

Fluoropolymers and Their Nanohybrids As Energy Materials: Application to Fuel Cells and Energy Harvesting

Om Prakash,[§] Shivam Tiwari,[§] and Pralay Maiti*[§]



Cite This: *ACS Omega* 2022, 7, 34718–34740



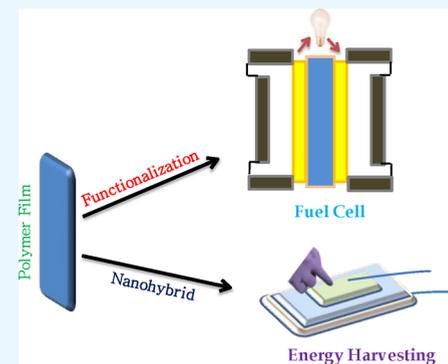
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The current review article provides deep insight into the fluoropolymers and their applications in energy technology, especially in the field of energy harvesting and the development of fuel cell electrolyte polymeric membranes. Fluoropolymers have gained wide attention in the field of energy applications due to their versatile properties. The incorporation of nanofillers within the fluoropolymer to develop the nanohybrid results in an enhancement in the properties, like thermal, mechanical, gas permeation, different fuel cross-over phenomena through the membrane, hydrophilic/hydrophobic nature, ion transport, and piezo-electric properties for fabricating energy devices. The properties of nanohybrid materials/membranes are influenced by several factors, such as type of filler, their size, amount of filler, level of dispersion, surface acidity, shape, and formation of networking within the polymer matrix. Fluoropolymer-based nanohybrids have replaced several commercial materials due to their chemical inertness, better efficacy, and durability. The addition of certain electroactive fillers in the polymer matrix enhances the polar phase, which enhances the applicability of the hybrid for fuel cell and energy-harvesting applications. Poly(vinylidene fluoride) is one of the remarkable fluoropolymers in the field of energy applications such as fuel cell and piezoelectric energy harvesting. In the present review, a detailed discussion of the different kinds of nanofillers and their role in energy harvesting and fuel cell electrolyte membranes is projected.



1. INTRODUCTION

Energy is a prime need in the current era for different purposes including portable and nonportable electronic devices. An increase in electronic-based devices has led to a higher consumption of energy that is dependent on the usage and power consumption of devices.^{1,2} Technological advancements in different fields, such as education, agriculture, hospitals, transportation, etc., require a large amount of energy, and further, the depleting conventional resources have pushed the world toward alternative energy sources to meet the requirements of the different sectors.^{3,4} The major cause of this depletion of energy sources is the rapid increase of the world's population.⁵ Petroleum/fossil fuels are the main source of nonrenewable energy sources; unfortunately, these sources are being reduced drastically. They also emit toxic gases, such as carbon dioxide, carbon monoxide, sulfates, nitrates, etc., which cause environmental problems.^{6,7} Rising environmental pollution has led to adverse effects on the survival of mankind, which has led us to switch to renewable resources like wind energy, geothermal energy, bioenergy, solar energy, hydro-power, and ocean energy.^{8–10} Apart from these, other sources like biofuels, fuel cells, and energy harvesting are also considered to be potential sources of energy. Organic materials, especially polymers, have attracted keen interest among researchers due to their versatile nature for use in nonconventional energy sources. Among the polymers,

fluoropolymers like poly(vinylidene fluoride) (PVDF) and its copolymers like PVDF-TrFE, PVDF-HFP, and PVDF-CTFE (Figure 1) based energy applications have made a major contribution in the field of alternative energies, one of which is the fuel cell which is drawing attention as a good alternative energy resource.^{11,12} The polymer electrolyte membrane is the key component of proton-exchange membrane fuel cells (PEMFCs), and it plays the most crucial role in fuel cell technology as it allows the ions (protons) to repel the electrons for the outer circuit.¹³ The role of the polymer membrane (thin plastic film) is to act as both a separator and electrolytes.¹⁴ The functional membrane can be prepared by introducing the ionic group into the polymer chain, like sulfonate, phosphonate, and chlorinate ions, etc., which in turn helps the transport of ions through the membrane.^{15–17} Nafion (a fluoropolymer with sulfate ionomers) is a commercial electrolyte of the PEMFCs with higher conductivity ($\geq 10^{-2}$ S cm^{-1}) and low-temperature applicability developed by DuPont

Received: July 28, 2022

Accepted: September 9, 2022

Published: September 22, 2022



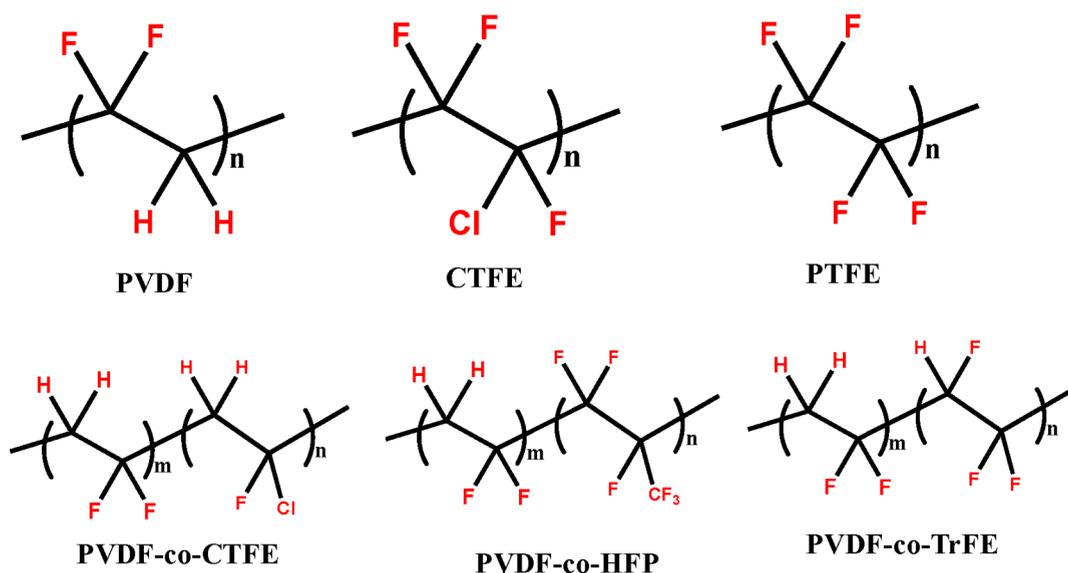


Figure 1. Common fluoropolymers with their chemical structures.

Inc.^{15,18} It has many drawbacks like high cost, higher methanol permeability, thermal and mechanical stability, etc.¹⁹ Layered silicate–polymer nanohybrids are an alternative polymer electrolyte membrane (PEM) that has lately attracted a great deal of interest due to the improvement in mechanical, thermal, and gas barrier properties and proton conductivity as compared to pristine polymers.^{20–22} Many polymer–inorganic nanohybrid membranes show much lower fuel permeability along with almost similar or enhanced proton conductivities due to the dispersion of the nanodimensional layered silicates throughout the polymer matrix.²³ Recently, Jana et al. showed the proton conductivity (σ) of $6.2 \times 10^{-2} \text{ S cm}^{-1}$ of the layered silicate dispersed HFP nanohybrid membrane.¹⁴ Another researcher developed a membrane of the graft fluorinated poly(arylene ether ketone) containing highly dense sulfonic-acid-functionalized pendants with a proton conductivity of $16.6 \times 10^{-2} \text{ S cm}^{-1}$.²⁴ The addition of nanofiller affects the cell performance in two ways: one is that the uniform distribution of the layered silicate produced the winding diffusion path which hindered the fuel transfer through the membrane, and the other is the structure with functionalization which facilitates the proton conduction through the membrane.^{25–27} Further, the smaller particle size increases the surface area of dispersed nanodimensional particles within the polymer matrix, which can alter the crystallinity of the polymer and thereby contribute to the ionic mobility that eventually increases the proton conduction.^{28,29}

Energy harvesting or energy scavenging is currently gaining much attention due to its application in self-powered or wearable devices. It is a process where energy is drawn from the waste mechanical or other sources and is converted to electrical energy and used for some low-powered devices. The sources to draw such energy can be mechanical stress, vibrations, movement of body parts, and so on. Certain materials are required to convert mechanical or vibrational energy to electrical energy. Piezoelectric materials are the most used materials in such applications. Piezoelectricity is the phenomenon where applied stress is converted to electrical outputs or strain or vice versa. Of the different piezoelectric materials, polymers have been the most studied due to their flexibility, biocompatibility, and high mechanical properties.

PVDF is the most common polymer material used in such applications. PVDF has the capability to get transformed into an electroactive phase when subjected to some alterations like processing or addition of fillers which generates the polar phase in the system. The polar phase leads to a piezoelectric-based energy-harvesting mode of application where the application of any mechanical stress produces electrical output. A detailed discussion will be done in a later part of this review.

Fluoropolymers like poly(vinylidene difluoride) (PVDF) have many salient features such as high mechanical, thermal, and chemical resistance and UV, nuclear, abrasion, and aging resistance properties, while their piezo and pyroelectric properties makes them versatile for applications such as energy harvesting, sensors, actuators, and some medical applications.^{30,31} PVDF is a highly nonreactive, insulating thermoplastic. It is interesting because of its availability of different crystalline polymorphisms. It exists in five different crystalline phases, i.e., α -, β -, γ -, δ -, and ϵ -phases, and it has three modes of molecular conformation, such as *TGTG'* (nonpolar), *TTTT* (polar), and *TTTGTTG'* (partially polar).^{22,32} Among all these phases, the nonpolar α -phase is the most common and thermodynamically stable phase, and the polar β -phase is a thermodynamically metastable phase.³³ The conversion of the polar phase has electrical/energy prospective and is more important because of the polar β - and γ -phases responsible for the piezoelectric properties.³⁴ There are different techniques used for the polar β -phase conversion, such as melt crystalline, stretching in unidirection/bidirection, poling at high voltage, growth on a special substrate with the help of the inorganic filler, spin coating, and electrospinning, etc. The present review discusses the nucleation of the electroactive phase with the dispersion of the silicate nanoclay followed by film/fiber preparation.^{35,22,36,37}

Electrospinning is a unique technique to prepare nanofibers, and the advantages possessed by electrospinning, such as its low cost and capability of a moderately high production rate, make it a highly potential system for producing nanohybrid fibers.³⁸ The prepared fibers have several advantages over film fabrication because they are extremely long and have a large surface area, complex pore size, and intriguing alignment. Either woven or nonwoven fibers possessed by electrospun

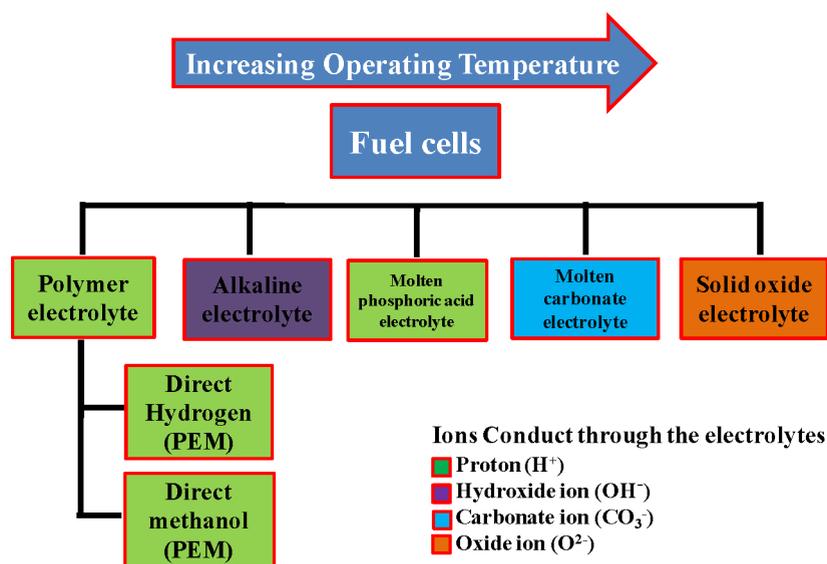


Figure 2. Broad classification of fuel cells based on the electrolytes and fuels.

nanofibers make them suitable for various applications.³⁹ Thus, the combination of the nanoparticle with the polymer (PVDF) matrix subsequently makes the fiber a better piezo electric β/γ -phase in comparison to pristine PVDF or its copolymer.²² The large sheet of nanofibers is used as a polymer electrolyte membrane or a device for energy harvesting.^{40,41} However, in this review, the role of the PVDF polymer and its required modifications will be discussed in two broad applications: fuel cell nanohybrid membrane followed by single cell fabrication and piezoelectric energy harvesting using nanofiller along with some of its applications.

At present, water, health, and energy are equally important topics for researchers. Among these, energy is of prime importance because of its dependency on almost every sector. Life without energy is unimaginable, and the ever depleting conventional sources of energy are drawing attention to develop some alternative sources for a sustainable future. Fluoropolymers such as PVDF and its copolymers play a very important role in energy fields. Fluoropolymers are extensively used in the fields of fuel cells as well as in energy harvesting, which are potential alternatives for sustainable energy demands.

2. FUEL CELLS

2.1. Fuel Cells - The Next Generation of Energy.

Electrochemical cells and allied systems play a key role worldwide in different sectors such as education, industries, and medical, etc. Electrochemical devices are critical, enabling technology for renewable energy, energy management, conservation and storage, pollution control/monitoring, and greenhouse gas reduction.^{42,43} A large number of electrochemical devices have been developed in the last few decades, and these systems optimize the cost, durability, and performance, leading to their simultaneous expansion into existing and emerging markets. Based on the electrochemical technologies, some established systems such as deep cycle batteries, sensors, and large-scale lithium-ion batteries in addition to emerging devices such as fuel cells play an important role in the present electrochemical devices.⁴⁴ Fuel cell technology is based on the electrochemical cell, in which the chemical energy is transferred into electrical energy. A wide variety of fuel cell

systems of various scales of power generation (few mW to MW range) are now commercially available, and their operating authorities have widely varying performances and characteristics, as discussed in the literature.⁴⁵ Fuel cells can be classified according to operating temperature, and the details of the classifications are shown in Figure 2.

Polymer electrolyte membrane fuel cells (PEMFCs) typically have the lowest operating temperature (LT) (below 100 °C), and solid oxide fuel cells (SOFCs) have the highest operating temperature (HT) at around 800 °C.^{46,47} The operating temperature in fuel cells is an important parameter, along with the type of fuel used, material choice, user application, and their electrical efficiency.^{48,49} High-temperature systems (such as MCFs and SOFCs) operate at relatively high temperature with total electrical efficiencies between 45 and 60% to allow internal reforming of hydrocarbon fuels at high temperature. In variance, the LT fuel cell systems operate to reform and clean (removing greenhouse and dangerous gases) hydrocarbon fuels utilized within the system. This class of fuel cell results in lower electrical efficiencies (~35–40%) due to very low reforming hydrocarbons. Therefore, such systems lead to lower electrical efficiencies.⁶ Intermediate temperature fuel cells (typically operating between 150 and 350 °C) are in general quite flexible to fuel impurities and require lower catalyst-loaded electrodes in comparison to the low-temperature system. The electrical efficiency is similar to the LT systems, but the durability of such a system is relatively higher than that of the LT system. The electrical efficiency of such systems can be enhanced by the use of ultrapure hydrogen gas. Table 1 shows the comparative study of the different types of fuel cells (conventional fuel cells) with electrical efficiency followed by their advantages and disadvantages and electrode reactions.

Besides all the above conventional fuel cells, some other classes of fuel cells, such as microbial and direct carbon fuel cells, play an important role in recent fuel cell technology. In microbial fuel cells (MFCs), the organic materials are converted into electrical energy through microbe metabolism, using electrochemical processes. The use of the microbe to generate electricity has been explored since the 1970s, but nowadays the MFCs are used for stationary power generation

Table 1. Classification of the Fuel cells

Fuel cell	Electrolytes	Operating temperature (°C)	Electrode reactions	Working efficiency (%)	Advantages	Disadvantages	Application	Refs
Polymer electrolyte membrane fuel cells (PEMFCs)	Polymer membrane (Nafion 117)	70–100	Anode $H_2 = 2H^+ + 2e^-$ Cathode $1/2O_2 + 2H^+ + 2e^- = H_2O$	35–60	LT, quick startup, reduced corrosion due to solid film	Expensive catalyst, highly pure fuel used	Transportation, stationary, portable electronic devices	15
Direct methanol fuel cell (DMFC)	Polymer membrane	30–70	Anode $H_2 + 2OH^- = H_2O + 2e^-$; Cathode $H_2O + 2e^- = 2OH^-$	20–25	LT, quick startup, reduced corrosion due to solid film	Expensive catalyst	Transportation, stationary, portable electronic devices	50
Alkaline fuel cell (AFC)	Aqueous solution of KOH/NaOH or anion exchange membrane	≤100	Anode $H_2 + 2OH^- = H_2O + 2e^-$ Cathode $1/2O_2 + 2H^+ + 2e^- = H_2O$	~60	Low cast and fast electrode reactions in alkaline medium	Sensitive to air and CO ₂ , electrolyte management and design of cells	Transportation, stationary, portable electronic devices	51
Phosphoric acid fuel cell (PAFC)	Phosphoric acid	150–200	Anode $H_2 = 2H^+ + 2e^-$ Cathode $1/2O_2 + 2H^+ + 2e^- = H_2O$	~40	Enables CHP due to high temp., increases the turbulence of fuel	Long startup time, Pt catalyst, design of the cell	Military, stationary power generation output in the range 100–400 kW	52
Molten carbonate fuel cell (MCFC)	Molten K ₂ CO ₃ and Li ₂ CO ₃	~650	Anode $H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^-$ Cathode $CO_2 + 2e^- + 1/2O_2 = CO_3^{2-}$	40–45	High efficiency, fuel flexibility, enables CHP, variety of the catalyst	Long startup time, high-temperature corrosion of the fuel cell components	Transportation, distributed power energy	53
Solid oxide fuel cell (SOFC)	Ytria-stabilized zirconia (YSZ), lanthanum gallate, doped Bi ₂ O ₃ , doped ceramic, etc.	~500–800	Anode $H_2 + O^{2-} = H_2O + 2e^-$ Cathode $1/2O_2 + 2e^- = O^{2-}$	~60	High efficiency, fuel flexibility, high temperature, nonmobile catalyst	Long startup time, size and design, high-temperature corrosion of the fuel cell components	Distributed power energy, auxiliary power units in vehicles, and stationary power generation	47

for small portable devices because of the high power density of such electronic devices. MFCs convert organic materials into electrical energy via the microbes' metabolic pathway. Recently, power sources for small and portable electronic gadgets^{54,55} use direct carbon fuel cells as the power sources and electrochemically consume hydrocarbon or mainly carbon-rich species with oxygen, which releases carbon dioxide gas. This offers many advantages over the conventional fuel cells, which include the potential to enhance the electric efficiency of the fuel cell systems, fuel cost, and availability.^{56–58} From the comparison of table and literature studies, one can conclude that the polymer electrolyte membrane has several advantages such as low temperature operation, quick startup, easy design of the cell, and application in transportation, stationary power, and portable device applications. However, some of the major disadvantages like electrical efficiency, expensive catalyst, and fuel purity need to be rectified.

2.2. Techniques Used for the Development of Functionalized Membranes. For the application of PEMFCs, the polymeric membranes should possess the following properties such as high ionic conductivity (H⁺, OH⁻, etc.), low fuel crossover, good thermal properties, electrochemical stability in acidic as well as basic medium, and outstanding mechanical properties in both the dry and hydrated states, but the thermal properties are more important in wet conditions for better proton conductivity, sufficient water uptake and moderate swelling, suppressed water transport through diffusion and electro-osmosis, the stability of the membrane material at premelting to form the MEA, and, more importantly from a practical point of view, a competitively cheaper price as compared to the commercial membrane and sufficient long-term durability.⁵⁹ To achieve these properties in the polymer matrix/membrane, some modifications are needed, such as chemical modification, blending of the base proton exchange materials such as the Nafion membrane, and swift heavy ion (SHI) irradiation.

2.2.1. Chemical Tagging/Grafting-Based Proton Exchange Membrane. Direct grafting of the polymer backbone and subsequent introduction of the ionomer followed by membrane formation lead to enhanced ionic conductivity of the functionalized membrane. There are several literature reports available for such kinds of functionalization. Direct functionalization of the poly(vinylidene fluoride-co-hexafluoro propylene) leads to a proton conductivity of 3.70×10^{-2} S cm⁻¹ and open-circuit voltage of the functionalized membrane of 0.63 V, corresponding to the power density of 48.34 mW/cm².³ Polybenzimidazole (PBI) random copolymers containing alicyclic and aromatic backbones were synthesized using two different dicarboxylic acids (viz., cyclohexane dicarboxylic acid and terephthalic acid) by varying their molar ratio, and the cyclohexyl-based PBI possessed a lower proton conductivity (114 mS cm⁻¹) than terephthalic acid based PBI (220 mS cm⁻¹).⁶⁰ Multiblock copolymers were synthesized by coupling carboxyl functionality in aromatic poly(arylene ethers) with *ortho*-diamino functional PBI oligomers. The maximum proton conductivity obtained was only 47 mS cm⁻¹.⁶¹ Therefore, chemical modification is one of the important routes to tailor the proton conductivity of the functionalized membrane by varying the grafting as well as doping concentration for better polymer electrolyte membranes for fuel cell technology.

2.2.2. Polymer-Composite-Based Proton Exchange Membrane. Physical mixing of the constituents is employed to enhance the ion conductivity,⁶² and these composite

membranes include macrocomposites,⁶³ nanocomposites, and hybrid organic–inorganic membranes with organic/inorganic materials incorporated as modified fillers.^{64,65} On the other hand, the modifiers participate in forming the membrane structure in the blending method.⁶⁶ Intensive efforts have been made to modify Nafion with inorganic and organic materials. Generally, inorganic materials are used in Nafion (standard commercial membrane) modification and are classified under the categories of inert hygroscopic filler, proton-conductive filler, and hydrophilic and proton-conductive bifunctional filler, etc.^{67–69}

2.2.3. Radiation-Induced Grafting for Polymer Proton Exchange Membranes. Swift heavy ions are involved in particle radiation when passing through the polymeric membrane matrix, and two important interactions occur: ion–electron interactions and ion–nucleon interactions. Due to these interactions, the path of the heavy ions is amorphous on the polymeric membrane, and different physical and chemical changes are incorporated on the polymer chain, such as the chain scission, double bond formation, reactive gas evolution, cross-linking, and reactive site free radical formations, etc. We utilized the free radical for the grafting of the conducting monomer, such as styrene, 3-hexyl thiophene, pyridine, etc., and the grafting was done by the chemical or radical introduced.^{70,14,15,71,72} Membrane preparation by radiation-induced grafting provides a cost-effective option because inexpensive commercial materials are used, such as PVDF, which is cheaper than the commercial Nafion membrane, one of the most important reasons for choosing the PVDF. It is also a fluorinated material like Nafion and has high mechanical strength and an easy industrial preparation procedure.^{47,73} The radiation-induced grafting methodology has major advantages: commercially available, polymer membrane material easily modified and adjustable, and experimental parameters are available such as radiation dose/type, temperature, and film thickness. From these advantages, it is clear that tailorability and customization are available in this methodology.^{74,75} There are three main steps involved in the preparation of the PEMCs. We initially prepared the base matrix, followed by ion bombardment to generate free radicals. After that, the grafting of the conducting monomers such as styrene, thiophene, pyrrole, etc. was done onto the matrix, and subsequently we introduced the ionomer sulfate group.⁴⁷

2.3. Fabrication of Conducting Nanochannels Using Swift Heavy Ions. Polymeric membranes are microporous films which act as semipermeable barriers to separate two different phases or selectively allow specific chemicals. The applicability of these membranes increases with the introduction of different functional groups in the areas of filtration⁷¹ (heavy ions and radioactive cations and anions), drug delivery,⁷⁶ gas permeation,^{77,78} electrolysis,⁷⁹ redox flow batteries,⁸⁰ and proton exchange membranes/anion exchange membranes, etc. The polymer should have appropriate properties such as mechanical properties (mechanically stiff and tough), thermal stability, being anticorrosive in acid as well as basic medium, and stability in different organic solvents, etc. Most of these properties do exist in thermoplastic polymers which are electrically insulating, while electrical/ionic conductivity is one of the prime requirements in the field of energy and some specific filtration purposes. Hence, the electrical/ionic conductivity of the insulating polymers (PE, PCPET, PVDF, and their copolymers) needs to be enhanced for the above applications.⁸¹ Therefore, functionalization of the

polymer is of prime importance to produce membranes for different purposes. In the present scenario, several research groups have explored the advanced functionalized membranes to replace the commercial membranes, minimize the cost, and ease the process and for a greater temperature window for operation.⁸² Swift heavy ions (SHIs) are one of the best choices for the fabrication of nanochannels in functionalized polymeric membranes.⁷⁴ Different chemical as well as physical changes are observed in the polymer membrane after swift heavy ion bombardment on the polymeric film, producing various species as shown in Figure 3.^{15,82}

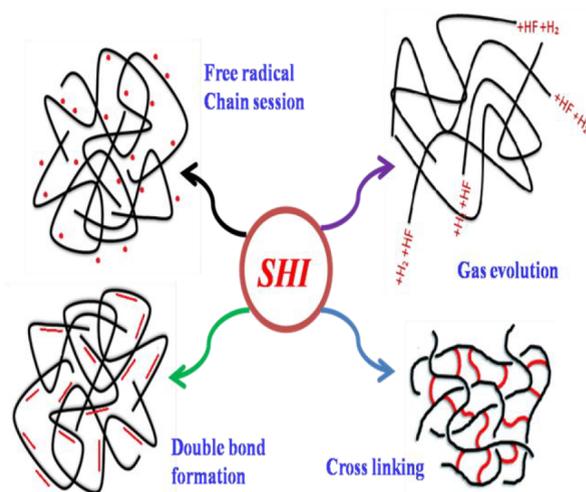


Figure 3. Formation of various chemical species upon SHI irradiation on fluoropolymers. Reprinted with permission from ref 15. Copyright 2017 John Wiley and Sons.

Among these species, the reactive free radical formation is important for chemical reactions, especially polymerization. Polymer grafts possibly use the reactive free radicals after bombardment. Further, the graft polymer membrane can be functionalized suitably for better conduction.⁸³ The polymer membranes in PEMFC technology use functionalized membranes with different functionalities, such as sulfonates, phosphates, chlorides, nitrites, quaternary ammonium salts, quaternary phosphonium salts, etc., to achieve high ionic conductance of the membranes.^{84,85,3,16} These nanochannels are exclusively ion conducting and termed as conducting nanochannels. Significant progress has been made worldwide to overcome the challenges and achieve the use of the target materials in PEMFCs, mainly in portable power generation including the automobile industry.

The fabrication of nanochannels in poly(vinylidene fluoride) (PVDF) and its nanohybrid (NH) (composites having organically modified layered silicate uniformly dispersed in a polymer matrix) was carried out using high-energy swift heavy ion (SHI) irradiation to create a latent track of nanometer dimensions in the films, followed by selective chemical etching to take out the amorphous zone exclusively.⁸⁶ It is worth mentioning that the passage of high-energy ions through the polymer film melts the surrounding area (tens of nanometer diameters) due to the ion–polymer matrix interactions, and their rapid quenching converts them into an amorphous track along with the generation of free radicals in the polymer chains, as shown in Figure 4a.³ The amorphous zone of the latent track was oxidized using the optimized conditions of the

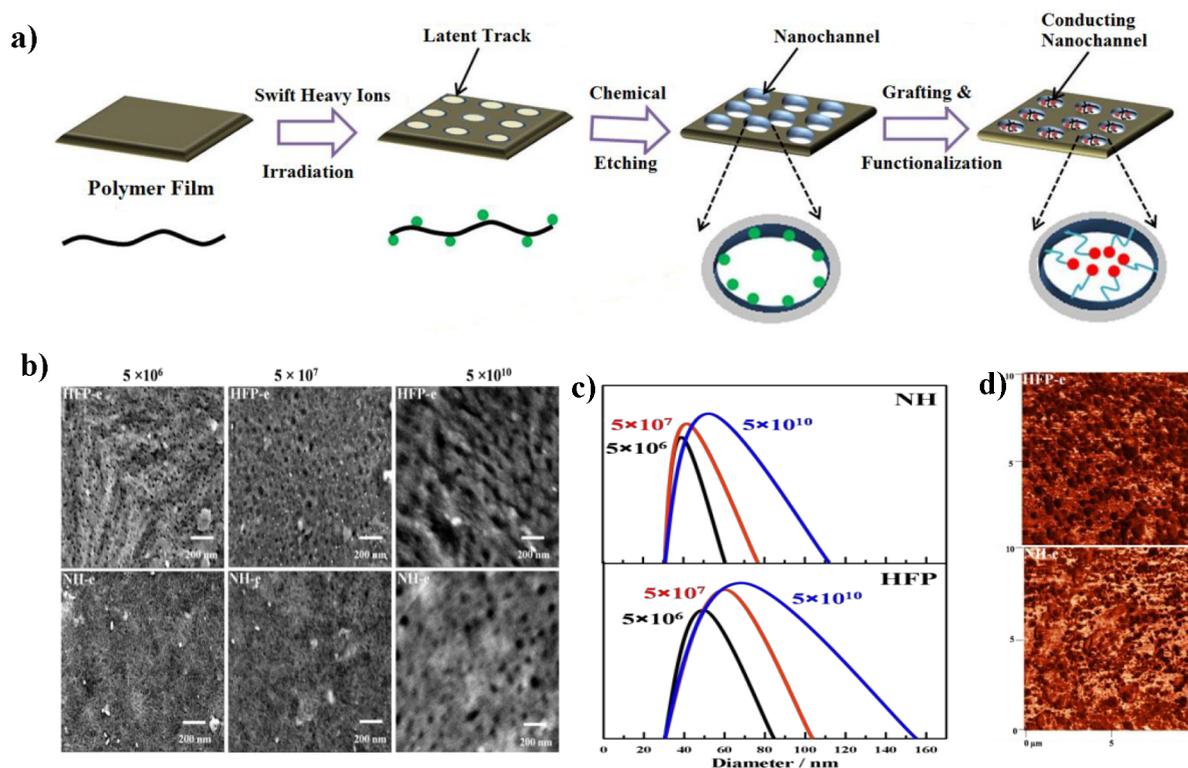


Figure 4. (a) Schematic of the swift heavy ion irradiation, latent track formation, reactive free radical followed by the grafting of the conducting monomer, and subsequent sulphonation of the nanochannels.³ (b) SEM images of the HFP (top column) and NH surfaces (bottom column) after etching at different fluences. (c) Distribution of nanochannel diameters of the irradiated etched HFP-e and NH-e at three different fluences. (d) AFM images of HFP-e and NH-e at a fluence of 5×10^{10} ion/cm².⁵⁰

selective chemical etchants, potassium permanganate, and alkaline sodium hydroxide solution at 65 °C for 4 h.⁸⁷ The pore size created by swift heavy ions can be altered by using the fluence of the heavy ions, the nature of the heavy ions, bombardment conditions like a direct beam or scattered beam, the polymer matrix, and the etching conditions such as temperature and time which influence the pore dimensions.⁷⁴ Nanochannel dimensions are significantly varied in the nanohybrid membrane as compared to the pristine PVDF membrane. This variation in the channel dimension is due to the dispersion of 2D-layered silicate in pristine PVDF which intercalates the polymer chain and gives the mechanical strength and toughness of the membrane.⁸⁸ The role of the nanoclay is to control the channel dimension and uniformity of the channel.¹⁴ The channel size of the membrane can be controlled by using either different size swift heavy ions or fluence (number of ions per unit area).^{89,50,90} The average channel dimension in HFP is 45 ± 7 nm, while 2D-layered silicate dispersed nanohybrids show around 34 ± 5 nm at 1×10^7 ions/cm² fluence. Larger channel dimension has been found at higher fluence (1×10^{10} ions/cm²); approximately 44 ± 6 nm in NH against 60 ± 6 nm (channel distribution shown in Figure 4c) in HFP. The SEM and AFM images with channel distribution are shown in Figure 4b,d. At higher fluence, the chances of irradiation of subsequent ions in a similar location are more probable, resulting in overlapping of ion tracks which cause larger channel dimension after etching.⁵⁰ Jana et al. varied the size of the swift heavy ions (Li^+ and Ag^+), keeping the fluence constant at 5×10^7 ions/cm² in a nanohybrid membrane, showing 30 ± 5 nm using a Li^+ ion as opposed to 60 ± 5 nm using a Ag^+ ion.^{89,90} Further, uniform distribution

and controlled size nanochannels are observed in nanohybrids. The channel dimension and number density are also influenced by the variation of temperature and time of etching. The surface pore diameter was around 180 nm for the track-etched membranes prepared through an etching temperature of 120 °C, while lower-temperature treatment exhibited smaller pores of approximately 100 nm, which indicates that the heating pretreatment accelerates the pore growth in the range of hundreds of nanometers.⁷⁴ Grasselli et al. have prepared an etched track membrane by the bombardment of a Sn heavy ion beam on the piezoelectric β -phase PVDF foil and reported the variation of the channel dimension depending on the etching time and etchant concentration at constant temperature and fluence.⁷³

2.4. Fabrication of Conducting Nanochannels and Structural Change.

A nanometer dimension nanochannel was formed after removing the amorphous zone created by high-energy swift heavy ions on thin polymer membranes. The amorphous zone was removed using the oxidizing agents potassium permanganate and sodium hydroxide, leading to the formation of a free radical on the surface as well as inside the nanochannels. The shape of the nanochannel may be either conical or cylindrical. It depends on the size of the ion beam and the scattering angle of the ion beam.⁸⁷ The surface reactive free radicals are oxidized with atmospheric air but inside free radicals remain at the periphery of the channel and are available for the polymerization reaction with vinyl monomers (e.g., styrene, pyrrole, 3-hexyl thiophene etc.). Subsequently, the chemically etched films are kept in various monomer solutions with optimized conditions. The polymerization and

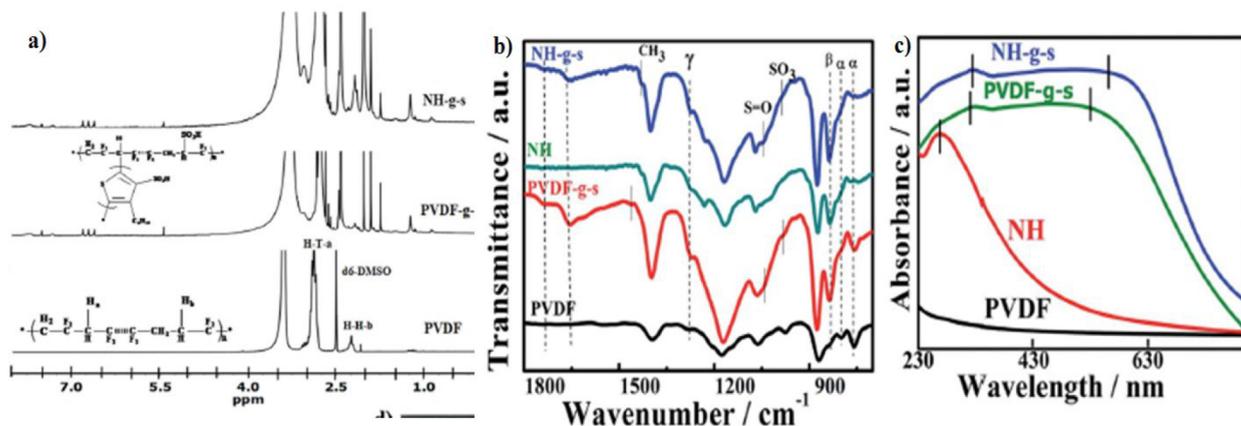


Figure 5. (a) ^1H spectra of pristine PVDF, PVDF-g-s, and NH-g-s measured using 500 MHz magnetic field NMR. Respective proton positions are indicated in the chemical structure (inset) and spectrum. (b) FTIR spectra of pristine PVDF, PVDF-g-s, NH, and NH-g-s, indicating various peak positions. (c) UV–vis absorption spectra of PVDF, NH, PVDF-g-s, and NH-g-s, showing the peak position by vertical lines.³

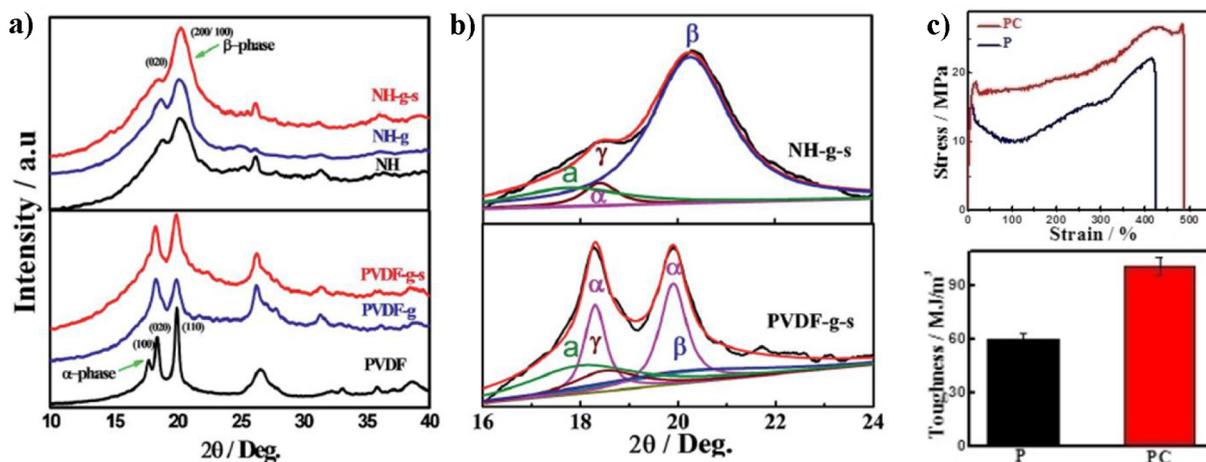


Figure 6. (a) XRD of the pristine PVDF and its nanohybrid before and after the grafting followed by the sulfonation. (b) Deconvolution of functionalized and pristine membranes.³ (c) Mechanical property increments after the dispersion of the silicate nanoclay. Reprinted with permission from ref 32. Copyright 2017 John Wiley and Sons.

subsequent functionalization are confirmed through various spectroscopic techniques.

2.4.1. Spectroscopic Measurements. The grafting and functionalization through nanochannels were confirmed through ^1H NMR, UV–visible, and infrared spectroscopy against the pristine PVDF. Prakash et al. fabricated through nanochannels after the irradiation of high energy silver ions on the thin pristine PVDF and its nanohybrid film as per previous discussions where free radicals inside the channel act as initiators.³ The grafting with PVDF chains was designed using the 3-HT monomer, leading to the filling of the nanochannel cylinder with the conducting P3HT polymer, followed by the sulfonation of the exclusively grafted films to make the nanochannels better ion conductors. The grafting followed by sulfonation led to the appearance of peaks at $\delta = 2.80$ and 1.95 ppm for the grafting of P3HT on PVDF chains, at $\delta = 7.90$ ppm for the grafting sulfonation in P3-HT chains, and at $\delta = 8.2, 7.7, 7.2,$ and 5.6 ppm for the sulfonate protons, as shown in the NMR spectra in Figure 5a.^{91–93} The grafting and sulfonation were also confirmed through FTIR measurements by the appearance of peak positions at 1649 and 1730 cm^{-1} due to the corresponding $-\text{C}=\text{C}-$ and $-\text{C}=\text{S}$ symmetrical stretching vibrations of the thiophene aromatic ring attached to

the PVDF chain (Figure 5b).^{94,95} The sulfonation in the grafted nanochannel was visualized through the peak positions at 1047 and 989 cm^{-1} due to the SO_2 and SO_3^- vibration peaks attached to the PVDF chain, respectively.⁹¹ Similar results are also verified through UV–visible spectra. After the grafting followed by sulfonation, a strong broad band appears at 513 nm in the spectrum of PVDF-g-s, which is assigned to the $\pi-\pi^*$ transition of the conjugated backbone of the 3-HT graft, along with an absorption band of the sulfonate group as compared to no absorption in pristine PVDF (Figure 5c).^{96,89}

2.4.2. Structural Change. Structural modification has been confirmed through wide-angle powder X-ray diffraction. The XRD spectra of the pristine PVDF shows peaks at $2\theta = 17.6$ (100), 18.5 (020), and 19.9° (110), indicating the α -phase (TGTG) of the polymer.³⁰ The nanohybrid membrane exhibits a structural modification with a peak at $2\theta = 20.3^\circ$ corresponding to the $(200/110)$ plane due to the piezoelectric β -phase (all trans conformation) (Figure 6a). In a lower range, the peak at $2\theta = 6.1^\circ$ indicates the sandwiching of 2D-layered silicate with a polymer chain.^{3,31} It has been observed that the piezoelectric β -phase content gradually increases after SHI irradiation, chemical etching, and subsequent grafting of the conducting monomer followed by the sulfonation. The fraction

Table 2. Comparative Study of the Characteristic Parameters of the Modified PEMFC Membrane against Nafion 117^a

Membrane	Thickness (μm)	(% WU)	IEC mmol/g	(% DS)	($k^m/\text{S cm}^{-1} \times 10^{-2}$)	Refs
Nafion@117	175	38	0.9	27	9.56	101
PVDF-s	130	22	0.36	27	0.06	91
PVDF-NH-s	130	27	0.50	32	0.50	91
HFP-18	80	12	0.78	18	3.72	16
PVDF-sty-s	30	10	0.22	14	0.05	71
NH-sty-s	30	14	0.33	16	0.13	71
PVDF-3HT-s	50	15	-	25	4.59	3
NH-3HT-s	50	20	-	30	4.21	3
HFP-3HT-s	30	-	-	-	5.5	14
NH-3HT-s	30	-	-	-	6.2	14
CTFE-sty-Ag ⁺	25	18	0.38	25	2.55	85
NH-sty-Ag ⁺	25	20	0.41	38	3.46	85
CTFE-sty-Li ⁺	25	10	0.30	-	1.22	85
NH-sty-Li ⁺	25	15	0.32	-	1.74	85

^aWU, water uptake; IEC, ion exchange capacity (mmol/g); DS, degree of sulphonation; k^m , proton conductivity; PVDF-s, direct sulphonation of poly(vinylidene fluoride); PVDF-NH-s, direct sulphonation of the PVDF nanohybrid membrane; HFP-18, direct sulphonation of the poly(vinylidene fluoride-co-hexafluoro propylene) membrane, sty- styrene; 3HT, 3-hexyl thiophene; CTFE-sty-Ag⁺, poly(vinylidene fluoride-co-chlorotrifluoro ethylene) irradiated with silver ions; NH-sty-Ag⁺, poly(vinylidene fluoride-co-chlorotrifluoro ethylene) nanohybrid irradiated with silver ions; CTFE, sty-Li⁺-poly(vinylidene fluoride-co-chlorotrifluoro ethylene) irradiated with lithium ions; NH-sty-Li⁺, poly(vinylidene fluoride-co-chlorotrifluoro ethylene) nanohybrid irradiated with lithium ions.

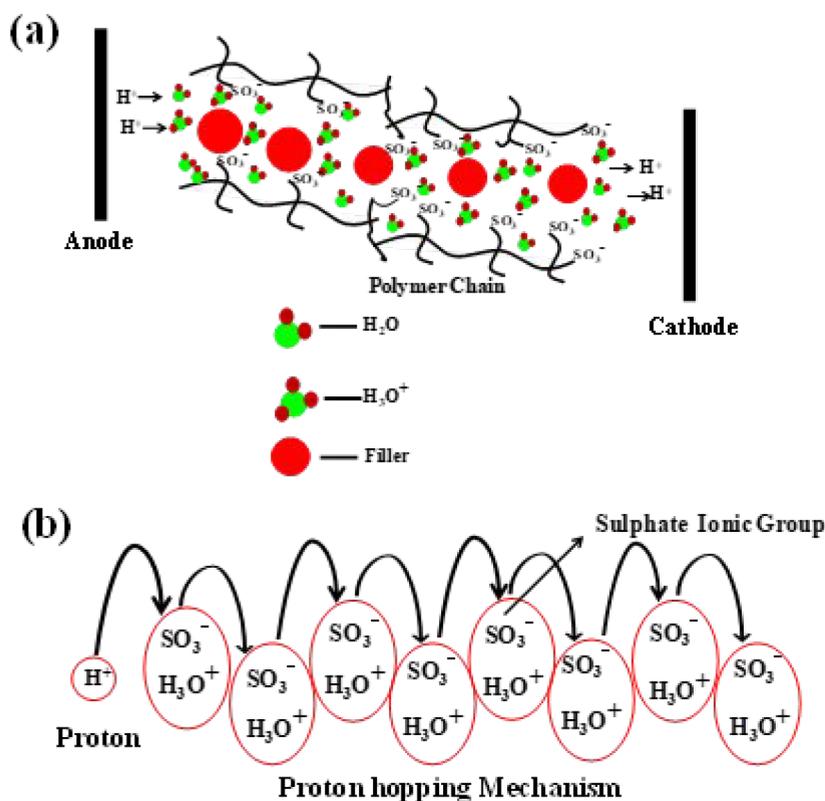


Figure 7. (a) Proton transport across the modified membrane obeying the electro-osmotic vehicular mechanism. (b) Proton transport across the membrane following the Grothous mechanism.

of the β -content is calculated through the deconvolution of the XRD spectra as shown in Figure 6b. A significant increase in the β -content in NH-g-s (72%) is reported as opposed to the minimal presence of the polar β -phase in pristine PVDF (4%) under quasiconditions.³ It is worth mentioning that PVDF did not possess any piezoelectric phase before the irradiation, while $\sim 25\%$ of the polar β -phase was observed in nanohybrids. The presence of the nanoclay in the pristine CTFE nanohybrid enhances the piezoelectric β -phase (78%),⁸⁵ and the presence

of a silicate nanoclay alters the β -phase content (75%)³⁵ in the HFP nanohybrid membrane. The dispersion of the nanoclay enhances the mechanical strength of the polymeric membrane as shown in Figure 6c. From the above discussion, it is clear that the organically modified nanoclay alters the crystal structure of the PVDF and its copolymer after suitably dispersing the nanoclay in the polymer matrix.³²

2.5. Membrane Characteristics for the PEMFCs. For the polymer electrolyte membrane fuel cells (PEMFCs), two

Table 3. Comparative Study of the Characteristic Properties of the Anion Exchange Membrane^a

Membrane	Thickness (μm)	Ion exchange capacity (IEC)/meq g^{-1}	Ionic conductivity (IC) at 25 $^{\circ}\text{C}/\text{S cm}^{-1}$	Refs
QAPPESK	50–100	-	0.052	107
QAPVA	~300	-	0.073	108
FEP-g-PVBTMAOH	~50	1.0	0.011	109
FEP-g-PVBTMAOH	~60	0.7	0.021	110
QPPESEN-2	~200	2.12	0.067	111
FPAES-Im-52	-	1.92	0.036	112

^aQAPPESK, quaternized poly(phthalazinon ether sulfone ketone); QAPVA, novel cross-linked quaternized poly(vinyl alcohol) (PVA) membranes; FEP-g-PVBTMAOH, radiation grafting of vinyl benzyl chloride onto poly(hexafluoro propylene-co-tetrafluoro ethylene) films with subsequent conversion to alkaline anion-exchange membranes; QPPESEN, synthesis of quaternized phenolphthalein-based poly(arylene ether sulfone nitrile); and FPAES, Im-52-synthesis of fluorene-containing poly(arylene ether sulfone) with imidazolium groups (FPAES-Im- x) and preparation of the membranes.

types of functionalized membranes are designed: the cationic membrane for proton conduction and the anionic membrane for hydroxide conduction. The details of these functionalized membranes and their characteristic properties are described below.

2.5.1. Cation Exchange Membrane (CEM) and Its Characteristics. Proton conductivity is a key parameter for the PEMFC membrane. The ionic conductivity of the modified matrix should be high for better fuel cell performance, and another important characteristic is the hydrophilicity of the modified matrix; i.e., the matrix should uptake a sufficient amount of water content.^{97,98} Besides these two parameters, the ion exchange capacity (IEC) of the modified membrane matrix also supports the better performance of PEMFCs.⁹⁹ Usually, the greater the IEC, the greater the proton conductivity. The Nafion membrane exhibits excellent proton conductivity as well as a sufficient amount of water uptake and ion exchange capacity.¹⁰⁰ The proton conductivity of the Nafion membrane is high at lower/ambient temperature, but the proton conductivity decreases with an increase of temperature. The temperature variation of the proton conductivity of the Nafion membrane as compared to the functionalized PVDF-g-s/NH-g-s polymer membrane is reported in the literature.⁷¹ Generally, the proton conductivity increases with the increment of the temperature in pristine Nafion 117 up to 70 $^{\circ}\text{C}$, while the conductivity decreases with a further increase of temperature. This drawback of Nafion can be alleviated by the modification of the Nafion matrix using some hydrophilic inorganic filler (SiO_2 , TiO_2 , ZrO_2 , zeolite, etc.), which facilitates the proton conduction through the membrane and is capable of absorbing water molecules. The role of humidity on the fuel cell performance is known, and the cell performance decreases at lower humidity.²³ Among all these parameters, the degree of ionomer plays an important role in the conduction of ions. The comparative study of these key parameters against the different modified membrane materials as well as standard Nafion 117 is shown in Table 2.

Proton conduction through the membrane is an important parameter of the polymer electrolyte membrane. There are two major mechanisms involved in the conduction of proton through the membrane: one is due to diffusion of ions from one side to the other side of the membrane, the so-called vehicle (electro-osmotic vehicular) mechanism, where the proton is combined with one or more water molecules (H_3O^+) present in electrolytes and then diffuses through the membrane. The schematic of the vehicle mechanism is shown in Figure 7a. The second is the Grotthuss mechanism where proton conduction occurs through a hopping/stepping

process and the movement of the proton across the membrane. One hydrolyzed ionic group is favored over the other ionic group when the extent of the ionic group is much higher. The schematic of the Grotthuss mechanism is given in Figure 7b. The activation energies required for proton conduction to occur are $E_{\text{act}} > 0.5$ eV by a vehicle mechanism and $0.1 < E_{\text{act}} < 0.4$ eV for the Grotthuss mechanism.^{102,103}

It is noted that the increases in water molecules, ion content, and also cell temperature are major factors in the enhancement of proton conduction. The high ionic density inside the matrix polymer will increase the region of hydrophilicity which is beneficial for enhancing the conductivity of the polymer electrolyte membrane. However, water content should be at optimum levels to avoid adverse effects such as swelling, mechanical strength reduction, and methanol crossover in the membrane.

2.5.2. Anion Exchange Membrane (AEM) and Its Characteristics. The different classes of fuel cells are discussed in the Introduction part, along with their electrochemical reactions, advantages, disadvantages, and operating conditions followed by their electrical efficiencies. The alkaline fuel cell (AFC) is a class of fuel cells in which the polymer membrane with functional groups such as ammonium salts, phosphonium, sulfonium, and other positively charged species works as the driving force of the hydroxide ion transport through the membrane. In principle, the AFC is similar to PEM, which allows the hydroxide ions to pass through the membrane and inhibit the electron transport through the membrane. The electron is transferred through the external circuits, which is responsible for the electric power generation. The AFC offers some advantages over the PEM, such as high reaction kinetics which results in higher cell voltages, causing higher electrical efficiency. The higher electrical efficiency permits a lower quantity of noble metal catalyst loading, such as platinum (Pt) and ruthenium (Ru) which minimize the cost of the cell.¹⁰⁴ Another advantage is the movement of OH^- anions which is the opposite direction of the movement of methanol during AEMFC running, so the methanol permeability of these anion exchange membranes should decrease. Some drawbacks of the AFC include: being very sensitive to CO_2 when air is used instead of pure oxygen, and the hydroxide ions may react with CO_2 and form carbonate which reduces the cell performance.¹⁰⁵ The alkaline medium may cause β -elimination of the functionalized membrane, which leads to a change in the cell performance and durability of the cell, and other drawbacks such as fuel crossover, similar to that for PEM.⁷⁹ Alkaline fuel cells are the oldest technology, and the AFC was the first fuel cell device known as an alkaline battery starting in the 20th

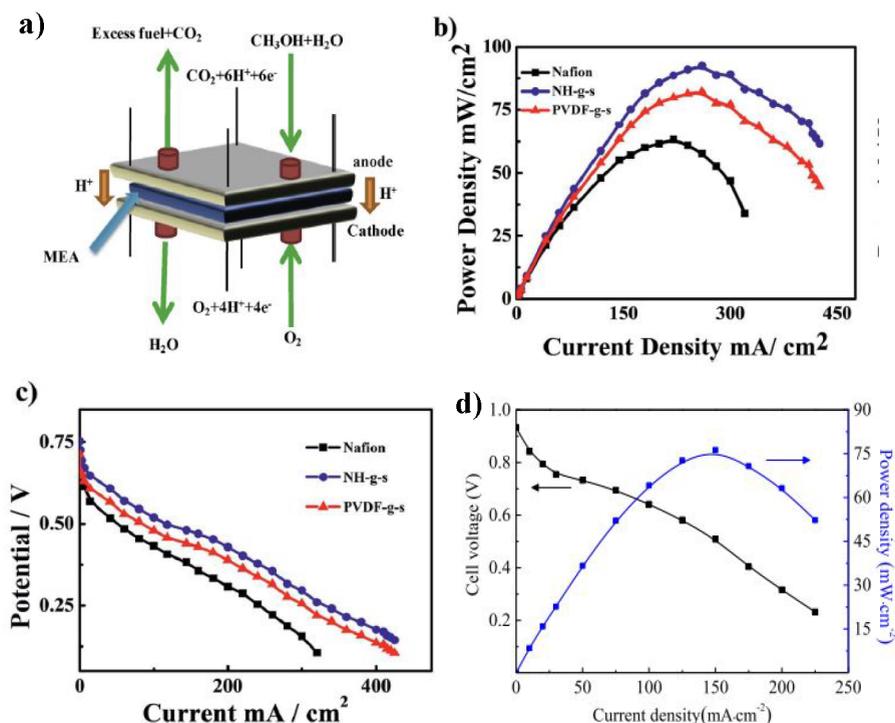


Figure 8. (a) Schematic of the direct methanol fuel cell (DMFC) principle with performance assessment of MEAs with PVDF-g-s and NH-g-s. Reprinted with permission from ref 16. Copyright 2018 Elsevier. (b) Power and current density curve of the cation exchange membrane. (c) Polarization curve of the cation exchange membrane.³ (d) Polarization curve with power density. Reprinted with permission from ref 111. Copyright 2020 Elsevier.

century.¹⁰⁶ However, there are many advantages over the liquid electrolytes which reduce the cost, fuel crossover, CO₂ poisoning of the electrolytes, etc. Like proton conduction in PEM, ionic conductivity (IC) is the key component of the alkaline membrane. The ionic conductivity (IC) and ion exchange properties (IEC) of different functionalized anionic membranes are presented in Table 3.

2.6. Applications of the Conducting Nanochannel.

Nanoporous/nanochannel-fabricated polymeric membranes have many applications like filtration, ion transport, reverse osmosis, and proton exchange membranes, etc. This review deals with the fabrication of conducting nanochannels. In the nanoporous membrane, the depth is a bit smaller to the pore diameter, while the pore diameter is smaller than its depth in the nanochannel. The conducting nanochannels have some important applications, e.g., sensing of biomolecules (proteins, lipids, etc.) and selective ion transportation in the field of energy.^{113,114} PVDF nanocomposites exhibit piezoelectric properties because of their high β -phase content which is highly polar and responsible for the piezoelectricity. Therefore, the PVDF nanohybrid membrane can be used as a smart membrane where the variation of potential can trigger the nanochannel dimension which in turn can be used as a selective ion transportation.¹¹⁵ The fabricated conducting nanochannel membrane can be used in PEMFCs due to its suitable properties.

2.7. Fabrication of Direct Methanol Fuel Cells Using the Nanohybrid Membrane. The direct methanol fuel cell (DMFC) is a quite new member of the fuel cell family. It is closely related to the polymer electrolyte membrane fuel cell (CEM/AEM), and the polymer membrane acts as an electron separator for electrolytes.¹¹⁶ However, the anodic catalyst such

as the Pt–Ru complex on a carbon cloth is used in DMFCs, which oxidize the liquid methanol to a proton (H⁺), electron, and carbon dioxide, eliminating the fuel reformer process. The proton transfers through a conducting nanochannel and combines the oxygen and electron to complete the redox reaction.⁷¹ The reason for the ruthenium used in the anode is to minimize the CO₂, and before the formation of carbon dioxide in the anode, it forms carbon mono-oxide (CO). The ruthenium carries out the complexation reaction with CO and minimizes carbon dioxide poisoning.¹¹⁷ Therefore, electricity is generated with the formation of water as a byproduct. A schematic of the direct methanol fuel cell is presented in Figure 8a. Efficiencies of the direct methanol cell are expected to be ~40%, typically at the operating temperature range of 40–90 °C. The efficiencies of such kinds of fuel cells increase by increasing the operating temperature, and some other parameters such as fuel, catalyst, and humidity also play important roles in cell efficiencies.¹¹⁸ The development of a high-temperature stable polymer membrane is desirable and still challenging. Shen et al. illustrate the direct methanol fuel cell performance using functionalized membranes of PVDF, ETFE, and LDPE after γ -radiation, followed by grafting of a styrene monomer and subsequent sulfonation to fabricate the membrane electrode assembly (MEA) and obtain a maximum power density of 58 mW cm⁻² in PVDF-functionalized membranes, slightly better than the standard Nafion 117 at similar conditions (the maximum power density of 37 mW cm⁻²).¹¹⁹ The performance of the fabricating nanochannel through an accelerator and P3HT grafting followed by sulfonated specimens of PVDF and its nanohybrid membrane indicate their superior membrane properties in DMFC technology. Through single-cell setup (DMFC), the perform-

Table 4. Proton Conductivity (k^m), Activation Energy (E_a), Methanol Permeability (P), Selectivity Parameter (SP), Open-Circuit Voltage (OCV), Maximum Power Density (MPD), and Maximum Current Density (MCD)

Membrane	k^m ($\times 10^{-2}$ S cm $^{-1}$)	E_a (kJ mol $^{-1}$)	P ($\times 10^{-7}$ cm 2 s $^{-1}$)	SP ($\times 10^5$ S s cm $^{-3}$)	OCV (V)	MPD (mW/cm 2)	MCD (mA/cm 2)	Refs
PVDFNF-Nafion	6.0	3.0	-	-	0.89	240	470	120
Anion-conductive block poly(arylene ethers)s	-	-	-	-	0.71	161	446	121
Cross-linked poly(vinyl alcohol) Nafion/PTFE	3.42	2.69	1.14	3.00	-	-	-	122
Nafion 117	-	-	-	-	0.975	-	1400	123
Nafion 117	9.56	6.52	13.10	0.72	0.73	51.2	140	101
HFP-sty-s	5.5	6.36	2.91	3.7	0.60	28	140	15
HFP-NH-sty-s	6.2	5.79	1.84	1.8	0.63	31	140	15
CTFE-sty-s	2.55	8.2	4.54	0.56	0.60	30	200	90
CTFE-NH-sty-s	3.46	8.3	4.43	0.78	0.53	44	200	90
HFP-3HT-s	7.8	6.09	5.86	1.3	0.66	39	140	14
HFP-NH-3HT-s	8.8	4.74	6.76	1.3	0.68	45	140	14
PBI/PVDF blend (90:10)	14.0	22.42	-	-	-	-	-	124
PBI/PVDF-HFP blend (90:10)	16.4	19.05	-	-	-	-	-	125

ance of such membranes was examined by recording the polarization curve ($I-V$), and the OCP of such membranes (NH-g-s) was 0.75 V, which is higher than the value of standard Nafion 117. The slow decay of the cell potential after applying the load indicates better performance.³ The power and current density of such membranes is calculated from an $I-V$ polarization curve. The NH-g-s membrane shows the highest power density of 92 mW cm $^{-2}$ at a current density of 253 mA cm $^{-2}$, as shown in Figure 8b,c. Nafion 117 membrane cell performance produces a power density of 63 mW cm $^{-2}$ at similar conditions, corresponding to the current density of 220 mA cm $^{-2}$, demonstrating the excellent DMFC performance using a nanohybrid membrane.³ The basic reason behind the better fuel cell performance lies in the extent of functionalization and nanoclay as a filler, which holds a sufficient amount of water even at a higher operation temperature. Selectivity parameter (SPs) of the fuel cell membrane refer to the efficiency of the cell performance and are defined as the ratio of proton conductivity (k^m) and methanol permeability (P) of any membrane. A greater value of SP indicates better efficiency of the cell performance, and a higher SP value of the nanohybrid membrane (NH-g-s) indicates its superior cell performance as compared to Nafion 117, the standard DMFC electrolyte membrane. The comparative study of DMFC performance and other parameters of different functionalized membranes is shown in Table 4.

Methanol permeability usually occurs through the nano-channel in membranes from the anode to cathode side of the DMFC, which decreases the open-circuit potential by increasing the thermal load on the DMFC cell, leading to a decrease in current and power density. Subsequently, after some time the cell becomes inactive. The high fuel permeability of commercial Nafion is a major drawback which is considerably reduced by the use of a silicate nanoclay dispersed functionalized nanohybrid membrane. The methanol permeability of the different functionalized membranes is compared in the above table and concludes that the dispersion of the inorganic nanofiller leads to the decrement of the cell fuel permeability. Lai et al. prepared grafting of a flexible ionic group on multiblock copolymers or anion exchange through the direct methanol fuel cell membrane and fabricated the membrane electrode assembly, measured the electrical efficiencies of the membrane, and found an open-circuit voltage (OCV) of 0.93 V against the maximum power density

of 76.3 mW cm $^{-2}$ achieved in a single fuel cell at 80 °C, whose polarization curve is shown in Figure 8d.¹¹¹ However, nanohybrid membranes of fluoropolymers are efficient as compared to existing standard commercial membranes.

3. ENERGY HARVESTING

The current scenario for the energy needs of the world is still mainly dependent on the conventional sources of energy. The need to establish alternative sources of energy for a sustainable future is a current hot topic of research. Several alternate sources have been formulated to overcome the gradual decrease in conventional sources of energy for a sustainable future. Of the many alternative sources developed, energy harvesting has made its mark because of its ever increasing applicability and environmentally friendly approach. Energy harvesting is a process where the waste or unused energies from various sources like vibrations, chemical sources, human motion, noise, or wind are stored or used to produce electrical energies which are able to be used up in miniature devices and low power electronics with better efficiency. It provides an alternative to replacing batteries and reduces their after use effects. It also saves on maintenance and replacement costs. The ability of this system to produce a considerable amount of power with minimal effort is of primary importance to the industries as well as to the researchers who are constantly putting in effort to broaden its area of application and reduce the dependency on batteries and conventional sources. An example of this system is Perpetuum, which is able to predict the failure of the rail wheel bearings by converting the vibration of the rolling stock to electrical power.^{126,127} With the advancement in the technologies, miniature and low power consumption-based devices are in high demand. Energy harvesting is an efficient method to produce a considerable amount of power to these small power-based devices with the advantage of low maintenance and almost negligible environmental impact. Now certain methods are a compromise in the broader context of energy harvesting, of which mechanical-based energy harvesting has gained widespread attention. Mechanical-based energy harvesting consists of energy produced from vibration and movements of the body or objects; for example, human body movement and movement of automobiles, motors, or acoustic waves generate a lot of power which if stored can be of high importance.^{128,129}

3.1. Piezoelectric-Based Energy Harvesting. The vibration to energy conversion consists of various mechanisms, of which piezoelectric-based mechanical energy harvesting has acquired higher attention because the piezoelectric materials are capable of producing high power densities in comparison to the other processes. This review mainly focuses on the piezoelectric-based energy harvesting over other methods in this section. Piezoelectric materials are smart materials which convert applied pressure to electrical energy output. These materials have the potential to convert produced mechanical vibrations into electrical energy through a direct piezoelectric effect. Also these materials undergo mechanical strain when exposed to electrical energy, which is known as an indirect piezoelectric effect. Here we will stick to the direct piezoelectric effect over the converse one.

The concept of piezoelectricity can be best understood considering a crystalline solid and its arrangement of ions along a unit cell. Based on crystal systems, of the 32 crystallographic classes, 11 are centrosymmetric, while 21 are noncentrosymmetric. Twenty of the 21 noncentrosymmetric classes show piezoelectric behavior. This lack of symmetry in the distribution of the ions of the crystalline materials leads to some dipole moments in these materials, which mark piezoelectricity, and as a result of the absence of the symmetry, these materials possess a well-defined polar axis. Now for a piezoelectric material to be capable of being used in energy-harvesting applications, it must be able to generate charge and potential on the application of stress. Hence, in the presence of the polar axis in piezoelectric materials, the energy harvesting depends on the direction of the applied strain relative to the polar axis on these materials. For the mechanical-based energy harvesting, a direct piezoelectric effect is of importance where the mechanical strain leads to electrical energy generation.^{126,130,22,131} Figure 9 depicts the charge separation

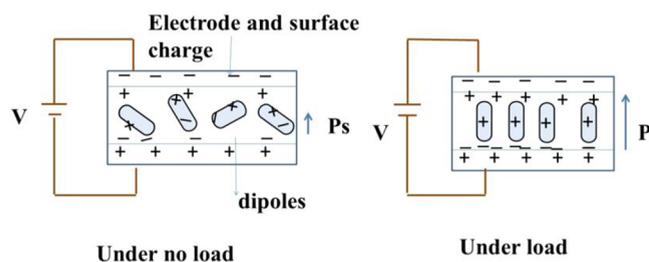


Figure 9. Charge separation mechanism. Reprinted with permission from ref 132. Copyright 2019 Elsevier.

mechanism under load and no load systems.¹³² The piezoelectric materials consist of polarization along with electric dipoles and domains which results in the presence of free charges on the surface of these materials. The dipoles remain random when no mechanical stress is applied on these materials; as a result, they cancel each other out, and hence, no electrical output is obtained. When a mechanical load is applied, the positive and negative charges get separated, resulting in alignment of dipoles which leads to a potential difference in the material, and thus electrical output is obtained in the direction of the applied stress. To obtain a better response from the materials, it is necessary to impart pressure along the direction of the dipole alignment.^{133–135}

Considering various sources for piezoelectric-based energy harvesting, the human body is one of the potential sources for

such applications. A normal person (average weight around 68 kg) produces about 67 W of power from their heel during walking; the lung motion while breathing produces around 1 W of power; and the finger motion of a normal person can produce around 6.9–19 mW of power.^{128,136} If a system can be developed which could harness around 5–10% of the power produced from different movements across the body, it could operate various wearable devices. In order to achieve maximum energy conversion efficiency from the source, the choice of material plays an important role. The key points while choosing a material should be (a) better energy conversion efficiency, (b) better coupling with the storage unit with minimal energy loss, (c) good conversion of power from AC to DC circuitry, and (d) better response time; i.e., the signal produced should not decay immediately. Better applications can be nurtured from a system when a proper material is used in the device form, which could harness maximum energy from the source. For a material to be of higher efficiency in the field of piezoelectric energy harvesting, an important parameter to be considered is piezoelectric coefficients (d_{xy}). Piezoelectric coefficients indicate the charge produced when a stress is applied on the material. This physical parameter indicates the net polarization produced per unit of the mechanical load applied to the piezoelectric material, or conversely, it explores the amount of mechanical strain experienced by the piezoelectric material per unit of the applied electric field. The most common and important coefficient is the 33-mode (d_{33}); i.e., the applied stress and the polarization are along the same direction. Other modes which can be utilized for energy harvesting are d_{31} , where the stress applied is perpendicular to the polarization and d_{15} which is a shear-based mode.

The total charge generated (Q) across the opposite ends of the material when a stress is applied ($\Delta\sigma$) over the piezoelectric material area (A) can be equated as^{126,127}

$$Q = A \times (d_{33})(\Delta\sigma) \quad (1)$$

The piezoelectric energy-harvesting performance depends on the amount of charge generated across the two faces of the material which is the function of the piezoelectric coefficient and applied stress. To obtain higher efficiency from the system, the coupling between the piezoelectric material and the source of mechanical input is an important parameter. Electro-mechanical coupling factor (k^2) relates the material's capability to sustain the mechanical pressure applied on it and the strain recovered. It provides the interchange in electrical and mechanical energy.^{126–128}

$$k^2 = \text{produced electrical energy}/\text{input mechanical energy} \quad (2)$$

Table 5 presents the values of piezoelectric coefficients for some common piezoelectric materials.

The piezoelectric materials generally fall into two groups: piezoelectric crystals and piezoelectric polymers. The piezoelectric phenomenon was first developed into single crystals and ceramic materials. The piezoelectric crystal is mainly comprised of single or polycrystalline ceramics. Polycrystalline ceramics are highly studied and explored for piezoelectric-based energy-harvesting applications. The piezoelectric ceramic materials possess high dielectric constant and d_{33} values (Table 5), which lead them to this field of applications.^{137,138} These materials include ferroelectric materials like lead zirconia titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$), barium titanate (BaTiO_3), and lead titanate (PbTiO_3) as well as nonferroelectric materials

Table 5. Electromechanical Parameters for Some Common Piezoelectric Materials^{126,127}

Piezoelectric material	d_{33} (pC/N)	ϵ_r	Electromechanical coupling factor (k_{33})
PZT	593	3400	0.75
PMN-PT	2820	8200	0.94
BaTiO ₃	149	1200	0.49
ZnO	12.4	11	0.48
Quartz	-2.3 (d_{31})	4.6	0.1
GaN	3.7	-	-
AlN	5	12	0.23
CdS	10.3	10.3	0.26
LiNbO ₃	6	28.7	0.23
PVDF	-33	7.6	0.19

like zinc oxide (ZnO) and AlN. Among the developed ceramic materials, PZT is the most widely used ceramic because it possesses an extremely high value of dielectric constant, piezoelectric coefficients, and coupling factor. In PZT, a large spontaneous polarization is produced due to the displacement of the positively charged metal atoms with the negatively charged oxygen atoms. The efficiency and physical properties of the PZT are further increased with the addition of some dopants like Mn, Ta, and Nb, etc.^{128,139,140} Although these ceramic materials possess extremely high piezoelectric properties, they also have some limitations which restrict their use in some applications. These inorganic materials are extremely hard, stiff, and brittle and have the potential to fail at low tensile strain. PZT having high values of piezoelectric parameters currently stands out among all ceramic materials but is toxic in nature due to the presence of lead which restricts its use in biomedical applications.¹⁴¹⁻¹⁴³

For wide applicability of the piezoelectric materials for energy-harvesting applications, the higher d_{33} value is the primary need for efficient energy conversion. However, most human movements like walking, hand tapping, respiration, heartbeat, and swinging of the arms require the material to be bendable or stretchable. Based on the application point of view, only considering the d_{33} values should not be mandatory, and the piezoelectric material should be flexible, biocompatible, and cost efficient. To harness the energy from body movements, the wearable device should be able to generate power with minimal effort from the body. As a result, flexible and mechanically sound piezoelectric materials become the choice over brittle ceramic materials. Flexibility helps in natural integration of the organs or soft clothing materials with different human motions, and as a result maximum energy can be generated.¹²⁸ The other class of piezoelectric materials is polymeric materials. Polymeric materials exhibiting piezoelectric property are preferred over the ceramic or inorganic materials because of their diverse properties like flexibility, biocompatibility, effective toughness, low density, economical, mechanical robustness, and ease of preparation at different temperatures. The biocompatible nature of some of the polymers makes them useful for implantable and wearable energy harvesters.¹⁴⁴⁻¹⁴⁶ Though polymers possess a lower value of dielectric constant and d_{33} values than ceramics, still their high piezoelectric voltage constant (g_{33}) and flexible and superior mechanical character make them a suitable material for implantable and wearable applications. A wearable device was made of polymer, which was used to capture the energy produced from the stretching or bending of the limbs or

expansion of the cavity and lungs during the respiration process.¹²⁸ Polymer-based piezoelectric or electroactive materials have been found to have wide application in the field of sensors, actuators, transducers, and storage devices. The electroactive polymers possessing a high level of polarization due to the availability of the net dipole moment in their macromolecular arrangements are of interest for energy-harvesting applications.¹²⁶ Polymers are generally of three types: crystalline, semicrystalline, and amorphous polymers. Semicrystalline and amorphous polymers have the favored properties to be applicable in piezoelectric applications. Semicrystalline polymers have a higher content of polar phase as compared to amorphous polymers due to their better mechanical orientation, thermal annealing, and high dipole moment. Those polymers which possess dipoles and can orient themselves on the application of mechanical stress and align into the favored direction have an edge for piezoelectric-based energy-harvesting applications. Different types of polymers based on their structure, like fluoropolymers, polyamides, polyureas, polythioureas, polylactides, elastomers, or naturally occurring polymers like cellulose, proteins, wood, and bones, have the potential for energy-harvesting applications. Piezoelectricity in polymers was first reported in 1963 in two polymers: poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC).^{146,147} The development of piezoelectricity in poly(vinylidene fluoride) (PVDF) by Kawai in 1969 gave a new dimension to electroactive polymers for such applications which were dominated primarily by inorganic materials.¹⁴⁸ Table 6 demonstrates the important piezoelectric parameters of some common polymers which suggests a wide diversity in the field of piezoelectric polymers.

Table 6. Dielectric Constant and d_{33} Values for Some Common Piezoelectric Polymers^{146,149-153}

Polymer	d_{33} (pC/N)	ϵ_r
PLA	9.82	3-4
Polyhydroxybutyrate	1.6-2.0	2-3.5
Polyamide-11	4	5
PVDF	-24 to -33	6-12
P(VDF-TrFE)	-38	18
P(VDF-HFP)	-24	11
P(VDF-CTFE)	140	13
P(VDF-TrFE-CTFE)	-	65
Cellulose (wood)	0.1	-
Chitin (lobster apodeme)	1.5	-
Collagen (bone)	0.2	-
Keratin (horn)	1.8	-
PAN	2	38
Polyurethane	-	6.8

PVDF is a highly efficient, par excellence polymer which has the highest dipole moment per unit among polymers, which makes it the most effective polymer for piezoelectric-based energy-harvesting applications. Piezoelectric property in PVDF originates from the noncentrosymmetric unit cell and net dipole moment and polarization in the material.^{154,155}

3.2. PVDF. Poly(vinylidene fluoride) is a semicrystalline, thermoplastic fluoropolymer obtained from the polymerization of the monomer vinylidene fluoride. PVDF consists of exceptional properties like flexibility, biocompatibility, chemical resistance, and high mechanical strength along with excellent piezoelectric, ferroelectric, and pyroelectric proper-

ties, which make it one of the most important polymers in the field of energy-harvesting applications.^{156,157} PVDF possesses an alternating chain of $-\text{CH}_2$ and CF_2 , which leads to dipole moment generation in the polymer. The fluorine atom possesses negative charges, while the hydrogen atom has positive charges which are at the two ends of the polymer. Due to this difference in charge, polarity is developed, which makes it a suitable material for the sensor-, actuator-, and transducer-based systems. When external field is applied opposite from the poled directions, PVDF stretches along its length. If the field is applied along the direction of the pole direction, the contraction phenomenon occurs in the polymer. These effects maximized its use in the piezoelectric-based energy-harvesting applications. Due to its unique molecular structure and arrangements, PVDF can exist in many conformations and structures. Basically, PVDF has five important crystalline phases, α , β , γ , δ , and ϵ . The hexagonal α -phase is thermodynamically stable, while the orthorhombic β -phase is kinetically more favorable. The α and δ phases possess TGTG' conformations, which lead to nonpolar nature and have no net dipole moment. The γ - and ϵ -phases have T₃GT₃G' conformation, which is semipolar in nature with a small dipole moment, whereas the electroactive β -phase consists of all trans (TTTT) planar zigzag conformations with their dipoles parallel to the *b*-axis, which results in the highest dipole moment per unit cell. The β -phase is the most significant phase for the piezoelectric property of the PVDF.^{126,146,151,158} Naturally PVDF consists mainly of the α -phase which is nonelectroactive but possesses the tendency to get converted to the β -phase and γ -phase which have electroactive character. The maximum transformation of the nonpiezo phase to the piezoelectric active phase leads to efficient piezoelectric property in the system, which leads to its use in sensors, actuators, batteries, energy storage devices, biomedical applications, etc.^{159,160} Several techniques have been implemented to raise the fraction of the electroactive phase in PVDF, of which the poling and mechanical stretching have been the most effective. Poling is a process where the external field is applied often at higher temperatures to align the dipoles along the polar axis of the applied field, which is further cooled to achieve permanent polarization. Mechanical stretching is a process where the polymer is stretched across the length for alignment of the molecular dipoles along the applied stress.^{161,162} Gaur et al. studied the changes in the pristine PVDF film when subjected to external poling and stretching. The stretched and poled films were of higher efficiency as compared to the pure PVDF due to a rise in the electroactive phase content.¹⁶³

Apart from poling and stretching, other methods have also been used to increase the β -phase content, like electrospinning, forming composites using electroactive fillers, copolymerization or blend formation, annealing of polymers, and change in molecular structure. Based on the molecular configurations of PVDF, certain tailoring with its elemental arrangements lead to some of its copolymers which were even better than the homopolymer. PVDF has four basic copolymers: P(VDF-TrFE), P(VDF-HFP), P(VDF-CTFE), and P(VDF-TrFE-CTFE). PVDF-TrFE (Figure 1) has a higher piezoelectric coefficient value and remnant polarization than PVDF since it possesses the highest degree of crystallinity and favored orientation of the crystallites. Due to these oriented molecular crystallites, it has the highest electromechanical coupling which leads to better piezoelectric properties.¹⁶⁴ Electrospinning is a

process which is the most effective and largely used technique to convert the nonpiezo phase to the electroactive phase. It is a process to prepare thin, flexible, and light scaffolds of polymers which have found use in different applications. In this process, uniaxial stretching and poling of the polymer solution is performed under the influence of high potential difference to draw into fibers of micron- to nanodimension. The electrospun fibers possess high mechanical strength, good electrical properties, and enhanced surface to volume ratio, which increases its applicability in diverse fields.^{130,165,166}

Based on the above methods to transform the paraelectric α -phase to the ferroelectric β -phase, certain modifications can be achieved in the piezoelectric properties which might be suitable for energy-harvesting applications, but the influence of stretching, poling, or electrospinning or other methods will only lead to a minimal change in the output power produced on mechanical stress. The addition of electroactive materials in the form of fillers which can induce piezoelectricity into the polymer through different processing techniques can also be an option to increase the applicability of these materials. With the addition of external material into the polymer matrix to achieve certain properties, such a combination is often called a composite. Composite formation with polymers has been the most efficient technique established to draw certain novel properties which might not be possible individually. For example, the nanocomposite prepared out of PVDF and PZT can lead to flexible, high electrical property material which can be used to harness energy for energy-harvesting applications.¹⁶⁷ Two types of processed substrates can be developed, which have wide application: films and fibers. The films can be prepared through solution casting or coprecipitation or compressed techniques, while fibers can be drawn using spinning and spraying methods. Since PVDF does not possess high dielectric and d_{33} values, the addition of certain electroactive fillers and then modifying the nature of the system using some methods can produce some excellent results. This review mainly focuses on the PVDF-based nanohybrids which can be used for piezoelectric energy-harvesting applications. There is a certain class of fillers which has been used to induce the piezoelectricity in the polymer. Some of the common classes of fillers are discussed with their importance in the field of energy harvesting.

3.3. Nanoparticle-Based Polymer Hybrids for Piezoelectric Energy Harvesting. Polymer-based hybrids have gained much attention in almost every field of scientific research. The addition of certain nanoparticles to the polymer matrix to achieve something exquisite due to the involvement of both materials has led to excellent applications, which might not be possible individually. Nanoparticles or nanofillers due to their small size and unique features have made a significant contribution in the field of energy harvesting since PVDF is a nonpiezoelectric material but possesses the potential to be electroactive when processed adequately. One of the techniques to induce piezoelectric behavior is the addition of electroactive fillers which can generate a dipole moment in the material; as a result, certain polarization is achieved which can be used to harness energy from the sources. Initially, the nanoparticles were directly added to the polymer matrix to gain piezoelectric nature, but with the advancement in the technologies, certain methods like functionalization, doping, and grafting were developed to increase the properties of the filler which produced better output than pristine nanofillers in most of the cases. There are many nanoparticles being

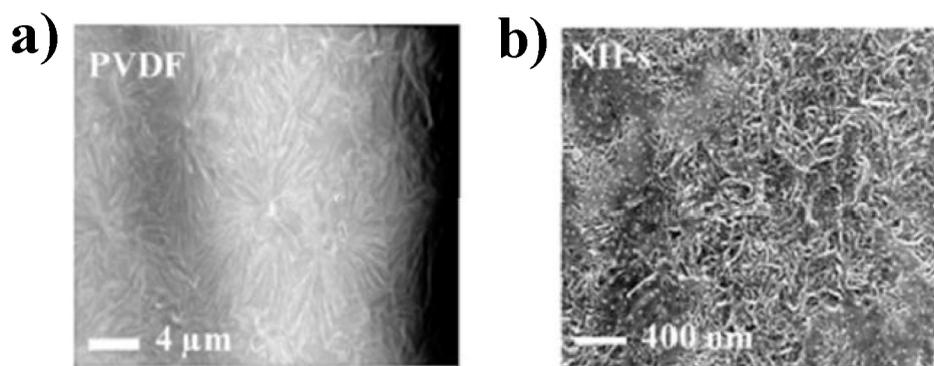


Figure 10. SEM morphology of (a) PVDF film and (b) PVDF nanohybrid through solution casting. Reprinted with permission from ref 30. Copyright 2013 American Chemical Society.

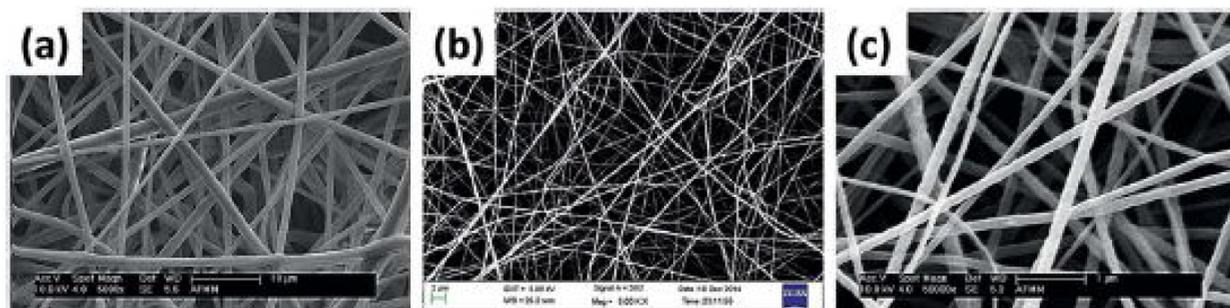


Figure 11. SEM micrographs of electrospun fibers of (a) PVDF, (b) PVDF-CNT, and (c) PVDF-CNT with Ag metal. Reprinted with permission from ref 177. Copyright 2016 Royal Society of Chemistry.

developed and are being used in the field of energy harvesting. Common fillers like carbon-based fillers which include graphene, carbon nanotubes (CNTs), and carbon nanofibers;^{168–170} inorganic fillers like PZT, BaTiO₃, and ZnO;^{167,171–173} 2D materials like nanoclays;^{30,174} and biofillers like fish scales, egg shell membranes, and others which have significantly improved the quality of the work with enhanced properties.^{132,175,176} Some of the fillers and their importance will be discussed here in the presence of PVDF for piezoelectric-based energy harvesting.

Carbon-based materials have significantly contributed to the field of scientific research due to their unique chemical and physical features and wide applicability. Their diverse electrical, mechanical, chemical, and optical properties have made a remarkable impact in the fields of fuel cell, energy harvesting, biomedical applications, solar cells, water treatment, and many other fields of scientific interests. Some other classes of fillers acting as nanoparticles for energy-harvesting applications are ceramic materials which possess very high values of dielectric constants and piezoelectric coefficients. The addition of a ceramic base to reinforce the polymer raises the electro-mechanical parameters and as a result enhances the efficiency of the system for such applications. Apart from these synthetic fillers, some natural materials also possess an enriched amount of electroactive phases which are capable of the transformation of the nonpiezo phases to piezo-active phases. These biomaterials have an added advantage of biocompatibility and cost-effectiveness, which makes them more applicable in some diverse fields of applications.

The addition of these nanoparticles leads to some alterations in the morphology, structure, and mechanical and thermal behavior, which suggests that incorporation of the electroactive

materials raises the potential of the system which produces enhanced output. Pristine PVDF has a spherulite-like morphology, which on some processing or the addition of some nanoparticles transforms to different appearances of needle-like morphology. Tiwari and co-workers prepared a film of PVDF and PVDF-nanoclay (Figure 10a,b), and on surface morphological analysis through SEM it was seen that addition of nanoclay leads to a change in the morphology of the material.³⁰ The change is also evident in the case of the electrospun fibers, where the fiber thickness and nature fluctuate under the impression of the nanoparticle. Electrospinning is a process where the material undergoes mechanical stretching and poling together which leads to a better system. In the presence of the electroactive fillers, the system gets charged, and thus better fibers are generated through the electrospinning process.^{22,169} Sharma et al. prepared electrospun fibers of PVDF-CNT with Ag (Figure 11) and found that the addition of a nanoparticle, CNT, leads to a decrease in the fiber diameter from 1.5 μm (pure PVDF) to 300 nm (PVDF-CNT). The decrease in the diameter is due to the rise in conductivity arising from the electroactive filler, while the fiber diameter increased to some extent on addition of the metal Ag which was due to the rise in viscosity of the system.¹⁷⁷ Yu et al. also achieved a similar observation when clay particles were added to the PVDF matrix. Lucentite (STN and SWN) was added to the polymer, and electrospun fibers were prepared out of it. The fibers with STN lead to reduction in its diameter (100–350 nm) as compared to pure PVDF (50–700 nm), which was attributed to the rise in conductivity of the solution on addition of the clay particles.¹⁶¹ The addition of electroactively charged particles has a profound effect on the morphology of the system. The electrospinning process leading

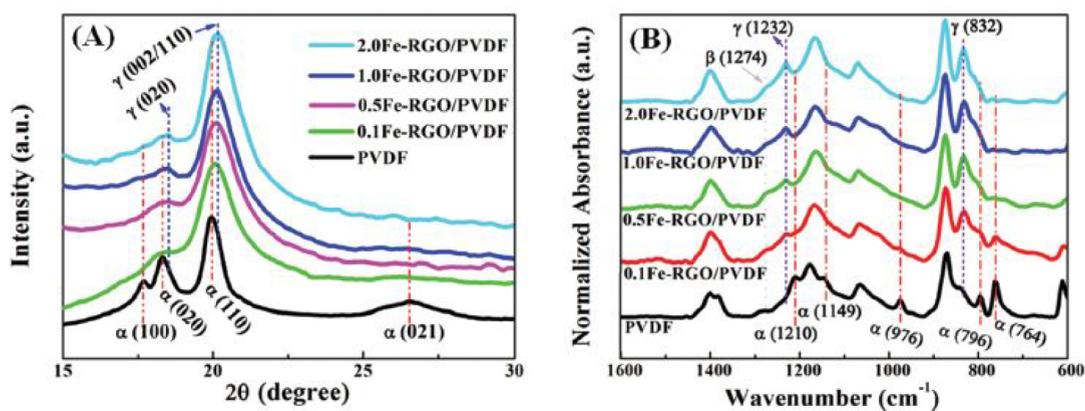


Figure 12. (A) XRD curve and (B) FTIR spectra of pristine PVDF and its composite with RGO at different concentrations of RGO. Reprinted with permission from ref 178. Copyright 2015 Royal Society of Chemistry.

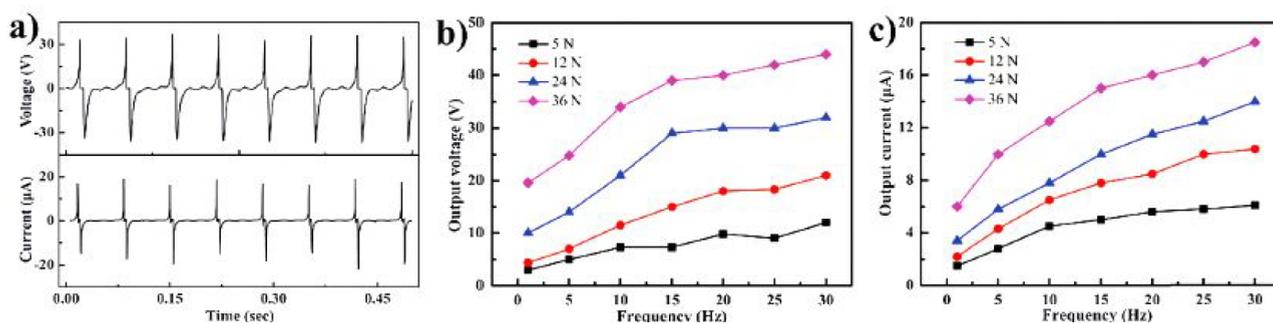


Figure 13. (a) Open-circuit voltage and short-circuit current w.r.t. time. (b) Output voltage and (c) output current with variable frequency. Reprinted with permission from ref 180. Copyright 2016 Royal Society of Chemistry.

to uniform fibers produces bead-free fibers when certain fillers are added to the polymer matrix, which leads to a rise in the piezoelectric phase content, and as a result the efficiency of the system gets enhanced.

The development of the crystalline phases on the addition of the nanoparticles is one of the outcomes which is related to the enhanced piezoelectric response of the PVDF-based devices. The transformation of the nonelectroactive phase or α -phase to the piezo-active phases (β and γ) is an important observation to confirm the role of fillers to achieve higher electroactive phase content. Karan et al.¹⁷⁸ were able to transform the α -phase to the γ -phase on addition of Fe-doped RGO in the PVDF matrix. The addition of Fe-rGO leads to a reduction in the nonpolar phase and a rise in the polar phases, which was evident from the XRD and FTIR results (Figure 12). The characteristic peaks of the γ -phase at 832 and 1232 cm^{-1} were evident for the reported transformation. It is conclusive that the incorporation of polar fillers leads to a higher content of electroactive phases, which enhances the applicability of the system. A change in morphology and the structure affects the piezoelectric parameters, like d_{33} values.

Wu et al.¹⁷⁹ observed a rise in the β -phase when CNT was added to the aligned system of PVDF fibers. The β -phase increased to $89 \pm 2\%$ from $79 \pm 3\%$ for the PVDF-CNT system in comparison to random fibers of PVDF. The rise in the polar phase leads to a rise in the d_{33} values. The d_{33} coefficient for pure random fibers of PVDF was 16.8 ± 1.4 pC/N, which increased to 31.3 ± 2.1 pC/N for the aligned PVDF-CNT composites. The rise in the piezoelectric coefficient can be attributed to the addition of fillers which enhance the

polarity and conductivity of the system, and as a result its electromechanical properties were enhanced. To prepare a material for piezoelectric energy-harvesting-based applications, the morphological and structural variation is a noteworthy observation based on which a highly efficient nanogenerator can be fabricated as suitable for such applications. An efficient piezoelectric nanogenerator or a device produces substantial electrical output in terms of voltage, current, power density, or conductivity, which presents a scenario to use it for some particular applications.

Li et al.¹⁸⁰ prepared a sandwiched structured device consisting of PVDF and PVDF-rGO membranes, which were able to harvest energy up to 46 V with a force of 36 N at the frequency of 15 Hz (Figure 13a). The maximum current and power density achieved were $18 \mu\text{A}$ and $18.1 \mu\text{W cm}^{-2}$. It was concluded that applying variable force at different frequencies generates variable electrical output. Figure 13b,c explains that on rising the force from 5 to 36 N the potential increased from 2 to 46 V, while the current reached to $18 \mu\text{A}$ from $2 \mu\text{A}$. The rise in the output voltage and short-circuit current suggests that the prepared device was able to convert mechanical energy to electrical output, which allows the piezoelectric generator to act as a sensor.

The rise in power density with the increase in the mechanical loads may be attributed to the larger amount of free charges generated on the surface of the material, which is easily transmitted through the electrodes. Hence, the better the charge generation from a developed piezoelectric system, the more efficient the device's application in various aspects will be. The development of wearable and portable piezoelectric

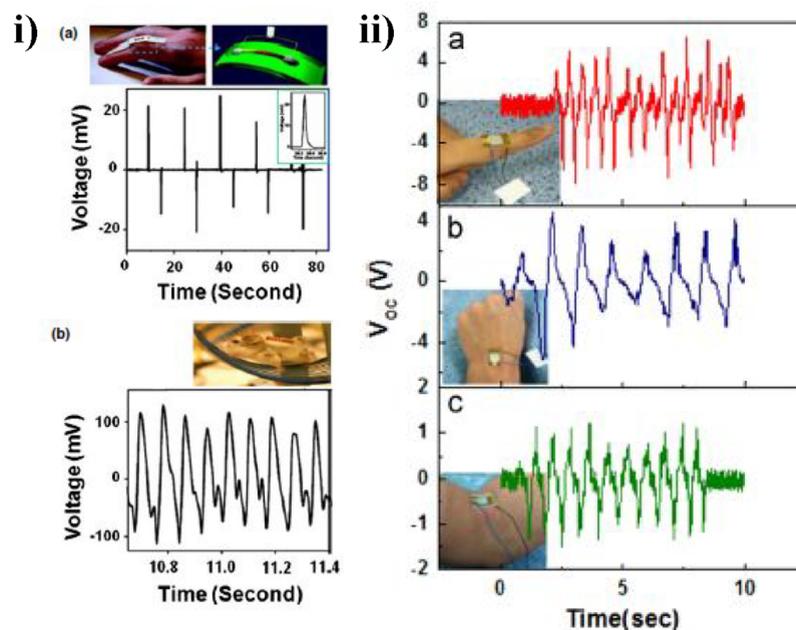


Figure 14. (i) Output voltage generated from (a) finger tapping and (b) hamster movement through a ZnO-based nanogenerator. Reprinted with permission from ref 181. Copyright 2009 American Chemical Society. (ii) Energy produced from different human body movements: (a) finger, (b) wrist, and (c) elbow. Reprinted with permission from ref 173. Copyright 2015 Elsevier.

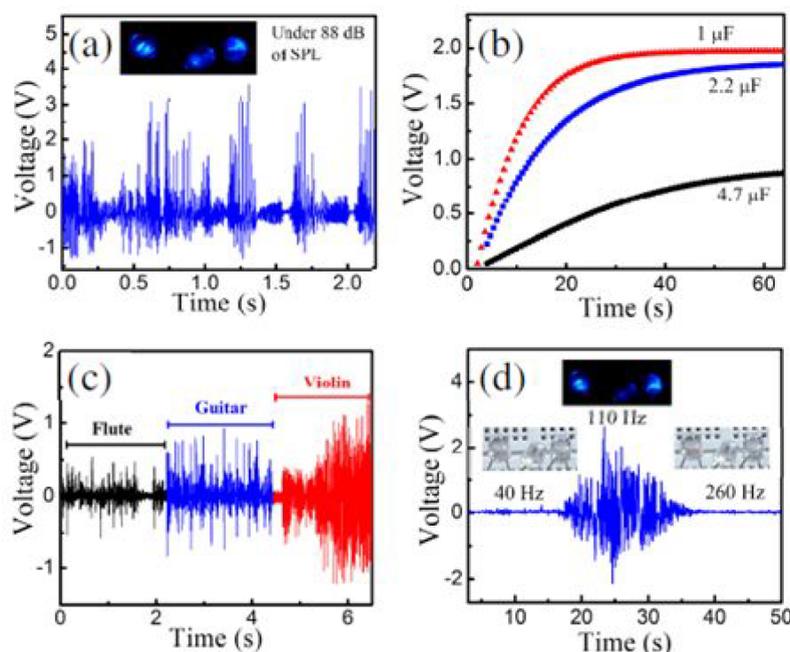


Figure 15. (a) Output voltage generated from sound energy of 88 dB with LEDs glowing in the inset. (b) Charging through different capacitors. (c) Output voltage produced from different musical instruments. (d) Frequency-based voltage generation with glowing of LEDs connected in series in the inset. Reprinted with permission from ref 169. Copyright 2016 American Chemical Society.

electronics has led to some advanced use of these products in real-life applications. Providing load on these devices generates some considerable output which can be used for small miniature-based electronics. The pressure required to generate such electrical outputs can be variable, like acoustics, wind, light, human body movements, or frequency based.

Developing portable and self-charged devices which could harvest energy from environmental sources will lead to a sustainable future with minimal energy requirements.¹⁶⁸

Siddiqui and co-workers¹⁷³ fabricated a system made of P(VDF-TrFE) and barium titanate nanoparticles, which was able to generate potential from different movements of the human body like the index finger, wrist, and elbow (Figure 14ii(a–c)). Garain et al.¹⁶⁹ generated a better level of energy from different sources, using the nanofibers of the Ce³⁺-doped PVDF/graphene composite. The prepared device was used to harvest energy from different types of load in the form of sound energy and pressure. Figure 15b shows that the prepared

device was also capable of storing charge against some load. Considerable output voltage was generated using acoustic energies of a pop song and musical instruments like the flute, guitar, and violin (Figure 15c). The generated energy was then also used to light up LEDs which showed the versatility of the device (Figure 15d). Even a low level of pressure can be sensed through these miniature devices, which make them a very important tool for the future. Rajala and co-workers¹⁸² developed shoe sensors made of PVDF and cellulose nanofibrils and an electromechanical film which could sense the movement of the human body and measure the plantar pressure distribution. Gaur and co-workers¹⁸³ were able to harvest a sufficient amount of energy from PVDF and orange peel biowaste, which produced a considerable amount of response for different human motions and also light up LEDs. PVDF-based devices are gaining attention in the field of piezoelectric energy harvesting due to its tunable and versatile properties. Generating something useful out of waste is needed for the coming future to partially solve the energy crisis, which might be a possibility.

It is thus conclusive that piezo polymers like PVDF have the capability to get transformed into an active polar piezo phase from the nonpolar phase when subjected to some modification in its structure/processing like stretching, poling, or adding electroactive fillers, etc. The role of nanoparticles is greatly studied because of their diverse applications and ease of processing. Adding suitable fillers leads to the generation of some quantitative electrical outputs, which in turn make a path for their various applications using different sources. The better activity of the polymer with these fillers has been used to prepare portable, self-chargeable miniature devices which provide a better option for energy conservation and generation for the sustainable future. Still modifications are being made to be able to harness energy from waste sources for larger application. Thus, it can be expected that using the piezo polymers one could be able to charge some of their basic needs, which can be a positive aspect for the near future to use these systems for an even broader context.

4. SUMMARY

The objective of this review is to report on modified poly(vinylidene difluoride) (PVDF) with copolymers (HFP, CTFE, and TrFE) and their nanohybrids for energy applications. The first application is the functionalized PVDF and its copolymer for the polymer electrolyte membrane fuel cells (PEMFCs), thereby making the functionalized membrane from the insulating PVDF/copolymers and silicate nanoclay dispersed nanohybrid membrane. SHI creates the free radical, olefinic bonds, chain scissions, and cross-linking in the PVDF after ion bombardment. Because of the catastrophic effect of SHI on the pure polymer, it can be carefully controlled using suitable nanoparticles. The bombardment of the SHI nucleates the electroactive phases and through-nanochannel crates by selective chemical etching, and subsequently the nanochannel is filled through in situ polymerization of the conducting monomers followed by sulfonation, making the nanochannel exclusively conducting and keeping the rest intact and mechanically and thermally stable. The high proton conductivity with low fuel permeability (methanol) of the conducting nanochannel makes them suitable for direct methanol fuel cells. With the design aspect of the single-cell membrane electrode assembly and through the measurement of the polarization curve, it is found to be suitable for

applications having lower cost and better cell performance as compared to the Nafion 117 standard membrane. It is concluded that the role of the nanoparticle is effective in generating polar phases in the PVDF, which leads to a better piezoelectric-based energy-harvesting system. The modifications in the polymer through some processing like stretching, poling, electrospinning, or composites are a better way to harvest energy, which provides certain optimism to use these systems for sustainable energy alternatives. PVDF-based materials are able to generate energy from different human body motions, vibrations, and other waste mechanical energy sources, which demonstrates its wide applicability and potential for the coming future.

■ AUTHOR INFORMATION

Corresponding Author

Pralay Maiti – School of the Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi 221005, India; orcid.org/0000-0002-6879-3591; Email: pmaili.mst@itbhu.ac.in

Authors

Om Prakash – Kashi Naresh Government PG College Gyanpur, Bhadohi 221304, India

Shivam Tiwari – School of the Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi 221005, India; orcid.org/0000-0002-9210-5955

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.2c04774>

Author Contributions

[§]O.P. and S.T. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.T. would like to thank the institute for providing the teaching assistantship. The research support grant from the Tata Innovation Fellowship (sanction no. BT/HRD/35/01/02/2020) is highly acknowledged.

■ REFERENCES

- (1) Tugrul Ogulata, R Energy sector and wind energy potential in Turkey. *Renew. Sustain. Energy Rev.* **2003**, *7* (6), 469–484.
- (2) Prakash, O.; Pandey, A. K.; Maiti, P. Functionalized Fluoropolymer Membrane for Fuel Cell Applications. *Nanoscale Eng. Biomater. Prop. Appl.* **2022**, 517–540.
- (3) Prakash, O.; Jana, K. K.; Manohar, M.; Shahi, V. K.; Khan, S. A.; Avasthi, D.; Maiti, P. Fabrication of a Low-Cost Functionalized Poly(Vinylidene Fluoride) Nanohybrid Membrane for Superior Fuel Cells. *Sustain. Energy Fuels* **2019**, *3* (5), 1269–1282.
- (4) Bhardwaj, R.; Prakash, O.; Tiwari, S.; Maiti, P.; Ghosh, S.; Singh, R.; Maiti, P. Efficient Herbicide Delivery through a Conjugate Gel Formulation for the Mortality of Broad Leaf Weeds. *ACS Omega* **2022**, *7*, 19964–19978.
- (5) Bailis, R.; Ezzati, M.; Kammen, D. M. Mortality and Greenhouse Gas Impacts of Biomass and Petroleum Energy Futures in Africa. *Science* **2005**, *308* (5718), 98–103.
- (6) Badwal, S. P. S.; Giddey, S. S.; Munnings, C.; Bhatt, A. I.; Hollenkamp, A. F. Emerging Electrochemical Energy Conversion and Storage Technologies. *Front. Chem.* **2014**, *2*, 79.
- (7) Gómez-García, M. A.; Pitchon, V.; Kiennemann, A. Pollution by Nitrogen Oxides: An Approach to NO_x Abatement by Using Sorbing Catalytic Materials. *Environ. Int.* **2005**, *31* (3), 445–467.

- (8) Goldemberg, J.; Teixeira Coelho, S. Renewable Energy - Traditional Biomass vs. Modern Biomass. *Energy Policy* **2004**, *32* (6), 711–714.
- (9) Devabhaktuni, V.; Alam, M.; Shekara Sreenadh Reddy Depuru, S.; Green, R. C.; Nims, D.; Near, C. Solar Energy: Trends and Enabling Technologies. *Renew. Sustain. Energy Rev.* **2013**, *19*, 555–564.
- (10) Gross, R.; Leach, M.; Bauen, A. Progress in Renewable Energy. *Environ. Int.* **2003**, *29* (1), 105–122.
- (11) Kim, J. R.; Choi, S. W.; Jo, S. M.; Lee, W. S.; Kim, B. C. Electrospun PVdF-based fibrous polymer electrolytes for lithium ion polymer batteries. *Electrochim. Acta* **2004**, *50* (1), 69–75.
- (12) Lehtinen, T.; Sundholm, G.; Holmberg, S.; Sundholm, F.; Bjornbom, P.; Bursell, M. Electrochemical characterization of PVDF-based proton conducting membranes for fuel cells. *Electrochim. Acta* **1998**, *43* (12–13), 1881–1890.
- (13) Prakash, O.; Bihari, S.; Keshav; Tiwari, S.; Prakash, R.; Maiti, P. Dehydrohalogenated Poly(Vinylidene Fluoride)-Based Anion Exchange Membranes for Fuel Cell Applications. *Mater. Today Chem.* **2022**, *23*, 100640.
- (14) Kumar, K.; Srivastava, A.; Parkash, O.; Avasthi, D. K.; Rana, D.; Shahi, V. K.; Maiti, P. Nanoclay and Swift Heavy Ions Induced Piezoelectric and Conducting Nanochannel Based Polymeric Membrane for Fuel Cell. *J. Power Sources* **2016**, *301*, 338–347.
- (15) Jana, K. K.; Tiwari, V. K.; Avasthi, D. K.; Paine, T. K.; Maiti, P. New Generation Fuel Cell Membrane Using Swift Heavy Ions. *ChemistrySelect* **2017**, *2* (22), 6413–6437.
- (16) Prakash, O.; Jana, K. K.; Jain, R.; Shah, P.; Manohar, M.; Shahi, V. K.; Maiti, P. Functionalized Poly(Vinylidene Fluoride-Co-Hexafluoro Propylene) Membrane for Fuel Cell. *Polymer (Guildf)* **2018**, *151*, 261–268.
- (17) Tripathi, B. P.; Kumar, M.; Shahi, V. K. Organic-Inorganic Hybrid Alkaline Membranes by Epoxide Ring Opening for Direct Methanol Fuel Cell Applications. *J. Membr. Sci.* **2010**, *360* (1–2), 90–101.
- (18) Walkowiak-Kulikowska, J.; et al. Polymers application in proton exchange membranes for fuel cells (PEMFCs). *Physical Sciences Reviews* **2017**, DOI: 10.1515/psr-2017-0018.
- (19) Ayyaru, S.; Dharmalingam, S. Development of MFC Using Sulphonated Polyether Ether Ketone (SPEEK) Membrane for Electricity Generation from Waste Water. *Bioresour. Technol.* **2011**, *102* (24), 11167–11171.
- (20) Tien, Y. I.; Wei, K. H. Hydrogen Bonding and Mechanical Properties in Segmented Montmorillonite/Polyurethane Nanocomposites of Different Hard Segment Ratios. *Polymer (Guildf)* **2001**, *42* (7), 3213–3221.
- (21) Tiwari, V. K.; Kulriya, P. K.; Avasthi, D. K.; Maiti, P. Poly(Vinylidene Fluoride- Co -Hexafluoro Propylene)/Layered Silicate Nanocomposites: The Effect of the Swift Heavy Ion. *J. Phys. Chem. B* **2009**, *113* (34), 11632–11641.
- (22) Tiwari, S.; Gaur, A.; Kumar, C.; Maiti, P. Enhanced Piezoelectric Response in Nanoclay Induced Electrospun PVDF Nanofibers for Energy Harvesting. *Energy* **2019**, *171*, 485–492.
- (23) Sahu, A. K.; Selvarani, G.; Pitchumani, S.; Sridhar, P.; Shukla, A. K. A Sol-Gel Modified Alternative Nafion-Silica Composite Membrane for Polymer Electrolyte Fuel Cells. *J. Electrochem. Soc.* **2007**, *154* (2), B123.
- (24) Xie, Y.; Liu, B.; Chen, Z.; Han, X.; Liu, B.; Zhang, H.; Pang, J.; Jiang, Z. Graft Fluorinated Poly(Arylene Ether Ketone)s Containing Highly Dense Sulfonic-Acid-Functionalized Pendants for Proton Exchange Membranes by C–N Coupling. *Polymer (Guildf)* **2017**, *131*, 84–94.
- (25) Singh, N. K.; Purkayastha, B. D.; Roy, J. K.; Banik, R. M.; Yashpal, M.; Singh, G.; Malik, S.; Maiti, P. Nanoparticle-Induced Controlled Biodegradation and Its Mechanism in Poly(ϵ -Caprolactone). *ACS Appl. Mater. Interfaces* **2010**, *2* (1), 69–81.
- (26) Giannelis, E. P. Polymer Layered Silicate Nanocomposites. *Adv. Mater.* **1996**, *8* (1), 29–35.
- (27) Tripathi, B. P.; Shahi, V. K. Progress in Polymer Science Organic – Inorganic Nanocomposite Polymer Electrolyte Membranes for Fuel Cell Applications. *Prog. Polym. Sci.* **2011**, *36* (7), 945–979.
- (28) Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. Nanocomposite Polymer Electrolytes for Lithium Batteries. *Nature* **1998**, *394* (6692), 456–458.
- (29) Golodnitsky, D.; Ardel, G.; Peled, E. Ion-Transport Phenomena in Concentrated PEO-Based Composite Polymer Electrolytes. *Solid State Ionics* **2002**, *147* (1–2), 141–155.
- (30) Tiwari, V. K.; Prasad, A. K.; Singh, V.; Jana, K. K.; Misra, M.; Prasad, C. D.; Maiti, P. Nanoparticle and Process Induced Super Toughened Piezoelectric Hybrid Materials: The Effect of Stretching on Filled System. *Macromolecules* **2013**, *46* (14), 5595–5603.
- (31) Tiwari, V. K.; Shripathi, T.; Lalla, N. P.; Maiti, P. Nanoparticle Induced Piezoelectric, Super Toughened, Radiation Resistant, Multi-Functional Nanohybrids. *Nanoscale* **2012**, *4* (1), 167–175.
- (32) Gaur, A.; Kumar, C.; Shukla, R.; Maiti, P. Induced Piezoelectricity in Poly(Vinylidene Fluoride) Hybrid as Efficient Energy Harvester. *ChemistrySelect* **2017**, *2* (27), 8278–8287.
- (33) Ranjan, V.; Yu, L.; Nardelli, M. B.; Bernholc, J. Phase Equilibria in High Energy Density PVDF-Based Polymers. *Phys. Rev. Lett.* **2007**, *99* (4), 047801.
- (34) Tiwari, V. K.; Kulriya, P. K.; Avasthi, D. K.; Maiti, P. Radiation-Resistant Behavior of Poly(Vinylidene Fluoride)/Layered Silicate Nanocomposites. *ACS Appl. Mater. Interfaces* **2009**, *1* (2), 311–318.
- (35) Gaur, A.; Shukla, R.; Kumar, B.; Pal, A.; Chatterji, S.; Ranjan, R.; Maiti, P. Processing and Nanoclay Induced Piezoelectricity in Poly(Vinylidene Fluoride-Co-Hexafluoro Propylene) Nanohybrid for Device Application. *Polymer* **2016**, *97*, 362–369.
- (36) Wang, B.; Huang, H. X. Incorporation of Halloysite Nanotubes into PVDF Matrix: Nucleation of Electroactive Phase Accompany with Significant Reinforcement and Dimensional Stability Improvement. *Compos. Part A Appl. Sci. Manuf.* **2014**, *66*, 16–24.
- (37) Wang, D.; Li, K.; Teo, W. K. Preparation and Characterization of Polyvinylidene Fluoride (PVDF) Hollow Fiber Membranes. *J. Membr. Sci.* **1999**, *163* (2), 211–220.
- (38) Teo, W. E.; Inai, R.; Ramakrishna, S. Technological Advances in Electrospinning of Nanofibers. *Science and Technology of Advanced Materials* **2011**, *12*, 013002.
- (39) Wu, J.; Wang, N.; Zhao, Y.; Jiang, L. Electrospinning of Multilevel Structured Functional Micro-/Nanofibers and Their Applications. *J. Mater. Chem. A* **2013**, *1* (25), 7290–7305.
- (40) Swallow, L. M.; Luo, J. K.; Siores, E.; Patel, I.; Dodds, D. A Piezoelectric Fibre Composite Based Energy Harvesting Device for Potential Wearable Applications. *Smart Mater. Struct.* **2008**, *17* (2), 025017.
- (41) Liao, Q.; Zhang, Z.; Zhang, X.; Mohr, M.; Zhang, Y.; Fecht, H. J. Flexible Piezoelectric Nanogenerators Based on a Fiber/ZnO Nanowires/Paper Hybrid Structure for Energy Harvesting. *Nano Res.* **2014**, *7* (6), 917–928.
- (42) Zhao, F.; Slade, R. C. T.; Varcoe, J. R. Techniques for the Study and Development of Microbial Fuel Cells: An Electrochemical Perspective. *Chem. Soc. Rev.* **2009**, *38* (7), 1926–1939.
- (43) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **2011**, *111*, 3577–3613.
- (44) Jana, K. K.; Thakur, A. K.; Shahi, V. K.; Avasthi, D. K.; Rana, D.; Maiti, P. Heavy Ion Irradiation for Fuel Cell Applications †. *J. Mater. Chem. A Mater. energy Sustain.* **2015**, *3*, 10413–10424.
- (45) Mahato, N.; Banerjee, A.; Gupta, A.; Omar, S.; Balani, K. Progress in Material Selection for Solid Oxide Fuel Cell Technology: A Review. *Progress in Materials Science*; Elsevier Ltd., 2015; pp 141–337.
- (46) Kraytsberg, A.; Ein-Eli, Y. Review of Advanced Materials for Proton Exchange Membrane Fuel Cells. *Energy and Fuels. American Chemical Society* **2014**, *28*, 7303–7330.
- (47) Ormerod, R. M. Solid Oxide Fuel Cells. *Chem. Soc. Rev.* **2003**, *32* (1), 17–28.

- (48) Kraysberg, A.; Ein-Eli, Y. Review of Advanced Materials for Proton Exchange Membrane Fuel Cells. *Energy Fuels* **2014**, *28* (12), 7303–7330.
- (49) Cullen, D. A.; Neyerlin, K. C.; Ahluwalia, R. K.; Mukundan, R.; More, K. L.; Borup, R. L.; Weber, A. Z.; Myers, D. J.; Kusoglu, A. New roads and challenges for fuel cells in heavy-duty transportation. *Nature energy* **2021**, *6* (5), 462–474.
- (50) Jana, K. K.; Thakur, A. K.; Shahi, V. K.; Avasthi, D. K.; Rana, D.; Maiti, P. A Poly(Vinylidene Fluoride-Co-Hexafluoro Propylene) Nanohybrid Membrane Using Swift Heavy Ion Irradiation for Fuel Cell Applications. *J. Mater. Chem. A* **2015**, *3* (19), 10413–10424.
- (51) Lin, B.; Qiu, L.; Lu, J.; Yan, F. Cross-Linked Alkaline Ionic Liquid-Based Polymer Electrolytes for Alkaline Fuel Cell Applications. *Chem. Mater.* **2010**, *22* (24), 6718–6725.
- (52) Sammes, N.; Bove, R.; Stahl, K. Phosphoric Acid Fuel Cells: Fundamentals and Applications. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8* (5), 372–378.
- (53) Dicks, A. L. Molten Carbonate Fuel Cells. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8* (5), 379–383.
- (54) Rabaey, J. *Low power design essentials*; Springer Science & Business Media, 2009.
- (55) Sun, M.; Mu, Z. X.; Chen, Y. P.; Sheng, G. P.; Liu, X. W.; Chen, Y. Z.; Zhao, Y.; Wang, H. L.; Yu, H. Q.; Wei, L.; Ma, F. Microbe-Assisted Sulfide Oxidation in the Anode of a Microbial Fuel Cell. *Environ. Sci. Technol.* **2009**, *43* (9), 3372–3377.
- (56) Cao, D.; Sun, Y.; Wang, G. Direct Carbon Fuel Cell: Fundamentals and Recent Developments. *J. Power Sources* **2007**, *167* (2), 250–257.
- (57) Giddey, S.; Badwal, S. P. S.; Kulkarni, A.; Munnings, C. A Comprehensive Review of Direct Carbon Fuel Cell Technology. *Prog. Energy Combust. Sci.*; Pergamon, 2012; pp 360–399.
- (58) Hackett, G. A.; Zondlo, J. W.; Svensson, R. Evaluation of Carbon Materials for Use in a Direct Carbon Fuel Cell. *J. Power Sources* **2007**, *168* (1), 111–118.
- (59) Einsla, B. R.; Yu, S. K.; Hickner, M. A.; Hong, Y. T.; Hill, M. L.; Pivovar, B. S.; McGrath, J. E. Sulfonated Naphthalene Dianhydride Based Polyimide Copolymers for Proton-Exchange-Membrane Fuel Cells: II. Membrane Properties and Fuel Cell Performance. *J. Membr. Sci.* **2005**, *255* (1–2), 141–148.
- (60) Kumar, S.; Sana, B.; Unnikrishnan, G.; Jana, T.; Kumar, S. Polybenzimidazole Co-Polymers: Their Synthesis, Morphology and High Temperature Fuel Cell Membrane Properties. *Polym. Chem.* **2020**, *11* (5), 1043–1054.
- (61) Lee, H. S.; Roy, A.; Lane, O.; McGrath, J. E. Synthesis and Characterization of Poly(Arylene Ether Sulfone)-b-Polybenzimidazole Copolymers for High Temperature Low Humidity Proton Exchange Membrane Fuel Cells. *Polymer (Guildf)* **2008**, *49* (25), 5387–5396.
- (62) Kiran Kumar, K.; Ravi, M.; Pavani, Y.; Bhavani, S.; Sharma, A. K.; Narasimha Rao, V. V. R. Investigations on the Effect of Complexation of NaF Salt with Polymer Blend (PEO/PVP) Electrolytes on Ionic Conductivity and Optical Energy Band Gaps. *Phys. B Condens. Matter* **2011**, *406* (9), 1706–1712.
- (63) Kouras, N.; Harabi, A.; Bouzerara, F.; Foughali, L.; Policicchio, A.; Stelitano, S.; Galiano, F.; Figoli, A. Macro-Porous Ceramic Supports for Membranes Prepared from Quartz Sand and Calcite Mixtures. *J. Eur. Ceram. Soc.* **2017**, *37* (9), 3159–3165.
- (64) Jung, D. H.; Cho, S. Y.; Peck, D. H.; Shin, D. R.; Kim, J. S. Preparation and Performance of a Nafion/Montmorillonite Nanocomposite Membrane for Direct Methanol Fuel Cell. *J. Power Sources* **2003**, *118*, 205–211.
- (65) He, Y.; Wang, J.; Zhang, H.; Zhang, T.; Zhang, B.; Cao, S.; Liu, J. Polydopamine-Modified Graphene Oxide Nanocomposite Membrane for Proton Exchange Membrane Fuel Cell under Anhydrous Conditions. *J. Mater. Chem. A* **2014**, *2* (25), 9548–9558.
- (66) Arunbabu, D.; Sannigrahi, A.; Jana, T. Blends of Polybenzimidazole and Poly(Vinylidene Fluoride) for Use in a Fuel Cell. *J. Phys. Chem. B* **2008**, *112* (17), 5305–5310.
- (67) Mahreni, A.; Mohamad, A. B.; Kadhum, A. A. H.; Daud, W. R. W.; Iyuke, S. E. Nafion/Silicon Oxide/Phosphotungstic Acid Nanocomposite Membrane with Enhanced Proton Conductivity. *J. Membr. Sci.* **2009**, *327* (1–2), 32–40.
- (68) Chen, Z.; Holmberg, B.; Li, W.; Wang, X.; Deng, W.; Munoz, R.; Yan, Y. Nafion/Zeolite Nanocomposite Membrane by in Situ Crystallization for a Direct Methanol Fuel Cell. *Chem. Mater.* **2006**, *18* (24), 5669–5675.
- (69) Bébin, P.; Caravanier, M.; Galiano, H. Nafion®/Clay-SO₃H Membrane for Proton Exchange Membrane Fuel Cell Application. *J. Membr. Sci.* **2006**, *278* (1–2), 35–42.
- (70) Prakash, O.; Mhatre, A.; Tripathi, R.; Pandey, A.; Yadav, P. K.; Khan, S.; Maiti, P. Lithium-Irradiated Poly(Vinylidene Fluoride) Nanohybrid Membrane for Radionuclide Waste Management and Tracing. *ACS Appl. Polym. Mater.* **2021**, *3* (4), 2005–2017.
- (71) Prakash, O.; Mhatre, A. M.; Tripathi, R.; Pandey, A. K.; Yadav, P. K.; Khan, S. A.; Maiti, P. Fabrication of Conducting Nanochannels Using Accelerator for Fuel Cell Membrane and Removal of Radionuclides: Role of Nanoparticles. *ACS Appl. Mater. Interfaces* **2020**, *12* (15), 17628–17640.
- (72) Saikia, D.; Kumar, A.; Singh, F.; Avasthi, D. K. Study of Li³⁺ Ion Irradiation Effects in P(VDF–HFP) Based Gel Polymer Electrolytes for Application in Li-Ion Battery. *J. Phys. D: Appl. Phys.* **2006**, *39* (19), 4208–4214.
- (73) Grasselli, M.; Betz, N. Making Porous Membranes by Chemical Etching of Heavy-Ion Tracks in β -PVDF Films. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* **2005**, *236*, 501–507.
- (74) Rohani, R.; Yamaki, T.; Koshikawa, H.; Takahashi, S.; Hasegawa, S.; Asano, M.; Maekawa, Y.; Voss, K. O.; Trautmann, C.; Neumann, R. Enhancement of Etch Rate for Preparation of Nano-Sized Ion-Track Membranes of Poly(Vinylidene Fluoride): Effect of Pretreatment and High-LET Beam Irradiation. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2009**, *267* (3), 554–557.
- (75) Varcoe, J. R.; Slade, R. C. T.; Lam How Yee, E.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. Poly(Ethylene-Co-Tetrafluoroethylene)-Derived Radiation-Grafted Anion-Exchange Membrane with Properties Specifically Tailored for Application in Metal-Cation-Free Alkaline Polymer Electrolyte Fuel Cells. *Chem. Mater.* **2007**, *19* (10), 2686–2693.
- (76) Rao, V.; Amar, J. V.; Avasthi, D. K.; Narayana Charyulu, R. Etched Ion Track Polymer Membranes for Sustained Drug Delivery. *Radiat. Meas.* **2003**, *36*, 585–589.
- (77) Kulshrestha, V.; Awasthi, K.; Vijay, Y. K. Swift Heavy Ion (SHI) Irradiated Polymer Blend Membranes for Hydrogen Permeation. *Int. J. Hydrogen Energy* **2007**, *32* (14), 3105–3108.
- (78) Kulshrestha, V.; Awasthi, K.; Acharya, N. K.; Singh, M.; Avasthi, D. K.; Vijay, Y. K. Swift Heavy Ion Irradiated Polymeric Membranes for Gas Permeation. *J. Appl. Polym. Sci.* **2006**, *102* (3), 2386–2390.
- (79) Manohar, M.; Das, A. K.; Shahi, V. K. Alternative Preparative Route for Efficient and Stable Anion-Exchange Membrane for Water Desalination by Electrodialysis. *Desalination* **2017**, *413*, 101–108.
- (80) Kumar, S.; Bhushan, M.; Shahi, V. K. Cross-Linked Amphoteric Membrane: Sulphonated Poly(Ether Ether Ketone) Grafted with 2,4,6-Tris(Dimethylaminomethyl)Phenol Using Functionalized Side Chain Spacers for Vanadium Redox Flow Battery. *J. Power Sources* **2020**, *448*, 227358.
- (81) Maiti, P.; Nandi, A. K. Morphology of poly(vinylidene fluoride)/poly(methyl acrylate) blends: influence of chain structure. *Macromol. Chem. Phys.* **1998**, *199* (8), 1479–1484.
- (82) Vijay, Y. K.; Dhayal, M.; Awasthi, K.; Kulshrestha, V.; Acharya, N. K.; Choi, J. S. Surface Modification and Synthesis of Polymeric Membrane for Energy and Biological Applications. *J. Biomed. Nanotechnol.* **2006**, *2* (2), 144–151.
- (83) Balanzat, E.; Betz, N.; Bouffard, S. Swift Heavy Ion Modification of Polymers. *Nucl. Inst. Methods Phys. Res. B* **1995**, *105* (1–4), 46–54.

- (84) Kanjilal, D. Swift Heavy Ion-Induced Modification and Track Formation in Materials. *Curr. Sci.*; Current Science Association, pp 1560–1566.
- (85) Jana, K. K.; Prakash, O.; Shahi, V. K.; Avasthi, D. K.; Maiti, P. Poly(Vinylidene Fluoride-Co-Chlorotrifluoro Ethylene) Nanohybrid Membrane for Fuel Cell. *ACS Omega* **2018**, *3* (1), 917–928.
- (86) Balanzat, E.; Bouffard, S.; Le Moël, A.; Betz, N. Physico-Chemical Modifications Induced in Polymers by Swift Heavy Ions. *Nucl. Inst. Methods Phys. Res. B* **1994**, *91* (1–4), 140–145.
- (87) Cuscito, O.; Clochard, M. C.; Esnouf, S.; Betz, N.; Lairez, D. Nanoporous β -PVDF Membranes with Selectively Functionalized Pores. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2007**, *265* (1), 309–313.
- (88) Gaur, A.; Rana, D.; Maiti, P. Mechanical and Wear Behaviour of Poly(Vinylidene Fluoride)/Clay Nanocomposite. *J. Mater. Res. Technol.* **2019**, *8* (6), 5874–5881.
- (89) Jana, K. K.; Vishwakarma, N. K.; Ray, B.; Khan, S. A.; Avasthi, K.; Misra, M.; Maiti, P. Nanochannel Conduction in Piezoelectric Polymeric Membrane Using Swift Heavy Ions and Nanoclay. *RSC Adv.* **2013**, *3*, 6147–6159.
- (90) Jana, K. K.; Prakash, O.; Shahi, V. K.; Avasthi, D. K.; Maiti, P. Poly(Vinylidene Fluoride- Co -Chlorotrifluoro Ethylene) Nanohybrid Membrane for Fuel Cell. *ACS Omega* **2018**, *3* (1), 917–928.
- (91) Kumar, K.; Charan, C.; Shahi, V. K.; Mitra, K.; Ray, B.; Rana, D.; Maiti, P. Functionalized Poly (Vinylidene Fluoride) Nanohybrid for Superior Fuel Cell Membrane. *J. Membr. Sci.* **2015**, *481*, 124–136.
- (92) Yu, Y.-Y.; Chien, W.-C.; Ko, Y.-H.; Chen, C.-P.; Chang, C.-C. Preparation of Conjugated Polymer-Based Composite Thin Film for Application in Solar Cell. *Thin Solid Films* **2015**, *584*, 363–368.
- (93) Kumar, S.; Maurya, I. C.; Prakash, O.; Srivastava, P.; Das, S.; Maiti, P. Functionalized Thermoplastic Polyurethane as Hole Conductor for Quantum Dot-Sensitized Solar Cell. *ACS Appl. Energy Mater.* **2018**, *1* (9), 4641–4650.
- (94) Farrokhzad, H.; Kikhavani, T.; Monnaie, F.; Ashrafzadeh, S. N.; Koeckelberghs, G.; Van Gerven, T.; Van Der Bruggen, B. Novel Composite Cation Exchange Films Based on Sulfonated PVDF for Electromembrane Separations. *J. Membr. Sci.* **2015**, *474*, 167–174.
- (95) Gholamkhash, B.; Holdcroft, S. Toward Stabilization of Domains in Polymer Bulk Heterojunction Films. *Chem. Mater.* **2010**, *22* (18), 5371–5376.
- (96) Tiwari, V. K.; Rath, M. C.; Sarkar, S. K.; Patel, V. K.; Ray, B.; Maiti, B.; Maiti, P. Electron Beam-Induced Piezoelectric Phase in Poly(Vinylidene Fluoride) Nanohybrid: Effect at the Molecular Level. *Polym. Int.* **2015**, *64* (2), 212–221.
- (97) Peighambaroud, S. J.; Rowshanzamir, S.; Amjadi, M. Review of the Proton Exchange Membranes for Fuel Cell Applications. *Int. J. Hydrog. Energy* **2010**, *35*, 9349–9384.
- (98) Zhai, L.; Li, H. Polyoxometalate-Polymer Hybrid Materials as Proton Exchange Membranes for Fuel Cell Applications. *Molecules* **2019**, *24* (19), 3425.
- (99) Koók, L.; Žitka, J.; Bakonyi, P.; Takács, P.; Pavlovec, L.; Otmar, M.; Kurdi, R.; Bélafi-Bakó, K.; Nemesőthy, N. Electrochemical and Microbiological Insights into the Use of 1,4-Diazabicyclo[2.2.2]-Octane-Functionalized Anion Exchange Membrane in Microbial Fuel Cell: A Benchmarking Study with Nafion. *Sep. Purif. Technol.* **2020**, *237*, 116478.
- (100) Sigwadi, R.; Dhlamini, M. S.; Mokrani, T.; Nemavhola, F.; Nonjola, P. F.; Msomi, P. F. The Proton Conductivity and Mechanical Properties of Nafion/ ZrP Nanocomposite Membrane. *Heliyon* **2019**, *5* (8), e02240.
- (101) Tripathi, B. P.; Shahi, V. K. 3-[[3-(Triethoxysilyl)Propyl]-Amino]Propane-1-Sulfonic Acid–Poly(Vinyl Alcohol) Cross-Linked Zwitterionic Polymer Electrolyte Membranes for Direct Methanol Fuel Cell Applications. *ACS Appl. Mater. Interfaces* **2009**, *1* (5), 1002.
- (102) Ren, Y.; Chia, G. H.; Gao, Z. Metal-Organic Frameworks in Fuel Cell Technologies. *Nano Today* **2013**, *8* (6), 577–597.
- (103) Hogarth, W. H. J.; Diniz Da Costa, J. C.; Lu, G. Q. Solid Acid Membranes for High Temperature (>140° C) Proton Exchange Membrane Fuel Cells. *J. Power Sources* **2005**, *142* (1–2), 223–237.
- (104) Merle, G.; Wessling, M.; Nijmeijer, K. Anion Exchange Membranes for Alkaline Fuel Cells: A Review. *J. Membr. Sci.* **2011**, *377* (1–2), 1–35.
- (105) Güllow, E.; Schulze, M. Long-Term Operation of AFC Electrodes with CO₂ Containing Gases. *J. Power Sources* **2004**, *127* (1–2), 243–251.
- (106) Reid, J. H. *Process of Generating Electricity*; 1902.
- (107) Fang, J.; Shen, P. K. Quaternized Poly(Phthalazinon Ether Sulfone Ketone) Membrane for Anion Exchange Membrane Fuel Cells. *J. Membr. Sci.* **2006**, *285* (1–2), 317–322.
- (108) Xiong, Y.; Fang, J.; Zeng, Q. H.; Liu, Q. L. Preparation and Characterization of Cross-Linked Quaternized Poly(Vinyl Alcohol) Membranes for Anion Exchange Membrane Fuel Cells. *J. Membr. Sci.* **2008**, *311* (1–2), 319–325.
- (109) Herman, H.; Slade, R. C. T.; Varcoe, J. R. The Radiation-Grafting of Vinylbenzyl Chloride onto Poly(Hexafluoropropylene-Co-Tetrafluoroethylene) Films with Subsequent Conversion to Alkaline Anion-Exchange Membranes: Optimisation of the Experimental Conditions and Characterisation. *J. Membr. Sci.* **2003**, *218* (1–2), 147–163.
- (110) Danks, T. N.; Slade, R. C. T.; Varcoe, J. R. Comparison of PVDF- and FEP-Based Radiation-Grafted Alkaline Anion-Exchange Membranes for Use in Low Temperature Portable DMFCs. *J. Mater. Chem.* **2002**, *12* (12), 3371–3373.
- (111) Lai, A. N.; Zhuo, Y. Z.; Hu, P. C.; Zheng, J. W.; Zhou, S. F.; Zhang, L. Enhanced Ionic Conductivity of Anion Exchange Membranes by Grafting Flexible Ionic Strings on Multiblock Copolymers. *Int. J. Hydrogen Energy* **2020**, *45* (3), 1998–2008.
- (112) Shen, B.; Pu, H. Fluorene-Containing Poly(Arylene Ether Sulfone)s with Imidazolium on Flexible Side Chains for Anion Exchange Membranes. *Int. J. Hydrogen Energy* **2019**, *44* (21), 11057–11065.
- (113) Tian, Y.; Wen, L.; Hou, X.; Hou, G.; Jiang, L. Bioinspired Ion-Transport Properties of Solid-State Single Nanochannels and Their Applications in Sensing. *ChemPhysChem* **2012**, *13* (10), 2455–2470.
- (114) Sachan, R.; Cooper, V. R.; Liu, B.; Aidhy, D. S.; Voas, B. K.; Lang, M.; Ou, X.; Trautmann, C.; Zhang, Y.; Chisholm, M. F.; Weber, W. J. Forging Fast Ion Conducting Nanochannels with Swift Heavy Ions: The Correlated Role of Local Electronic and Atomic Structure. *J. Phys. Chem. C* **2017**, *121* (1), 975–981.
- (115) Jana, K. K.; Ray, B.; Avasthi, D. K.; Maiti, P. Conducting Nano-Channels in an Induced Piezoelectric Polymeric Matrix Using Swift Heavy Ions and Subsequent Functionalization. *J. Mater. Chem.* **2012**, *22* (9), 3955.
- (116) He, T.; Jia, R.; Lang, X.; Wu, X.; Wang, Y. Preparation and Electrochemical Performance of PVdF Ultrafine Porous Fiber Separator-Cum-Electrolyte for Supercapacitor. *J. Electrochem. Soc.* **2017**, *164* (13), E379–E384.
- (117) Simakov, D. S. *Renewable synthetic fuels and chemicals from carbon dioxide: fundamentals, catalysis, design considerations and technological challenges*; Springer, 2017.
- (118) Zhang, J., Ed. *PEM fuel cell electrocatalysts and catalyst layers: fundamentals and applications*; Springer Science & Business Media, 2008.
- (119) Shen, M.; Roy, S.; Kuhlmann, J. W.; Scott, K.; Lovell, K.; Horsfall, J. A. Grafted Polymer Electrolyte Membrane for Direct Methanol Fuel Cells. *J. Membr. Sci.* **2005**, *251* (1–2), 121–130.
- (120) Li, H. Y.; Liu, Y. L. Nafion-Functionalized Electrospun Poly(Vinylidene Fluoride) (PVDF) Nanofibers for High Performance Proton Exchange Membranes in Fuel Cells. *J. Mater. Chem. A* **2014**, *2* (11), 3783–3793.
- (121) Tanaka, M.; Fukasawa, K.; Nishino, E.; Yamaguchi, S.; Yamada, K.; Tanaka, H.; Bae, B.; Miyatake, K.; Watanabe, M. Anion Conductive Block Poly(Arylene Ether)s: Synthesis, Properties, and Application in Alkaline Fuel Cells. *J. Am. Chem. Soc.* **2011**, *133* (27), 10646–10654.
- (122) Saxena, A.; Tripathi, B. P.; Shahi, V. K. Sulfonated Poly(Styrene-Co-Maleic Anhydride) - Polyethylene Glycol - Silica

Nanocomposite Polyelectrolyte Membranes for Fuel Cell Applications. *J. Phys. Chem. B* **2007**, *111* (43), 12454–12461.

(123) Siu, A.; Schmeisser, J.; Holdcroft, S. Effect of Water on the Low Temperature Conductivity of Polymer Electrolytes. *J. Phys. Chem. B* **2006**, *110* (12), 6072–6080.

(124) Singha, S.; Jana, T. Effect of Composition on the Properties of PEM Based on Polybenzimidazole and Poly(Vinylidene Fluoride) Blends. *Polymer (Guildf)* **2014**, *55* (2), 594–601.

(125) Hazarika, M.; Jana, T. Novel Proton Exchange Membrane for Fuel Cell Developed from Blends of Polybenzimidazole with Fluorinated Polymer. *Eur. Polym. J.* **2013**, *49* (6), 1564–1576.

(126) Wan, C.; Bowen, C. R. Multiscale-Structuring of Polyvinylidene Fluoride for Energy Harvesting: The Impact of Molecular-, Micro- and Macro-Structure. *J. Mater. Chem. A* **2017**, *5* (7), 3091–3128.

(127) Bowen, C. R.; Kim, H. A.; Weaver, P. M.; Dunn, S. Piezoelectric and Ferroelectric Materials and Structures for Energy Harvesting Applications. *Energy Environ. Sci.* **2014**, *7* (1), 25–44.

(128) Qi, Y.; McAlpine, M. C. Nanotechnology-Enabled Flexible and Biocompatible Energy Harvesting. *Energy Environ. Sci.* **2010**, *3* (9), 1275–1285.

(129) Kong, L. B.; Li, T.; Hng, H. H.; Boey, F.; Zhang, T.; Li, S. *Waste Energy Harvesting*; 2014; Vol. 24.

(130) Yan, J.; Liu, M.; Jeong, Y. G.; Kang, W.; Li, L.; Zhao, Y.; Deng, N.; Cheng, B.; Yang, G. Performance Enhancements in Poly(Vinylidene Fluoride)-Based Piezoelectric Nanogenerators for Efficient Energy Harvesting. *Nano Energy* **2019**, *56*, 662–692.

(131) Chen, X.; Xu, S.; Yao, N.; Shi, Y. 1.6 v Nanogenerator for Mechanical Energy Harvesting Using PZT Nanofibers. *Nano Lett.* **2010**, *10* (6), 2133–2137.

(132) Kumar, C.; Gaur, A.; Tiwari, S.; Biswas, A.; Rai, S. K.; Maiti, P. Bio-Waste Polymer Hybrid as Induced Piezoelectric Material with High Energy Harvesting Efficiency. *Compos. Commun.* **2019**, *11*, 56–61.

(133) Chang, C.; Tran, V. H.; Wang, J.; Fuh, Y. K.; Lin, L. Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency. *Nano Lett.* **2010**, *10* (2), 726–731.

(134) Karan, S. K.; Bera, R.; Paria, S.; Das, A. K.; Maiti, S.; Maitra, A.; Khatua, B. B. An Approach to Design Highly Durable Piezoelectric Nanogenerator Based on Self-Poled PVDF/AIO-RGO Flexible Nanocomposite with High Power Density and Energy Conversion Efficiency. *Adv. Energy Mater.* **2016**, *6* (20), 1601016.

(135) Tiwari, S.; Gaur, A.; Kumar, C.; Maiti, P. Ionic Liquid-Based Electrospun Polymer Nanohybrid for Energy Harvesting. *ACS Appl. Electron. Mater.* **2021**, *3* (6), 2738–2747.

(136) Starner, T. Human-Powered Wearable Computing. *IBM Syst. J.* **1996**, *35* (3–4), 618–629.

(137) Cook-Chennault, K. A.; Thambi, N.; Sastry, A. M. Powering MEMS Portable Devices - A Review of Non-Regenerative and Regenerative Power Supply Systems with Special Emphasis on Piezoelectric Energy Harvesting Systems. *Smart Mater. Struct.* **2008**, *17* (4), 043001.

(138) Muralt, P. Ferroelectric thin films for micro-sensors and actuators: a review. *Journal of micromechanics and microengineering* **2000**, *10* (2), 136.

(139) Anton, S. R.; Sodano, H. A. A Review of Power Harvesting Using Piezoelectric Materials (2003 – 2006). *Smart Materials and Structures* **2007**, *16*, R1.

(140) Setter, N.; Damjanovic, D.; Eng, L.; Fox, G.; Gevorgian, S.; et al. Ferroelectric Thin Films: Review of Materials, Properties, and Applications. *Journal of Applied Physics* **2006**, *100* (5), 051606.

(141) Lazaridis, A. A numerical solution of the multidimensional solidification (or melting) problem. *Int. J. Heat Mass Transfer* **1970**, *13*, 1459–1477.

(142) Bonacina, C.; Comini, G.; Fasano, A.; Primicerio, M. Numerical solution of phase-change problems. *Int. J. Heat Mass Transfer* **1973**, *16* (10), 1825–1832.

(143) Fang, J.; Niu, H.; Wang, H.; Wang, X.; Lin, T. Enhanced mechanical energy harvesting using needleless electrospun poly

(vinylidene fluoride) nanofibre webs. *Energy Environ. Sci.* **2013**, *6* (7), 2196–2202.

(144) Yu, Y.; Sun, H.; Orbay, H.; Chen, F.; England, C. G.; Cai, W.; Wang, X. Biocompatibility and in vivo operation of implantable mesoporous PVDF-based nanogenerators. *Nano Energy* **2016**, *27*, 275–281.

(145) Chang, J.; Dommer, M.; Chang, C.; Lin, L. Piezoelectric Nanofibers for Energy Scavenging Applications. *Nano Energy*; Elsevier **2012**; pp 356–371.

(146) Costa, P.; Nunes-Pereira, J.; Pereira, N.; Castro, N.; Gonçalves, S.; Lanceros-Mendez, S. Recent Progress on Piezoelectric, Pyroelectric, and Magnetoelectric Polymer-Based Energy-Harvesting Devices. *Energy Technol.* **2019**, *7* (7), 1800852.

(147) Li, Q.; Wang, Q.; Li, Q.; Wang, Q. Ferroelectric Polymers and Their Energy-Related Applications. *Macromol. Chem. Phys.* **2016**, *217* (11), 1228–1244.

(148) Taylor, P.; Marutake, M. The Days When Piezoelectric PVDF Was Discovered. *Ferroelectrics* **1995**, *171*, 8–10.

(149) Fukada, E. History and recent progress in piezoelectric polymers. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control* **2000**, *47* (6), 1277–1290.

(150) Frübing, P.; Kremmer, A.; Spanoudaki, R. G.; Pissis, P.; Frübing, P.; Kremmer, A.; Gerhard-mulhaupt, R. Relaxation Processes at the Glass Transition in Polyamide 11 : From Rigidity to Viscoelasticity Relaxation Processes at the Glass Transition in Polyamide 11 : From Rigidity to Viscoelasticity. *J. Chem. Phys.* **2006**, *125* (21), 214701.

(151) Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. Electroactive Phases of Poly(Vinylidene Fluoride): Determination, Processing and Applications. *Prog. Polym. Sci.* **2014**, *39*, 683–706.

(152) Fukada, E.; Ando, Y. Piezoelectric Properties of Poly- β -Hydroxybutyrate and Copolymers of β -Hydroxybutyrate and β -Hydroxyvalerate. *Int. J. Biol. Macromol.* **1986**, *8* (6), 361–366.

(153) Hikosaka, S.; Ishikawa, H.; Ohki, Y. Effects of Crystallinity on Dielectric Properties of Poly(L-Lactide). *Electron. Commun. Japan* **2011**, *94* (7), 1–8.

(154) Sharma, A.; Won, L. D.; Buddhi, D.; Park, J. U. Numerical Heat Transfer Studies of the Fatty Acids for Different Heat Exchanger Materials on the Performance of a Latent Heat Storage System. *Renewable Energy* **2005**, *30*, 2179–2187.

(155) Chen, C. R.; Sharma, A.; Tyagi, S. K.; Buddhi, D. Numerical Heat Transfer Studies of PCMs Used in a Box-Type Solar Cooker. *Renewable Energy* **2008**, *33* (5), 1121–1129.

(156) Sukumaran, S.; Chatbouri, S.; Rouxel, D.; Tisserand, E.; Thiebaud, F.; Ben Zineb, T. Recent Advances in Flexible PVDF Based Piezoelectric Polymer Devices for Energy Harvesting Applications. *Journal of Intelligent Material Systems and Structures* **2021**, *32* (7), 746–780.

(157) Alluri, N. R.; Chandrasekhar, A.; Jeong, J. H.; Kim, S. J. Enhanced Electroactive β -Phase of the Sonication-Process-Derived PVDF-Activated Carbon Composite Film for Efficient Energy Conversion and a Battery-Free Acceleration Sensor. *J. Mater. Chem. C* **2017**, *5* (20), 4833–4844.

(158) Lovinger, A. J.; Laboratories, B.; Hill, M. *Fluoride Poly (Vinylidene Fluoride)* **2003**, 5934 (1981), 1–6.

(159) Costa, P.; Silva, J.; Sencadas, V.; Costa, C.M.; van Hattum, F.W.J.; Rocha, J.G.; Lanceros-Mendez, S. The Effect of Fibre Concentration on the α to β -Phase Transformation, Degree of Crystallinity and Electrical Properties of Vapour Grown Carbon Nanofibre/Poly (Vinylidene Fluoride) Composites. *Carbon* **2009**, *47* (11), 2590–2599.

(160) Fan, F. R.; Tang, W.; Wang, Z. L. Flexible Nanogenerators for Energy Harvesting and Self-Powered Electronics. *Adv. Mater.* **2016**, *28* (22), 4283–4305.

(161) Yu, L.; Cebe, P. Crystal Polymorphism in Electrospun Composite Nanofibers of Poly(Vinylidene Fluoride) with Nanoclay. *Polymer (Guildf)* **2009**, *50* (9), 2133–2141.

- (162) Bera, B.; Sarkar, M. D. Piezoelectricity in PVDF and PVDF Based Piezoelectric Nanogenerator: A Concept. *IOSR Journal of Applied Physics* **2017**, *9* (3), 95–99.
- (163) Gaur, A.; Kumar, C.; Tiwari, S.; Maiti, P. Efficient Energy Harvesting Using Processed Poly(Vinylidene Fluoride) Nanogenerator. *ACS Appl. Energy Mater.* **2018**, *1* (7), 3019–3024.
- (164) Ruan, L.; Yao, X.; Chang, Y.; Zhou, L.; Qin, G.; Zhang, X. Properties and Applications of the β Phase Poly(Vinylidene Fluoride). *Polymer* **2018**, *10* (3), 228.
- (165) Baji, A.; Mai, Y. W.; Li, Q.; Liu, Y. Electrospinning Induced Ferroelectricity in Poly(Vinylidene Fluoride) Fibers. *Nanoscale* **2011**, *3* (8), 3068–3071.
- (166) Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites. *Compos. Sci. Technol.* **2003**, *63*, 2223–2253.
- (167) Wankhade, S. H.; Tiwari, S.; Gaur, A.; Maiti, P. PVDF–PZT Nanohybrid Based Nanogenerator for Energy Harvesting Applications. *Energy Reports* **2020**, *6*, 358–364.
- (168) Kwon, J.; Sharma, B. K.; Ahn, J. H. Graphene Based Nanogenerator for Energy Harvesting. *Jpn. J. Appl. Phys.* **2013**, *52* (6), 06GA02.
- (169) Garain, S.; Jana, S.; Sinha, T. K.; Mandal, D. Design of in Situ Poled Ce³⁺-Doped Electrospun PVDF/Graphene Composite Nanofibers for Fabrication of Nanopressure Sensor and Ultrasensitive Acoustic Nanogenerator. *ACS Appl. Mater. Interfaces* **2016**, *8* (7), 4532–4540.
- (170) Hosseini, S. M.; Yousefi, A. A. Piezoelectric Sensor Based on Electrospun PVDF-MWCNT-Cloisite 30B Hybrid Nanocomposites. *Org. Electron.* **2017**, *50*, 121–129.
- (171) Gaur, A.; Tiwari, S.; Kumar, C.; Maiti, P. Flexible, Lead-Free Nanogenerators Using Poly(Vinylidene Fluoride) Nanocomposites. *Energy Fuels* **2020**, *34* (5), 6239–6244.
- (172) Dakua, I.; Afzulpurkar, N. Piezoelectric Energy Generation and Harvesting at the Nano-Scale: Materials and Devices. *Nanomaterials and Nanotechnology* **2013**, *3*, 21.
- (173) Siddiqui, S.; Kim, D. Il; Duy, L. T.; Nguyen, M. T.; Muhammad, S.; Yoon, W. S.; Lee, N. E. High-Performance Flexible Lead-Free Nanocomposite Piezoelectric Nanogenerator for Biomechanical Energy Harvesting and Storage. *Nano Energy* **2015**, *15*, 177–185.
- (174) Tiwari, S.; Maiti, P. 2D Materials–Polymer Composites for Developing Piezoelectric Energy-Harvesting Devices. *Eng. Polym. Nanocomposites Energy Harvest. Appl.* **2022**, 99–128.
- (175) Karan, S. K.; Maiti, S.; Paria, S.; Maitra, A.; Si, S. K.; Kim, J. K.; Khatua, B. B. A New Insight towards Eggshell Membrane as High Energy Conversion Efficient Bio-Piezoelectric Energy Harvester. *Mater. Today Energy* **2018**, *9*, 114–125.
- (176) Gaur, A.; Tiwari, S.; Kumar, C.; Maiti, P. Polymer Biowaste Hybrid for Enhanced Piezoelectric Energy Harvesting. *ACS Appl. Electron. Mater.* **2020**, *2* (5), 1426–1432.
- (177) Sharma, M.; Srinivas, V.; Madras, G.; Bose, S. Outstanding Dielectric Constant and Piezoelectric Coefficient in Electrospun Nanofiber Mats of PVDF Containing Silver Decorated Multiwall Carbon Nanotubes: Assessing through Piezoresponse Force Microscopy. *RSC Adv.* **2016**, *6* (8), 6251–6258.
- (178) Karan, S. K.; Mandal, D.; Khatua, B. B. Self-Powered Flexible Fe-Doped RGO/PVDF Nanocomposite: An Excellent Material for a Piezoelectric Energy Harvester. *Nanoscale* **2015**, *7* (24), 10655–10666.
- (179) Wu, C. M.; Chou, M. H.; Zeng, W. Y. Piezoelectric Response of Aligned Electrospun Polyvinylidene Fluoride/Carbon Nanotube Nanofibrous Membranes. *Nanomaterials* **2018**, *8* (6), 420.
- (180) Li, B.; Zhang, F.; Guan, S.; Zheng, J.; Xu, C. Wearable Piezoelectric Device Assembled by One-Step Continuous Electrospinning. *Journal of Materials Chemistry C* **2016**, *4* (29), 6988–6995.
- (181) Yang, R.; Qin, Y.; Li, C.; Zhu, G.; Wang, Z. L. Converting Biomechanical Energy into Electricity by a Muscle-Movement-Driven Nanogenerator. *Nano Lett.* **2009**, *9* (3), 1201–1205.
- (182) Rajala, S.; Salpavaara, T.; Tuukkanen, S. Testing and Comparing of Film-Type Sensor Materials in Measurement of Plantar Pressure Distribution. *Proc. Annu. Int. Conf. IEEE Eng. Med. Biol. Soc. EMBS* **2016**, 251–254.
- (183) Gaur, A.; Tiwari, S.; Kumar, C.; Maiti, P. Bio-Waste Orange Peel and Polymer Hybrid for Efficient Energy Harvesting. *Energy Reports* **2020**, *6*, 490–496.