. 2 — Subject wise documents published in the domain of piezo-self-charging supercapacitor.

layer of insulating material (carbon, plastic, or paper) immersed into an electrolyte solution. The performance of the supercapacitor can be altered using the chosen material for its electrodes[18]. Generally, low loading material is preferred for electrode plates to investigate the electrochemical properties of the materials. Also, the increment of external loading escalates the electrode thickness, but, due to having limitations in ionic conductivity, the issue of mass transfer occurs across the electrode. The material selection for SCPSCs electrode plays an imperative role in terms of stability, efficiency, and performance having high specific capacitance, higher surface area, controlled porosity, etc., higher thermal conductivity, and low cost[11]. Supercapacitors can be divided into (i) pseudo-supercapacitor and (ii) double-layered capacitors. Further, based on the mechanism and types of electrodes, this are further categorized into symmetric (having two similar parallel plates) as well as asymmetric (having two dissimilar parallel plates)[3].

2.1.1 Electrical Charge Cumulation

"The cumulation of an electrostatic charge is necessary to store the charge traps within so-called Helmholtz layers." The applied input voltage diffuses the ions in electrolyte via voids developed in opposite polarity electrodes. The accumulated charges produce two loaded layers between an electrode and an electrolyte, with a little interfacial separation. Thus, the high capacitance values result from the fact that the capacitance depends upon the surface area and the "inverse of separation among both the layers[19]. Also, using the carbon materials like graphene as an electrode enhances capacitive performance. These carbon-made graphene materials possess improved characteristics like large surface area and high and enhanced electrical and thermal conductivity. "An EDLC is the simplest and most commercially available supercapacitor, where the charge is physically stored by electrostatic charge adsorption at the interface between electrode and electrolyte" [20,21].

2.1.2 Pseudo-supercapacitance

Supercapacitors are also termed as 'electrochemical capacitors.' Pseudocapacitance is referred to as a faradaic process known as an electrochemical energy storage process where the absorbed ions gather the charges. In supercapacitors, a redox reaction occurs, and the transfer of ions is deposited all over the two layers. "Ruthenium dioxide (RuO2) was the first electrode material reported to exhibit pseudocapacitive behavior". The electrochemical behavior of pseudocapacitance energy storage is midway between pure electrostatic EDLCs and solid-state diffusion dominated by Faradaic reactions in bulk battery-type materials. The mechanism of energy storage for capacitive electrodes has been illustrated showing the electrochemical chemical features during various faradaic processes[21]. The electrochemical behavior of pseudocapacitance energy storage is midway between pure electrostatic EDLCs and solid-state diffusion dominated by Faradaic reactions in bulk battery-type materials.

2.2 Phenomenon of Piezoelectricity

Piezoelectric materials feature the electrical properties of materials that produce piezoelectric effect, as a result, the mechanical energy is converted into electrical energy. The piezoelectric materials are used as dielectrics that get polarized on mechanical loading/stress. All materials do not show the unique behavior of such energy conversion through the piezo-effect. There are two states of piezoelectric materials: polar and non-polar piezoelectric materials. Polar piezoelectric materials possess "non-zero dipole moment," whereas non-polar piezoelectric materials possess "total null moment. Initially, the material exhibits a neutral character. On external loading, deformation occurs in the material that induces an electric dipole by separating positive and negative charges. Further, the opposite induced poles neutralize each other, and some "definite charge is seen" on the surface of polarized materials, termed as "piezoelectric effect." Under influence of such effects, an electric field occurs on the polarization of the materials and helps "converting mechanical energy into electrical energy". On removal of applied external load, the induced charges vanish, the flow of charges takes place in reversed direction, and the induced polarity gets reversed[22]. Finally, the material gains its original state.

2.3 Self-charging Energy Storage Mechanism

The energy conversion from one form to another and its storage is a challenging issue occurring nowadays. In the case of SCPSCs, the energy is stored on the interface exposed between the electrode and electrolyte solution. During the energy storage mechanism, self-charging process depends piezo-effect. When a piezoelectric material experiences an external loading, it develops an internal field effect[23]. However, the 'Rochelle salt' is used in piezoelectric materials as well as in developing SC supercapacitors[24]. Figure 3 demonstrates the mechanism of supercapacitors. Initially, the system remains at discharged state in the absence of any external stimuli, Fig. 3(a). Then, applying small loading via hand, the piezo material gets polarized, and due to ions polarization, a potential difference is created throughout the separator on both sides of electrode.

As a result, cations pass through the piezo-field of an electrolyte solution, this percolates the potentials generated across the piezo-separator, as shown in Fig. 3(b). An electrochemical imbalance occurs when ions flow through electrodes and electrolyte solution, resulting the occurrence of redox reaction at both electrode surfaces, Fig. 3(c). The free flow electrons towards the negative electrode, ensuring charge balance and charging. Due to this continuous process, a state of chemical equilibrium is obtained and no further ions polarization occur.

On removal of external loading/compression force, the developed piezo-potential is dissipated through the piezo-separator made up of piezoelectric materials as delineated in Fig. 3(d), unsettles the equilibrium state of electrochemical systems. This is compensated by returning of ions to complete the charging after the occurrence of the redox reaction[24].

2.4 Mathematical Modelling of Piezoelectric Effect

According to the linear theory, at low mechanical stress the piezo-material has a linear profile at the low electric field. The piezoelectric materials exhibit linear behavior for a particular range of electric fields

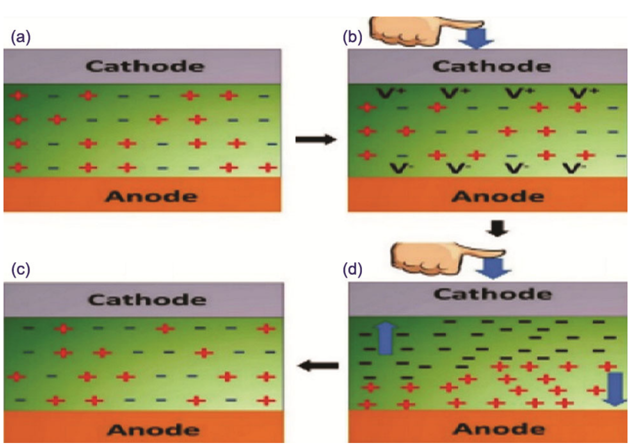

Fig. 3 — Schematic showing the SCPSCs mechanism: (a) discharge state, (b) piezo-effect due to external stimuli, (c) ions movement closer to the electrode surface, and (d) vanishing of piezo-effect on removal of external stimuli[24].

and mechanical stresses. A poled piezoelectric material becomes electrically polarized when it gets physically stretched/strained, resulting the electrical charges deposition on the material's surface. If the electrodes come into contact with the surface of the substance, the collected charges from the material surface get accumulated on these electrodes[25,26]. In piezo-materials, the accumulated electric charge density exhibits a proportional relationship with external stress. The mathematical relation for the same is given as:

$$\vec{P}_{pe} = \vec{d} \times \vec{T} \quad \ldots(1)$$

where, $\overrightarrow{P_{pe}}$ denotes polarization vector of piezo-materials, $\vec{d}$ is the strain coefficient of piezo-materials, and $\vec{T}$ represents the stress applied to piezo-material. Similarly, the reverse piezo-effect is also expressed as:

$$\vec{S}_{pe} = \vec{d} \times \vec{E} \quad \ldots(2)$$

Where, $\overrightarrow{S_{pe}}$ is mechanical strain under piezo-effect, $\vec{E}$is the magnitude of an applied electric field. Further, both direct and reversed piezo-effects could be structured under the consideration of elastic properties as:

$$\vec{P}_{pe} = \vec{d} \times \vec{T} = c \times S = e \times S \quad \ldots(3)$$

$$\vec{T}_{pe} = c \times \vec{S}_{pe} = c \times \vec{d} \times \vec{E} = e \times \vec{E} \quad \ldots(4)$$

2.5 Fabrication Techniques

For SCPSCs fabrication various techniques and methods are adopted. Sometimes for energy harvesting process, the smart piezo-materials are employed as a separator as well as electrolytes. For a SC capacitor, various methods such as electrospinning, mixed-oxide sintering, vapor induced phase separation, etc[12,26,27]. are being used to prepare piezo-materials for energy harvesting purposes. PVDF is a highly appreciated piezoelectric smart material utilized in SCPSCs. Various literatures have reported the PVDF films of different thicknesses, can be directly used as piezo-separator in the fabrication of SC supercapacitors. Besides the separator, piezo-materials are also utilized as electrolytes. Krishnamoorthy et al.[28] reported the idea of ion gel electrolyte made-up of piezoelectric materials for utilization in a supercapacitor.

However, the techniques of using the piezo-materials as a “piezo-separator and piezo-electrolyte” are very productive and functional. The choice of piezo-materials has proven their efficacy, high performance, and effective uses in manufacturing of SCPSCs and plays a vital role in their unmatched applications. Various piezo-materials such as potassium “sodium niobate (KNN),” $BaTiO_3$, ZnO, and PVDF are used to fabricate SCPSCs. Usually, inorganic materials like ZnO, quartz, $BaTiO_3$, PZT, and organic materials like PVDF exhibits the piezoelectric phenomenon. Among these, PZT and $BaTiO_3$ possess highest piezo-constant and demonstrate high efficacy. But, due to lead content in ZnO, the

$BaTiO_3$ is the only promising lead-free material with high piezoelectricity and biocompatibility for environmental concerns. Similarly, when compared to other organic polymers, PVDF possess higher piezoelectric capabilities that can be deformed without cracking, and has higher strength. Due to the chemical stability and inertness, it is used as a separator. This does not react with the electrolyte over a sizeable potential range. (Available the in-depth study on the development of SCPSCs)[27,29-32].

3 Results and Discussion

3.1 Advantages and Disadvantages

In this field, the materials proposed for manufacturing of SCPSCs are making strides. However, they have some flaws that limit their uses as a supercapacitor manufacturing candidate. A notable merits and demerits of SCPSCs based materials have been provided by Singh et al.[3]

3.2 Applications

Further, providing the applications perspective in implementation benefits is one of the major characteristics of utilization of such SCPSCs. The development and architectural design of such systems based on their usability are the current hour requirements and indeed incorporates various aspects such as human need, cost effectiveness and future materials[33] etc. At a high-end applications spectrum, the SCPSCs are being used in hybrid vehicles in order to enhance their efficiency. Also, these are potentially utilized in solar arrays and also in micro-energy harvesting applications which do not require much energy storage. Further, various MNCs are now a days involved in developing SCPSCs with higher efficiency that can be found in detail in[33].

3.3 Challenges

The world is suffering from an energy crisis, and the demand alternate energy sources are comparatively very high. The shortage of energy sources, their reasonable distribution and utilization is the primary concern for our researchers and scientists in today's era. The development of SCPSCs have grown as a demanding candidate in energy harvesting and storage systems. However, they possess some sort of limitations. SCPSCs also encounter some technical issues like “electrical parameter models, conducting consistency analysis and creating industry standards." However, there are many available supercapacitors, but these are insufficient and incapable of charging the devices for an extended time. Additionally, the low power density, design improvement, low power output, longevity, self-discharging, and the cycling life of such SCPSCs are the primary technical issues and demand high concerns.[3,34-36]

4 Conclusion

Over the last few decades, the demand for an alternate energy source have extensively investigated for sustainable, environment-friendly energy generation, storage systems and techniques. The energy harvesting and storage methods possess the long-term utilization of renewable energy resources for various applications. The current work discusses the SCPSCs construction and mechanisms for developing SC devices and summarizes the fabrication procedure along with challenges. various applications of SCPSCs in domain of “flexible/wearable technology,” advancing the ways of adaptable display facilities, “ecosystem management, cloud computing, military applications, and smart wearable electronic gadgets. The present work highlights different piezo-materials that facilitate the SC phenomenon in supercapacitors.” Various organic and inorganic materials with high piezoelectric constants such as PZT, ZnO, and $BaTiO_3$ are used as a PVDF. Among these materials, $BaTiO_3$exhibits its lead-free, environment-friendly characteristics. But, the lead content in ZnO made this undesirable material from environmental perspective. Still, ZnO possesses high performance, easy fabrication, low cost, and high piezoelectricity, made it suitable in wide range of applications. Due to exceptional properties, it is much advantageous towards the utilization in supercapacitors.

References

1 Huskinson B, Marshak M P, Suh C, Er S, Gerhardt M R, Galvin C J, Chen X, Aspuru-Guzik A, Gordon R G & Aziz M J, *Nat,* 505 (2014) 195.

2 Verma S, Gupta V, Khosla A, Kumar S & Arya S, *Nanotechnol,* 31 24 (2020) 245401.

3 Singh B, Padha B, Verma S, Satapathi S, Gupta V, & Arya S, *J Energy Storage, 47 (2022) 103547.*

4 Verma S, Arya S, Gupta V, Mahajan S, Furukawa H, & Khosla A, *J Mater Res Technol,* 11 (2021) 564.

5 Pu X, Li L, Song H, Du C, Zhao Z, Jiang C, Cao G, Hu W & Wang Z L, *Adv Mater,* 27 (2015) 2472.

6 Luther J M, Law M, Beard M C, Song Q, Reese M O, Ellingson R J, & Nozil A J, *Nano Lett,* 8 (2008) 3488.

7 Poudel B Hao, Ma Y, Lan Y, Minnich A, Yu B, Yan X, Wang D, Muto A, Vashaee D, Chen X, Liu J, Dresselhaus M, Chen G, & Ren Z, *Sci,* 320 (2008) 634.

8 Shao Z P, Haile S M, Ahn J, Ronney P D, Zhan Z, & Barnett S A, *Nat* 435 (2005) 795.

9 Cao X, Jie Y, Wang N, & Wang Z L, *Adv Energy Mater,* 6 (2016) 1600665.

10 Song Y, Cheng X, Chen H, Huang J, Chen X, Han M, Su Z, Meng B, Song Z, & Zhang H, *J Mater Chem* A, 37 (2016) 14298.

11 Xue X, Wang S, Guo W, Zhang Y, & Wang Z L, *Nano Lett,* 12 (2012) 5048.

12 Maitra A, Paria S, Karan S K, Bera R, Bera A, Das A K, Si S K, Halder L, De A, & Khatua B B, *ACS Appl Mater Interfaces,* 11 (2019) 5022.

13 Pazhamalai P, Krishnamoorthy K, Mariappan V K, Sahoo S, Manoharan S, & Kim S J, *Adv Mater Interfaces,* 5 (2018) 1800055.

14 Winter M, Brodd R J, *Chem Rev,* 104 (2004) 4245.

15 Robinson B H, *Sci Total Environ,* 408 (2009) 183.

16 Zhang Y, Xue X, Cui C, He B, Nie Y, Deng P, & Wang Z L, *Nanotechnology,* 25 (2014) 105401.

17 Stevic Z, *Supercapacitor Des Appl* (In-tech Open, London), ISBN: 978-953-51-2748-2 (2016) 89.

18 Pope M A, Korkut S, Punckt C, & Aksay I A, *J Electrochem Soc,* 160 (2013) 1653.

19 Okonkwo P C, Collins E, & Okonkwo E, *Biopolym Compos Electron,* (2017) 487.

20 Kim B K, Sy S, Yu A, Zhang J & Hand b, *Clean Energy Syst* (John Wiley & Sons Ltd., UK), (2015) 1.

21 Shao Y, El-Kady M F, Sun J, Li Y, Zhang Q, Zhu M, Wang H, Dunn B & Kaner R B, *Chem Rev,* 118 (2018) 9233.

22 Augustyn V, Simon P & Dunn B, *Energy Environ Sci,* 7 (2014) 1597.

23 Dubal P, Chodankar N R, Kim D H & Gomez-Romero P, *Chem Soc Rev,* 47 (2018) 2065.

24 Verma S, Arya S, Gupta V, & Khosla A, *Chem Eng J,* 424 (2021) 130567.

25 Sahoo S, Krishnamoorthy K, Pazhamalai P, Mariappan V K, Manoharan Sindhuja, & Kim S-J, *J Mater Chem A,* 7 (2019) 21693.

26 Parida K, Bhavanasi V, Kumar V, Wang J, & Lee P S, *J Power Sources,* 342 (2017) 70.

27 Lu Y, Jiang Y, Lou Z, Shi R, Chen D & Shen G, *Prog Nat Sci Mater Int,* 30 (2020) 174.

28 Pazhamalai P, Krishnamoorthy K, Mariappan V K, Sahoo S, Manoharan S & Kim S J, *Adv Mater Interfaces,* 5 (2018) 1800055.

29 Zhou D, Wang F, Yang J, & Fan L Z, *Chem Eng J,* 406 (2021) 126825.

30 Sharma M, Gaur A & Quamara J K, *Solid State Ion,* 352 (2020) 115342.

31 Pazhamalai P, Mariappan V K, Sahoo S, Kim W Y, Mok Y S & Kim S-J, *Micromachines,* 11 (2020) 198.

32 Samyal R, Bagha A K, Bedi R, Bahl S, Saxena KK, & Sehgal S, *Mater Res Express,* 8 (2021) 075302.

33 Goyal D, Dang R K, Goyal T, Saxena K K, Mohammed K A & Dixit S, *Materials,* 15(18) (2022) 6241.

34 Huang S, Zhu X, Sarkar S & Zhao Y, *APL Mater,* 7 (2019) 100901.

35 He W, Fu X, Zhang D, Zhang Q, Zhuo K, Yuan Z & Ma R, *Nano Energy,* (2021) 105880.

36 Liu Z, Li H, Shi B, Fan Y, Wang Z L & Li Z, *Adv Funct Mater,* 29 (2019) 1808820.