REVIEW ARTICLE | JULY 18 2024

Exploring electrospun Nafion nanofibers: Bibliographic insights, emerging possibilities, and diverse applications

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AIP Advances 14, 070701 (2024)
https://doi.org/10.1063/5.0206492

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Cite as: AIP Advances 14, 070701 (2024); doi: 10.1063/5.0206492
Submitted: 17 March 2024 • Accepted: 18 June 2024 •
Published Online: 18 July 2024

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ABSTRACT

Over the past several decades, there has been a significant surge in interest regarding the use of organic–inorganic hybrid polymers and nanocomposite membranes. The reasons for this are improved attributes, reduced costs, and the additional stability the influence membrane provides. This Review outlines the various techniques and methodologies used to prepare Nafion and its composites, delineating the promising benefits of the electrospinning process. Electrospinning has emerged as a versatile and promising technique for fabricating nanofibers with unique properties and wide-ranging applications. This study explores the electrospinning of Nafion, a perfluorosulfonic acid polymer widely known for its exceptional proton conductivity and chemical stability, into nanofibrous structures, unlocking new possibilities yet unknown features of its inherent properties. The morphology and chemical structure of the resulting nanofibers is analyzed. A thorough bibliographic analysis of electrospun Nafion was presented using the PRISMA approach for methodically presenting the report. Network visualization of connected authors and categorizing application-specific publications are also discussed. Moreover, the electrospinning parameters and blends are systematically investigated to optimize the production of Nafion nanofibers for various applications in fuel cells, water treatment, actuators, sensors, and energy harvesting. The challenges involved in electrospinning Nafion, Nafion nanocomposites, and their variants are also presented, with a discussion delineating the future scope. This work concludes by emphasizing the interdisciplinary character of the Nafion polymer and its composites, connecting materials science and the intricate issues presented by various sectors.

I. INTRODUCTION

The utilization of green energy, quality water, and sensing technologies has experienced a significant increase on a global scale since the beginning of the 21st century. The contemporary global landscape is confronted with an increasingly voracious need due to the progress of technology and the expansion of the people in residential, commercial, and industrial domains. The pace of sustainable energy technology deployment in 2022 has exhibited notable swiftness. According to the International Energy Agency (IEA), the projected investment in energy, compared to the anticipated requirements outlined in IEA scenarios for 2030, is estimated to amount to around 4.5 trillion USD. Furthermore, it is crucial to emphasize the significant potential of hydrogen in achieving global energy and climate objectives, as this may effectively attract investments and expedite the implementation of hydrogen technologies. Simultaneously, this approach will generate a substantial demand for hydrogen and hydrogen-based fuels.[1]

The industrial sector is a significant user of water. They use around 22% of the world's freshwater and as much as 60% in countries with high per capita gross domestic product (GDP). In the industrial sector alone, water consumption is predicted to rise by 400% by 2050. Typical wastewaters contain hardness, non-neutral pH levels, varying temperatures, salinity, turbidity, and heavy metal concentrations. Chemical precipitation, flotation, and ion exchange are the traditional procedures for extracting heavy metals from wastewater. However, these methods' poor removal efficiency, high energy consumption, and hazardous sludge formation prevent their widespread use.[2] However, anionic polymers are utilized in wastewater treatment to enhance the fusion capacity of a suspended substance, have a negative charge, and possess a high molecular weight. These polymers contain active groups that can attract positively charged ions in water. Moreover, anionic polymers are employed in wastewater treatment to facilitate the aggregation of organic debris, bacteria, and other particulate substances in the water. This significantly decreases the concentration of suspended particles in the water, facilitating the subsequent water-filtering procedure.[3]

Since the first identification of micro-electro-mechanical system (MEMS) based sensors in the 1950s, incorporating sensing and monitoring technologies has become essential to human civilization and well-being. These technologies have reached complete commercialization and are proliferating. Sensors, which find use in many domains such as residential, commercial, industrial, medical, and defense sectors, now need more support in their expansion owing to the absence of standardized testing and manufacturing processes.[4,5]

Although abundant resources are available in nature, there are only sometimes effective solutions for the difficulties stated above. Therefore, researchers have initiated investigations into several polymeric materials as multifunctional potential complements to the currently used conventional methods.[6] Among those polymers, Nafion is one of the anionic, semicrystalline, sulfonated tetrafluoroethylene-based fluoropolymer-copolymers, which was first discovered in the late 1960s by Dr. Walther Grot, an esteemed researcher at DuPont.[7] Taking into account its characteristics such as high mechanical strength and resistance to severe environmental conditions and high cationic conductivity, this material is favorable for various membrane-based applications, such as fuel cells,[8] water treatment,[9] and energy harvesters.[10] The membrane is vital for flow batteries (FBs), separating the FB feeds to prevent short-circuits and allowing selective ion transport to maintain charge balance. The key features of a membrane need for optimal FB performance, such as ion-exchange capacity, stability, perm selectivity, and water uptake.[11] Nafion exhibits a notable chemical stability temperature, reaching up to 190 °C, owing to incorporating ionic sulfonate groups within its PTFE backbone, meaning that the compound is comprised of a polytetrafluoroethylene (PTFE) backbone with hydrophobic properties, along with a perfluorinated vinyl ether pendant side chain that is hydrophilic, and forms an ionic bond with a sulfonic acid group ($-SO_3H$) shown in Fig. 1. However, its operational temperature range is moderately limited, with a softening point falling between 85 and 100 °C, allowing for practical use up to 100 °C.[12] For example, a family of hybrid ion-exchange membranes (IEMs), labeled [Nafion/(WO_3) x], was prepared by incorporating various amounts of tungsten oxide nanofiller into Nafion® and tested in a vanadium redox flow battery (VRFB). Compared to Nafion 212, [Nafion/(WO3) 0.587] demonstrated a higher Coulombic efficiency, energy efficiency, and capacity retention at 50 $mA \cdot cm^{-2}$.[13] Moreover, this fluorinated polymer's worries about sustainability are eased by the fact that it lasts a long time and can be used for many different things. Slack *et al.*[14] fabricated an electrospun nanofiber cathode mat in membrane-electrode-assembly (MEA) with Nafion/PVDF or Nafion/PAA binders, alongside a slurry cathode MEA with neat Nafion or a Nafion/PVDF binder. This is the mechanism behind PVDF's role in enhancing fuel cell durability, i.e., twofold.

Electrospinning is a highly adaptable and cutting-edge method used to manufacture nanofibers.[15] This process utilizes an electric field to attract charged polymer solutions or melts, forming fragile fibers with diameters generally ranging from nanometers to micrometers. The electrospinning method involves the creation of a Taylor cone at the end of a needle or spinneret, which emits a charged jet, as shown in Fig. 2.[16] This jet is then stretched into nanofibers by electrostatic forces. Moreover, electrospinning enables the adjustment of nanofiber characteristics by altering materials and processing parameters, which include polymer molecular weight, solution properties (viscosity, conductivity, and surface tension), and processing parameters (electric potential, flow rate, and distance between the capillary and the collector).[17] Electrospinning

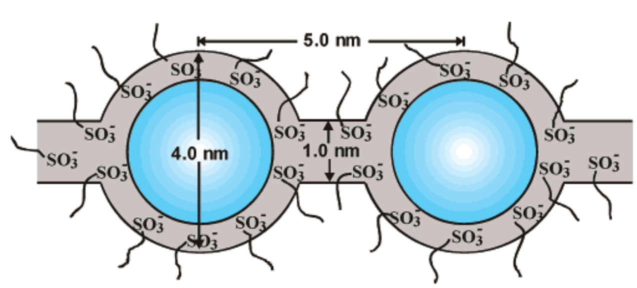

FIG. 1. Cluster-network model of Nafion. The image is reproduced with permission from Stanley Whittingham *et al.*, ACS Chem. Rev. **104**(10), 4243 (2004). Copyright 2004 American Chemical Society.

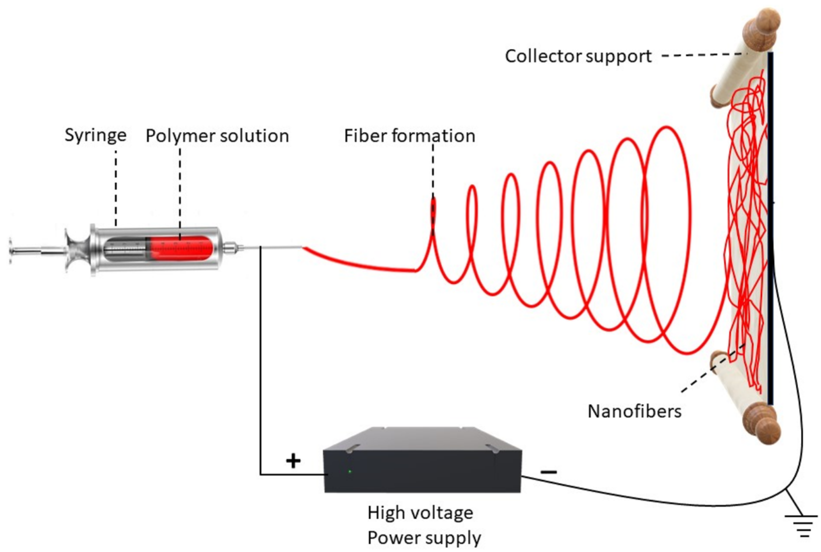

FIG. 2. Electrospun nanofiber preparation setup.

Nafion, a perfluorosulfonic acid polymer, may provide several benefits compared to other manufacturing techniques, especially in scenarios where nanofibrous structures are advantageous, such as energy, sensors, and wastewater treatment. Nafion is well recognized for its use in fuel cells and other electrochemical devices because of its exceptional proton conductivity.[18] Ketti Vizzu *et al.*[19] fabricated electrical relaxation and polarization phenomena of electrospun PVDF/Nafion blended fiber mats and membranes, which are compared with those of solvent-cast membranes of the same composition. This shows that electrospun materials exhibit a "reciprocal templating" phenomenon, resulting in different electrical behaviors compared to solvent-cast membranes. Furthermore, the electrospun membranes suggest smaller water clusters than those in pristine Nafion, with adsorbed water forming thin solvation shells around Nafion's polar side chains. Similarly, Nawn *et al.*[20] developed PVDF/Nafion nanofibers, resulting in that PVDF restricts Nafion's PTFE backbone, increasing its helical conformation, thereby affecting Nafion's water uptake and thermal properties. Dipole–dipole interactions also stabilize the β-phase of PVDF at higher temperatures. The benefits of using electrospun Nafion are practical proton transport, a large surface area, mechanical solid integrity and durability, the capacity to produce in large quantities with reduced amounts of Nafion, and cost savings. Furthermore, the production of electrospun Nafion nanofibers is well addressed in Sec. III A. Therefore, the primary aim of this Review is to provide a concise overview of the fabrication of electrospun Nafion nanofibers and their applications.

II. NAFION

A. Main properties

A precursor copolymer containing tetrafluoroethylene and a sulfonyl vinyl ether is used to make Nafion perfluorinated membranes as shown in Fig. 3. This copolymer has the generic chemical formula.[7]

Hydrophobic semicrystalline backbone chains make up the first section. The backbone gives the membrane its shape and makes it impermeable to water. The second part is an amorphous area comprising several sulfonic acid groups and certain side chains. Clusters of hydrophilic sulfonic acid groups, which are essential for proton conductance across the membrane, are found in the last area.[12] When Nafion becomes hydrated, the sulfonic acid groups attract water molecules and form hydrogen bonds. These bonded water clusters create pathways within the polymer structure, which help move protons through a hopping process.[7,10,14,21] The presence of these water clusters also contributes to Nafion's ion conductivity level. The transportation of protons in Nafion involves a combination of two mechanisms: vehicular and Grotthuss.

In the vehicular mechanism, protons move through the pathways by interacting with water molecules and hopping between them. Meanwhile, the Grotthuss mechanism facilitates proton transfer through acid groups by breaking and reforming hydrogen bonds with surrounding water molecules.[22] The extent to which Nafion allows the flow of protons relies heavily on how hydrated it is. When water is present, the clusters of water become more interconnected, resulting in improved transportation of protons. However, excessive

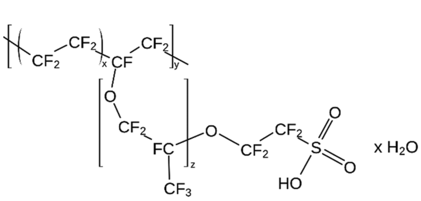

FIG. 3. Chemical structure of Nafion.

TABLE I. Physical parameters of various popular Nafion membranes used for multifunctional applications.

Membrane type	Thickness (μm)	Typical basis weight (g/m^2)
Nafion 112	51	100
Nafion 115	127	250
Nafion 117	178	360

hydration can cause Nafion membranes to swell and reduce their stability.[23] Moreover, the physical parameters of various popular Nafion membranes used for multifunctional applications are presented in Table I. The mechanical properties of Nafion membranes are affected by several factors, including hydration, temperature, and ion exchange. The mechanical properties presented in Table II are similar to those of other Nafion membranes.[24,25] However, the immersion of the Nafion membrane in water or various solutions of methanol or ethanol resulted in a decrease in Young's modulus when compared to the original state of the membrane[24] because of the lower intermolecular interaction between the ionic groups in the membrane.[25]

Similarly, the degree of elongation of Nafion soaked in ethanol/water mixture and ethanol is higher than that of the membrane soaked in water, indicating a lower modulus.[26] One possible explanation is that the water molecules or alcohol molecules can penetrate the Nafion membrane and disrupt the hydrogen bonding between the sulfonic acid groups and the polymer backbone, leading to a decrease in Young's modulus, or the water molecules or alcohol molecules can act as plasticizers and increase the free volume of the polymer chains, which also leads to a decrease in Young's modulus.[27] Furthermore, four transitions were seen in the Nafion membrane through dynamic mechanical studies conducted within a temperature ranging from −150 to 250 °C. The α peak was the most significant at a temperature of 150 °C. The observed peak was attributed to the glass transition temperature of the ionic areas.[14]

Nevertheless, a material's dielectric constant (ε) measures its ability to store electrical energy in an electric field. Nafion has a dielectric constant, typically 18 to 22.[28] This property is helpful in capacitive applications, as materials with higher dielectric constants can store more electrical charge. In addition, Paddison *et al.*[29] investigated the dielectric response of three different Nafion membranes—Nafion 105, Nafion 117, and Nafion 120—across a spectrum of water content. This investigation was conducted within the microwave frequency range spanning from 0.045 to 30 GHz. This study revealed a significant dependence of the dielectric constants and loss factors of these Nafion membranes on the amount of water present. This suggests that the presence of water has a notable influence on how these membranes interact with electromagnetic fields within the microwave frequency range. Such insights are essential for optimizing the design and performance of Nafion membranes in practical applications. The ionic conductivity of Nafion is related to its ability to transport ions under an electric field. It allows for the migration of protons (H+ ions) when hydrated, which is essential in applications such as proton exchange membrane fuel cells (PEMFCs).[30] Nafion has cation exchange properties due to its sulfonic acid groups. Its membranes can be incorporated into separation and filtration systems where metal ions must be selectively separated from water or other aqueous solutions.[31]

TABLE II. Some typical mechanical properties of Nafion™ 117 membranes at 25 °C.

Property	Dry	Hydrated
Tensile strength	15–20 MPa	2–5 MPa
Young's modulus	300–500 MPa	20–50 MPa
Elongation at break	100%–200%	500%–1000%

B. Preparation of Nafion, Nafion composites, and applications

Film-based membranes have been gaining more attention in a wide range of applications in various fields, including electronics,[32] materials science,[33–35] medicine,[36] sensors,[37] and energy[38–40] owing to their unique properties. Figure 4 shows some intelligent fabrication techniques that are highly popular for Nafion polymer and electrospinning.

Spin coating is a common thin-film deposition technique used to create uniform and controlled material coatings on various substrates. It is important to note that the choice of solvent, Nafion concentration, and spin-coating parameters (spin speed, acceleration, and duration) can all be adjusted to tailor the film's properties for specific research or application needs.[41] However, spin coating may not be the primary method for large-scale Nafion film production in industrial settings. The effects of varying the Nafion concentration and spin coating angular velocity on the thickness and morphology of the Nafion films were investigated.[42,43] Then, Mohamed *et al.*[42] focused on integrating Nafion into the catalyst layers, where fragile layers of the polymer are often formed on the catalysts of polymer electrolyte fuel cells (PEFCs). The experimental data suggest that the nanostructure of 23 nm thick spin-coated Nafion film is different from 220 nm thick film and also from 26 to 227 nm thick dip-coated films, possibly due to the preservation of the unique rod-like structure of Nafion in the dilute solution. To support the previous literature, Kusoglu *et al.* stated that the confinement of Nafion thin films is affected by both substrate and processing conditions; spin-cast films on gold exhibit less structural order and decreased swelling compared to self-assembled films, which can have implications for the design and optimization of fuel cells.[44] In addition, a spin-coated 150 nm Nafion thin film on a silicon (Si) substrate investigated interface proton transport. The results showed that the thin Nafion film on the Si substrate has a highly ordered structure with side chain sulfonic acid groups. Due to these strongly orientated features, the thin film had a poorer proton conductivity than the commercial Nafion membrane.[45]

Lithography is another process used in microfabrication to pattern parts of a thin film or the bulk of a substrate.[46,47] The typical optical lithography process sequence is as follows: substrate preparation, photoresist spin coat, prebake, exposure, post-exposure bake, development, and post-bake. The function of the lithography process in IC fabrication is to produce a multiple image on the resist and the wafer.[48] The method entails the transfer of a pattern from a photomask to a substrate. The process mainly uses

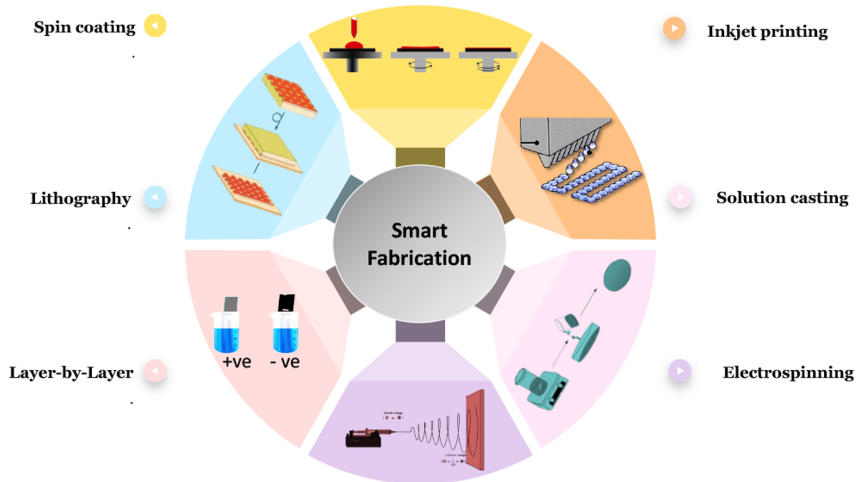

FIG. 4. Smart fabrication techniques.

stepper and scanner devices with optical light sources. Additional lithography variations encompass direct-write electron beam and nanoimprint techniques.[49] Other advanced lithography technologies are now being researched and developed, including extreme ultraviolet (EUV), multi-beam electron beam, and directed self-assembly (DSA).[50]

The fabrication of micro- and nanopatterned Nafion thin films with tunable mechanical and electrical properties using thermal evaporation-induced capillary force lithography involves the use of a thermal evaporation system to deposit a thin layer of gold on a silicon wafer, followed by the application of a Nafion solution. The Nafion solution is then patterned using capillary force lithography to create micro- and nanopatterned Nafion thin films. The resulting films exhibit superior mechanical and electrical properties that can be tailored for specific applications.[51]

Inkjet printing is a deposition method for liquid-phase materials that saves material. It is a better manner of regulating solution deposition than conventional approaches such as spray painting.[52] Inkjet printing was used to deposit Nafion ionomer as the transport medium onto the catalytic layer, resulting in membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells (PEMFCs).[53] The cyclic voltammetry findings revealed that inkjet printing outperforms spray painting by increasing catalyst efficiency. It was proved that with the suitable Nafion loading of 0.64 mg cm^{-2} via inkjet printing, this technology might be utilized to increase the performance of the MEA for PEMFCs.[54]

In the same way, Shukla *et al.* examined inkjet-printed platinum-loading polymer electrolyte fuel cell (PEFC) electrodes. Catalyst-coated membranes (CCMs) with 0.026 mg Pt/cm^2, 1.5–2 μm catalyst layer thickness, and variable Nafion loadings (NLs) was observed on cathode electrodes. Due to its lower CL thickness and reduced macro-scale transport losses, inkjet CCM at ambient pressure was ten times higher than spray-coated CCM. However, the hot-pressing conditions at 800 psi and 100 °C for 3 min show the better efficiency and power density of MEAs (membrane electrode assemblies) using Pt/MWCNT ink as a catalyst ink, applied directly onto the substrate Nafion membrane with a Pt loading of 0.2 mg cm^{-2} for both the anode and cathode.[55]

Solution casting is one of the methods used to fabricate Nafion membranes. In this process, Nafion is dispersed into a solution by heating in aqueous alcohol at 250 °C in an autoclave for subsequent casting into thin films or used as a polymeric binder in electrodes. Furthermore, the Nafion resin, in its solid form, was dissolved in several solvents, including DMAc, DMF, NMF, methanol–H_2O, ethanol–H_2O, and IPA–H_2O, and cast on a copper grid that had a 400-mesh carbon layer to form a thin layer. The findings of the experiments indicated that Nafion 117 exhibited qualities similar to solution-casting membranes generated from alcohol–H_2O solvents.[56] In addition, a study by Zeynali *et al.* investigated the solvent composition effects on the average particle size and polydispersity of the commercial perfluorinated sulfonic acid (PFSA) membrane, i.e., Flemion, in different solution mixtures.[57] The particle size decreases as the solvent becomes more compatible with the Flemion. The average particle size of the solute rose as the water concentration in the propanol/water combination increased. When three solution combinations were compared, the mean particle size rose when the solvent was changed from ethanol to methanol to propanol. As a result, the solubility and performance of the filler in the Nafion solution are the primary issues while producing a Nafion composite-based casting membrane since they may cause a drop in proton conductivity and durability in fuel cells. This effect may be reduced by utilizing a multilayer membrane created by the hot press or dip coating.[58]

Layer-by-layer (LbL) self-assembly is another way of producing membranes with multilayers. LbL assemblies are a flexible method that provides control at the nanoscale level, producing stable and durable coatings.[59] This technique involves electrostatically adsorbing anionic and cationic polymeric electrolytes (PEs) on the surface of a substrate in alternating cycles to produce LBL assembly membranes.[60] However, when constructing functional ultrathin films, covalent LbL assembly is a potent approach that offers nanoscopic structural accuracy, componential variety, and variable design. LbL films prepared using covalent cross-linking offer several distinct advantages compared to conventional LbL films constructed using multiple noncovalent interactions. These advantages include the following: (i) increased film endurance or rigidity; (ii) improved componential diversity when uncharged species or small molecules are stably built into the films by forming covalent bonds; and (iii) increased structural diversity when covalent cross-linking is employed in componential, spatial, or temporal (labile bonds) selective manners.[61]

The LbL method has the potential to be applied in various applications, including forming multi-composite films, nanoparticle modification, enzyme process, optic development, sensors, membranes for water treatment, and fuel cells.[62] In one study, Nafion-based LbL coatings were created with antimicrobial activity. The coatings were made of Nafion layered alongside compounds with a well-established antimicrobial activity: lysozyme, chitosan, and carbon dots (C-dots). Nafion was coated with molecules shown to have antimicrobial action, such as lysozyme, chitosan, and carbon dots (CDots). Both sets of systems were formed by combining these components. The antibacterial activity of both trilayer systems was shown to be exceptional when tested against the Gram-negative and Gram-positive species *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), respectively, of the representative species.[63] An LbL film of Nafion/polyethyleneimine/SiO_2 nanoparticles[64] had a potential application in water/oil separation, detergent-free cleaning, and oil-repellent anti-fogging; their fabrication is challenging because of the lower surface tension of oil than that of water.

Electrospinning: A wide variety of organic polymers may be effectively prepared into fibers or fiber mats using electrospinning, a basic approach that has been utilized successfully. During the electrospinning process, an electric field is applied to a polymer solution that is kept in place at the end of a capillary tube by the surface tension of the polymer. A solid fiber is produced as the intensity of the electric field rises. This occurs because the electrified jet is continually stretched due to the electrostatic repulsions between the surface charges and the evaporation of the solvent.[65–67] Electrospinning technology has been used to fabricate and assemble nanofibers into membranes, which have extended the range of potential applications in various fields such as biomedical,[68] environmental protection,[69,70] nanosensors,[71] electronic/optical,[72,73] and protective clothing.[74] *Compared to other fabrication methods, electrospun materials have several distinctive characteristics that make them potential candidates for various applications in biomedicine and engineering. These characteristics include a high surface-to-volume ratio, flexibility, high mechanical strength, high porosity, and the ability to adjust the distribution of nanofibers and pores across the material,*[75] as shown in Fig. 5.

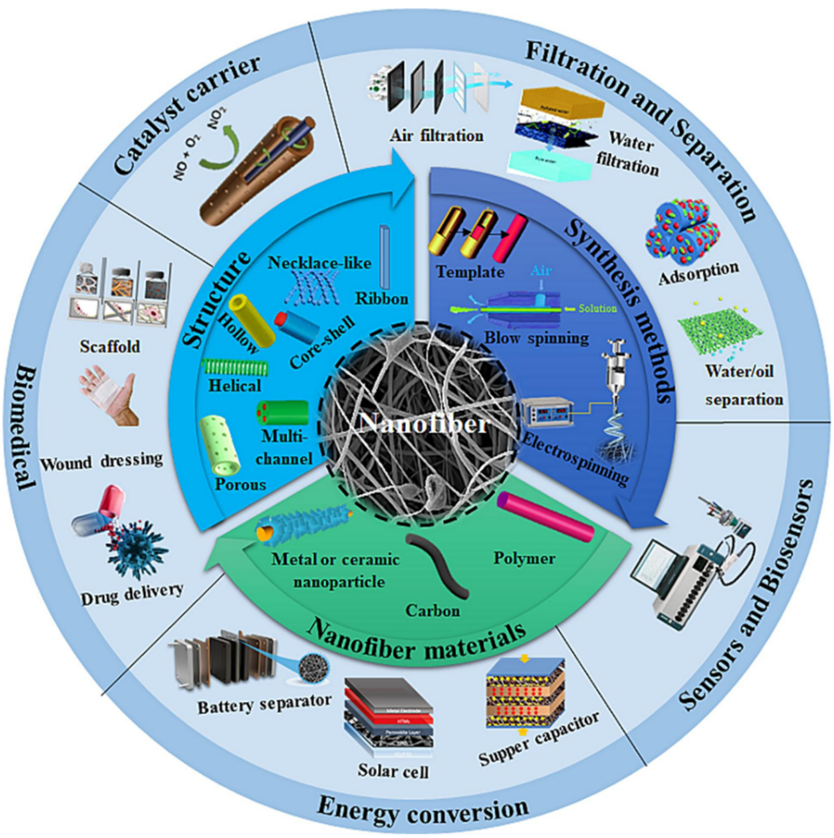

FIG. 5. Applications mostly applicable for nanofibers made of Nafion and its composites. The image is reproduced with permission from Elsevier Maleki *et al.*, Microchem. J. **197**, 109799 (2023). Copyrights Elsevier B.V. All rights reserved.

III. BIBLIOMETRIC ANALYSIS FOR ELECTROSPUN NAFION

The information was obtained and compiled from the Scopus and Web of Science (WOS) databases. Both options were selected based on the databases, including high-quality studies.[76] Furthermore, the present study utilized the PRISMA approach for methodical report analysis. The literature was queried for this investigation utilizing Boolean expressions. The search terms "Nafion AND Nanofibers" and "Nafion AND Electrospinning" were entered. The phrases were searched in both databases for the years leading up to 2023 without employing any particular filters. In total, 323 research articles were identified as findings. Following a PRISMA-based review shown in Fig. 6, 83 articles were selected for further analysis. Figure 7 illustrates the growth of research in the disciplines of "Nafion nanofibers" or "electrospun-based Nafion nanofibers" over time, as measured by the number of publications.

The primary obstacle in producing membranes for water filtration applications is the creation of nanofibers from pure Nafion while simultaneously enhancing the hydrophilicity and antifouling

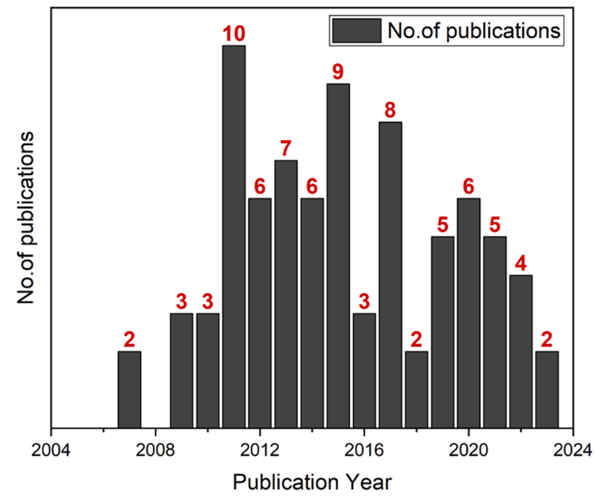

FIG. 7. Publications in the fields of electrospun-based Nafion over time each year.

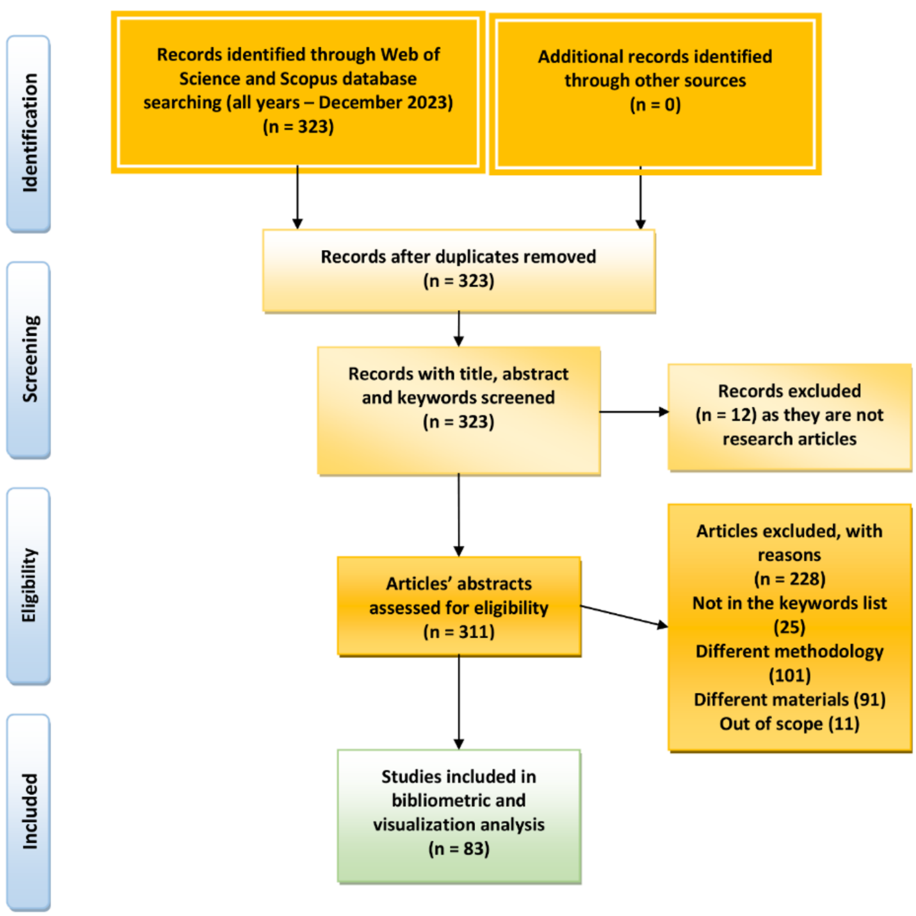

FIG. 6. Flow chart of the PRISMA criteria applied to the publications selected for this study.

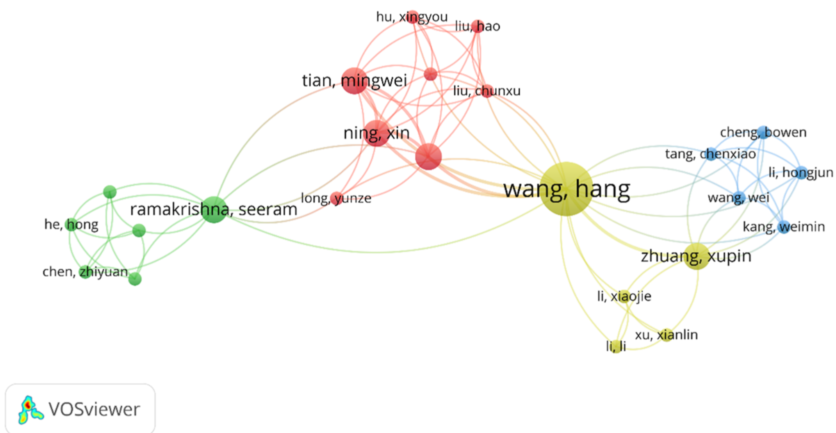

FIG. 8. Network visualization based on the largest set of connected authors (if yes).

qualities of the manufactured membranes, which have yet to be reported. Nevertheless, with their connections shown in Figs. 8 and 9, only a few researchers have used the spinning nanofiber technique through blending. These nanofibers have found extensive usage in various fields, such as fuel cells, sensors, actuators, and others, as shown in Fig. 10.

A. Fabrication of electrospun Nafion membranes (ENMs)

Due to growing enthusiasm for nanoscience and nanotechnology, researchers initiated fresh inquiries into manufacturing nanofibers using the electrospinning process. The quantity of papers and patents associated with electrospinning has significantly increased since 2003. Currently, the manufacturing of nanofibers, which have diameters ranging from tens to hundreds of nanometers and possess regulated shape and function, has been successfully achieved by utilizing synthetic and natural polymers.[77] Electrospun fibers are proven for their potential use in many applications, as shown in Fig. 4.

Here are some examples of the applications of electrospun nanofibers:

- Catalytic supports: Electrospun nanofibers have been used as catalytic supports for various reactions.[78,79]
- Energy storage/heritage components: Electrospun nanofibers have created energy storage components such as batteries.[80]
- Bright mats: Electrospun nanofibers have been used to create intelligent mats that can detect changes in temperature or humidity.[81,82]

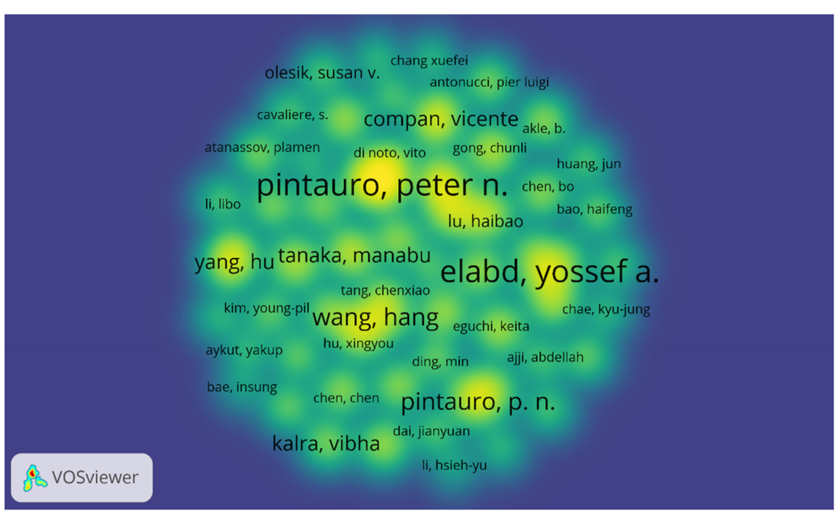

FIG. 9. Network visualization based on the largest set of connected authors (if no).

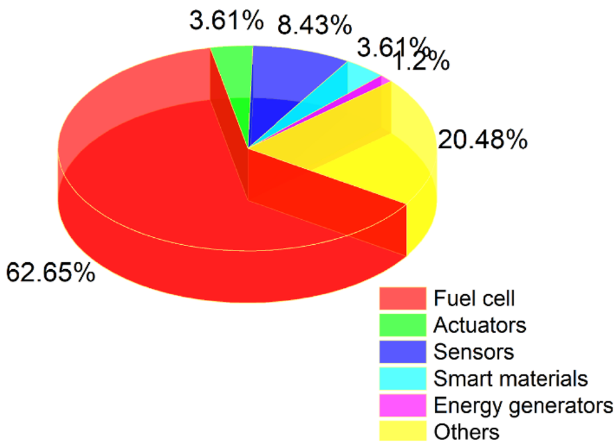

FIG. 10. Applications of electrospun Nafion nanofibers.

However, the possibilities are endless. When ionic polymers such as *perfluorosulfonic acid (PFSA), Nafion, Flemion, Aquivion*, and other sulfonated polymers can electrospun, it may be difficult to transform them into nanofibers since they often have a low viscosity and high conductivity. This presents a problem for the electrospinning process. Consequently, it is essential to integrate other compatible polymers into the process to generate composites or alter them with various molecules to improve their spinnability. In addition, few attempts were made to electrospun pure Nafion using a variety of polymer concentrations, solvents, neutralization, and electrospinning settings; nevertheless, the results were electrospraying rather than electrospinning.[83–85] There have been reports of a Nafion blend polymer solution that includes poly(vinylidene fluoride) (PVDF),[86] polyvinyl alcohol (PVA),[87] polyethylene oxide (PEO),[88] polyacrylonitrile (PAN),[89] polyvinylpyrrolidone (PVP),[90] cellulose monoacetate,[91] and polyacrylic acid (PAA)[92] as a carrier polymer. Two methods have successfully produced Nafion electrospun fibers: either by directly adding a carrier polymer to a Nafion solution with a solvent or by adding a 2-propanol/water solvent to the Nafion solution and then evaporating the solution to create Nafion powder, which is subsequently electrospun with the addition of a carrier polymer[87,88] represented in Fig. 11. However, research gaps regarding Nafion nanocomposites are enormous, especially in water/air purification and medical applications.

Initially, Nafion electrospinning tests resulted in polymer droplets due to insufficient polymer chain entanglement. One method to encourage fiber production is to raise the concentration of polymer solutions. This was achieved by either gently heating the commercial solution to evaporate solvents or incorporating a polymer with a high molecular weight into the solution, which can facilitate fiber formation. In 2007, Laforgue *et al.*[78] fabricated the ionomer membrane using Nafion, employing the electrospinning apparatus. A homogeneous 5% DuPont Nafion 117 solution (USA) for electrospinning was prepared by incorporating a minute quantity (1%) of PEO shown in Fig. 12 (1). However, the exceptional quality of Nafion nanofibers was obtained through electrospinning with only 0.1 weight percent of PEO polymer.[81] It was seen that protons could flow at more than 1 S/cm through a 400-nm wide fiber, as shown in Fig. 13.

Similarly, by adding 2% PVA,[78] high-quality, beads-free nanofibers were formed, as presented in Fig. 12 (2). The electrospinning tests were conducted by manipulating the electric field to flow rate ratios to get a stable electrospinning jet. Beaded fibers are produced, and conductivity is substantially increased by adding PVA. Further escalation of the PVA content results in a regression of the conductivity. In addition, ENMs possess superior mechanical properties compared to the homogeneous recast Nafion film.[93] Alternatively, Nafion powder was first prepared according to the procedure depicted in Fig. 9. Subsequently, a 30 wt. % Nafion solution was obtained by dissolving the Nafion powder in a mixture of 2-propanol and water (in a weight-to-weight ratio of 2/1). Electrospinning was then carried out by incorporating either PVP as an additive polymer dissolved in a specific quantity of dimethylacetamide (DMAc). This process yielded Nafion membranes with a sponge-like structure. However, Nafion nanofibers were electrospinning without needles using foam electrospinning by adding poly(acrylic acid) as a carrier polymer,[92,94] as shown in Fig. 14. The needleless electrospinning technique generates many

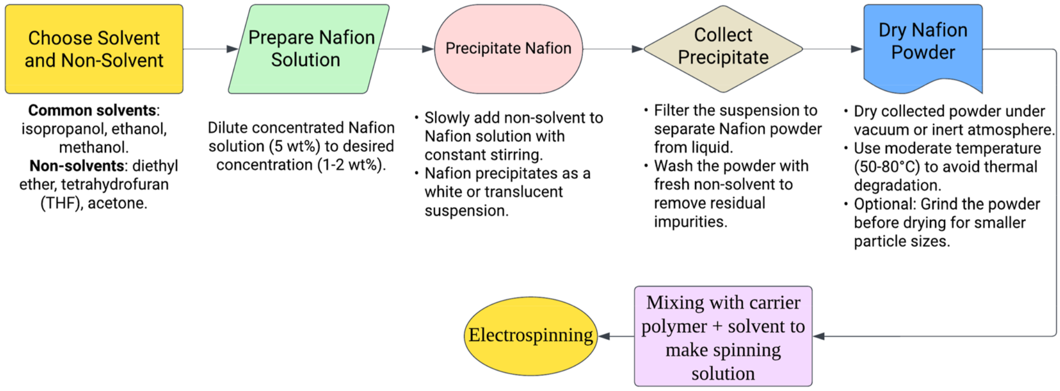

FIG. 11. Process flow of generating Nafion electrospun nanofibers.

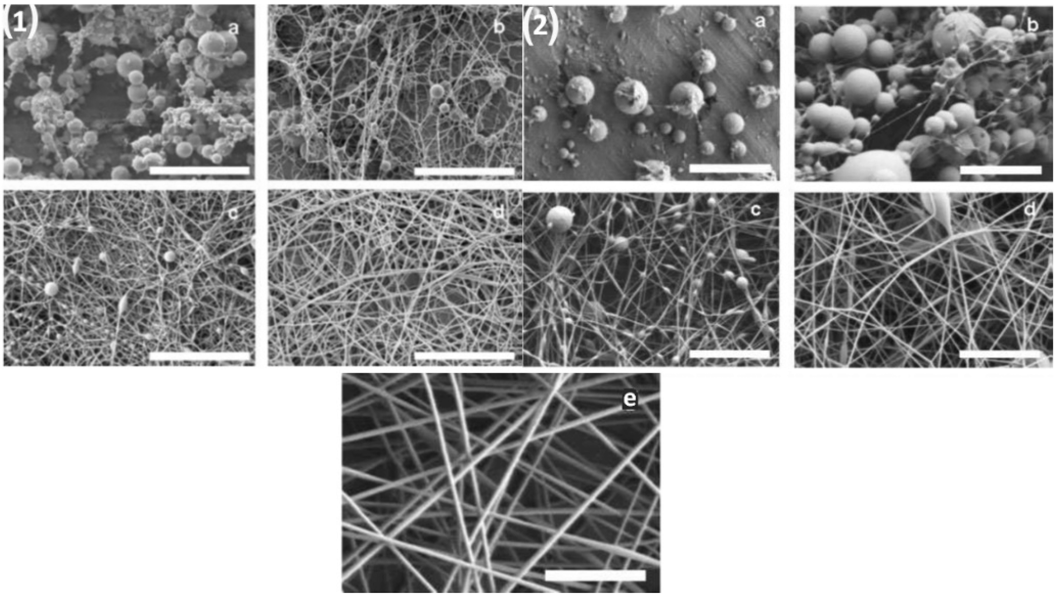

FIG. 12. SEM images illustrating the electrospun structure morphology as produced by (1) Nafion–PEO solutions with (a) 0.25, (b) 0.5, (c) 0.75, and (d) 1 wt. %, and (2) Nafion–PVA solutions with (a) 0.25, (b) 0.5, (c) 0.75, (d) 1, and (e) 2 wt. %. This image is reproduced with permission from *Laforgue et al.*, Macromol. Mater. Eng. **292**, 1229–1236 (2007). Copyright 2007 John Wiley and sons.

electrospinning sites, which facilitates achieving high productivity and purity. The entanglement occurs easily during electrospinning because of the greater polymer concentrations at the surface of tiny bubbles in the solution. Moreover, compared to needle electrospinning, there is a difference of two orders of magnitude in the fiber mats generated by needleless electrospinning and exhibited greater Young's modulus and proton conductivity. Therefore, a carrier polymer with a high molecular weight is significant throughout the electrospinning process of Nafion,[94] whatever the process is.

B. Electrospun Nafion nanofiber applications

1. Fuel cell

Fuel cells use catalysts to transform chemical energy into electrical energy via anode–cathode redox processes. They are gaining popularity as an alternative energy source because their efficiency and lack of pollution-direct methanol fuel cells (DMFCs) and proton exchange membrane fuel cells (PEMFCs) appear promising. Their excellent power density and low operating temperatures are advantageous. Innovative fuel cell designs use electrospun nanofibers

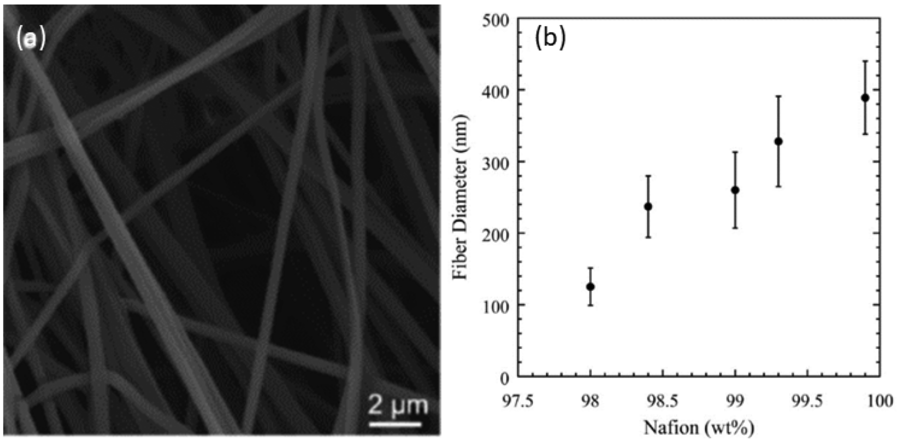

FIG. 13. SEM images of high-purity Nafion nanofibers electrospun with high molecular weight PEO (Mw—8000 kg/mol) at (a) 99.9 wt. % Nafion and (b) fiber diameter with respect to composition in wt. % Nafion. This image is reproduced with permission from Dong *et al.*, Nano Lett. **10**(9), 3785–3790 (2010). Copyright 2010, American Chemical Society.

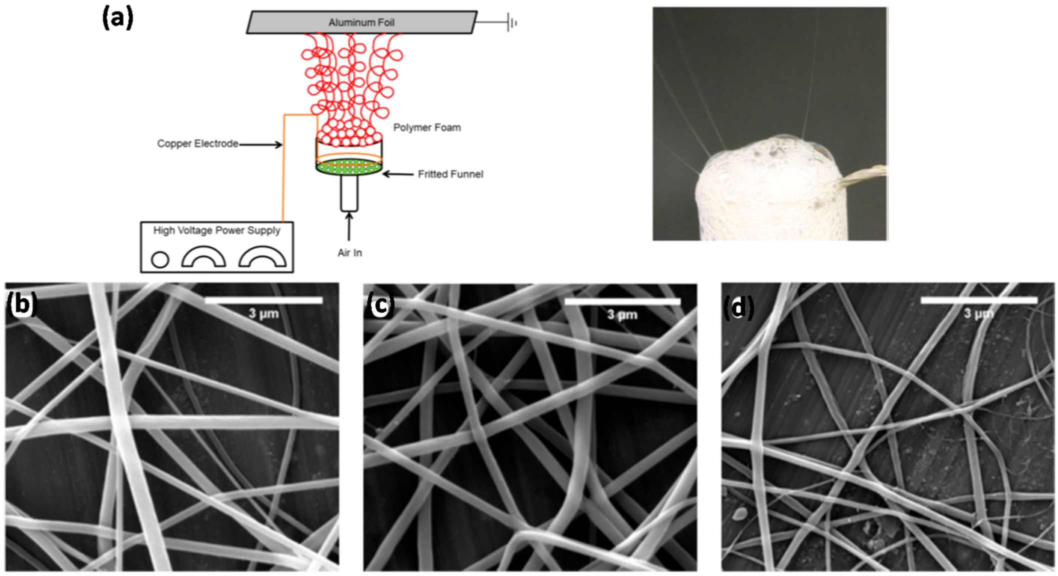

FIG. 14. (a) Representation of needleless electrospinning processes and (b)–(d) SEM images illustrating needleless electrospinning. The image is reproduced with permission from Hwang *et al.*, ACS Appl. Polym. Mater. **1**(10), 2731–2740 (2019). Copyright 2019, American Chemical Society.

as anodes, cathodes, or proton-conductive membranes to improve performance and efficiency.[95] Porous PVA electrospun mats were created by feeding an aqueous solution of PVA with cetyltrimethylammonium bromide (CTAB) as a surfactant.[96] The purpose of adding CTAB was to decrease the surface tension of water and enhance the electrospinning capability. After a 3-h heating process at a temperature of 170 °C in a vacuum environment with a pressure of 250 mbar, it shows a superior performance in methanol permeability of 5.33×10^{-7} cm^2 s^{-1}. Moreover, direct methanol fuel cells at various temperature and methanol concentration levels revealed that the highest level of performance was attained at a temperature of 95 °C and a methanol concentration of 2M. Woo Park *et al.*[86] experimented on H_2/Br_2 charge and discharge regenerative fuel cells at 25 and 45 °C. The results revealed that the power output was about 10% greater when using a thick nanofiber membrane containing more than 50% Nafion fibers than a thick Nafion 115 film. Similarly, a nanofiber network membrane made of Nafion was created for use in direct methanol fuel cells using the process of electrospinning. At 25 °C and 80% relative humidity, the membranes produced had a proton conductivity of 0.10 S/cm, and their permeability to methanol was 3.6×10^{-6} cm^2/s.[97] However, inorganic fillers, such as micro- or nanoparticles, have been introduced into polymer matrices to enhance water retention and thermal stability. Although this does increase the barrier capacity for methanol crossing when it is disseminated in acidic membranes, further study is required to fully understand this phenomenon.

2. Water treatment

One way to address water shortages is to treat alternate water sources, such as rainfall, ocean, and wastewater. Heavy metals, organic contaminants, gas, and bacteria, which are poisonous and carcinogenic, must be eliminated before water is safe for use. Electrospun materials are used as nano-absorbents to remove heavy metals due to their high porosity, active sites, and faster contaminant removal.[98] Moreover, electrospun nanofiber mat (membrane) filtration is used to eliminate suspended particles from water by exerting pressure to force water through a membrane.

Electrospun webs were fabricated by combining Nafion and PVA polymers, which had both elasticity (ability to stretch) and compressibility. Its thickness can be reduced to one-third of its original size. This web was used for the electrochemical detection of Cd(II) metal owing to its positive surface charge.[99] Thus, it may be inferred that Nafion has the potential to be beneficial for retaining positively charged metal ions in aqueous solutions, owing to the electrostatic force. Though it has been shown that Nafion and PAN are not compatible, Chau Tran and Vibha Kalra fabricated electrospun nanofibers by including 5 wt. % polyacrylonitrile (PAN) in Nafion thereby enabling the effective electrospinning of nanofibers due to increased intermolecular entanglements in the solution. The mechanical properties revealed that the Nafion/PAN nanofibers that were manufactured had a much higher tensile strength in comparison with the PAN nanofiber membranes, and a removal rate of 45% for Cr^{3+} metal ions was achieved using membrane, which shows an adsorption affinity for metal ions.[89]

3. Actuator/shape memory

Electrospun nanofiber-based actuators have better mechanoelectrical transduction than traditional IPMCs, making them appropriate for self-powered devices. In ionic polymer transducers, electrospun nanofiber mats accelerate actuator response. Adjusting the ionic liquid and membrane swelling level may change the nanofiber-based actuators' shape and transduction performance. Actuators

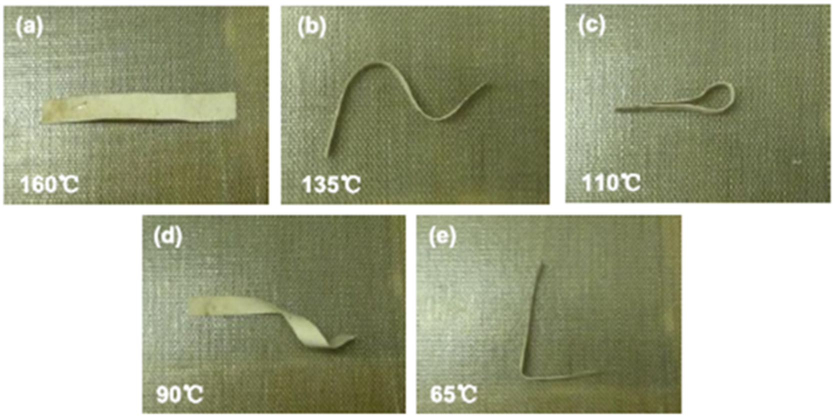

FIG. 15. Shape memory properties of the Nafion nanofiber membrane. The image is reproduced with permission from IOP Zhang *et al.*, Smart Mater. Struct. **22** 085020 (2013). Copyright 2013 IOP Publishing Ltd.

using ionic liquid-Nafion mats respond 46 s faster compared to film transducers by Nah *et al.*[100] Nafion-based ionic polymer–metal composite actuators, or IPMCs for short, are intriguing new materials with plenty of potential applications in biomimetics, microfluidics, and soft robotics.[101,102] The conducting nanoparticles, multiwalled carbon nanotubes (MWNTs), and silver were distributed in a Nafion solution and then electrospun. Therefore, IPMC equipped with Nafion and conducting nanoparticle electrospun webs exhibited enhanced displacements and blocking forces.[103] Furthermore, ionic conductivity is crucial for faster response in ionic polymer actuators. The ionic liquid-Nafion fiber composite had three times better conductivity than films. Not limited to that, heated electrospun Nafion nanofibers have good shape memory. After three shape memory cycles, the shape fixity and recovery rates are 96% and 89%, respectively, as presented in Fig. 15.[93,104] Shape memory polymers, such as Nafion nanofibers, may remember strain and thermomechanical history when deformed and recovered above 120 °C.[105] In addition, the electrospun Nafion cell has a unidirectional orientation of ionic conductivity, which improves the proton conductive thermoelectric cell. Recovering waste heat to electrical output is an up-and-coming economic option.[106]

4. Sensors

Enhanced mechanical and dielectric strength, surface area, and chemical characteristics may be achieved by designing electrospun nanofibers with well-organized microstructures. They are ideal for wearable electronics because of their high flexibility, stretchability, and breathability. Moreover, electrospun nanofibers are perfect for soft electronic platforms because of their reaction to mechanical

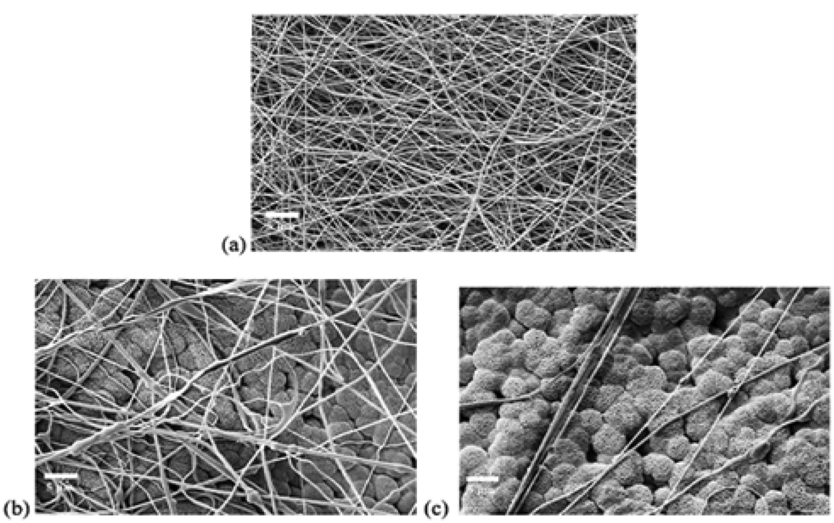

FIG. 16. FE-SEM images of (a) 2.5% CNT/Nafion 0%, (b) 2.5%CNT/Nafion 6%, and (c) 2.5%CNT/Nafion 8%. The image is reproduced with permission from Elsevier Guo *et al.*, J. Membr. Sci. **590**, 117265 (2019). Copyright 2019 Elsevier Ltd. All rights reserved.

deformation and body compatibility through blending or adding fillers.[107] Electrospinning with cellulose monoacetate (CMA) powder and ~5% Nafion in lower aliphatic alcohols and water solution was employed for the DNA biosensor. Recovering ammonia is made up to three times easier using the electrospun Nafion honeycomb porous membranes shown in Fig. 16.[108] The humidity sensor used electrospun MWCNT/Nafion nanofiber sheets, which exhibited a three-dimensional (3D) porous structure. The current sensor significantly improved relative humidity sensitivity and had outstanding linearity and repeatability with a quick reaction time of around 3 seconds.[109]

5. Energy harvesting

Electrospun nanofibers are a promising material for energy harvesting. In other words, they may transform mechanical stresses and acoustic signals into electrical energy.[110] Wearable and flexible nanofiber-based piezoelectric or triboelectric nanogenerators have also been developed to harvest energy from body motion, converting wasted mechanical vibrations into energy. These innovations open many possibilities for efficient and sustainable energy solutions for portable, wearable electronic applications.[111] The electrospun nanofibers of Nafion functionalized $BaTiO_3$ and PVDF were fabricated to create a TENG (triboelectric nanogenerator) device. The device's design is based on the contact-separation mode shown in Fig. 17. The device exhibits a high output voltage of 307 V, a current density of 1.8 $\mu A/cm^2$, and a power density of 1.12 mW/cm^2. Furthermore, it maintains a constant output performance after 10 000 cycles.[112]

IV. CHALLENGES

According to the available literature, several research studies have focused on using polymer-based nanocomposites for wastewater treatment and energy harvesting.[113–115] The fundamental challenge is the electrospinning of pure Nafion and polymer mixes. Due to the viscosity and high conductivity, the presence of water molecules affects agglomeration or dissemination in a spray-like way.[116] Despite attempts by academics and enterprises to increase the ability to spin Nafion and broaden its uses, there still needs to be a more significant gap in tackling particle clumping, especially at high amounts of inclusion. Nevertheless, Nafion electrospun nanofibers made of high molecular weight polymers can be used as a matrix for creating polymer nanocomposite materials with better spinnability.[117] The prepared Nafion-based blends and nanocomposite materials with fillers have improved the performance as proton exchange membranes in fuel cells, sensors, and actuators.[118] However, continuing research on the topic of achieving cost reductions related to the production of high-quality Nafion nanostructure membranes is something that will be investigated in the future. Because this has yet to be provided in the open literature, it is essential to consider the appropriate optimization parameters for electrospinning using the Taguchi experiment design. In addition, the incorporation of low-cost polymer mixes with a wide variety of organic and

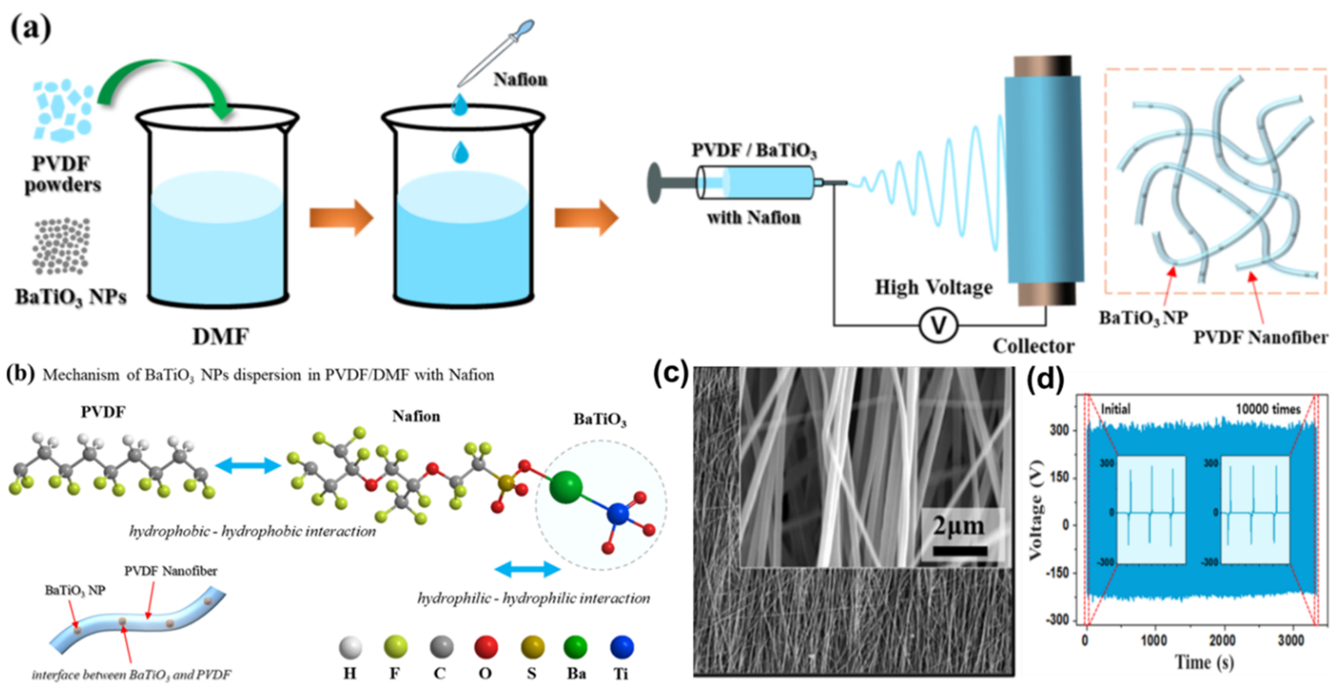

FIG. 17. (a) Diagram depicting the procedure for composite nanofibers made of $BaTiO_3$, PVDF, and Nafion, (b) chemical structure of Nafion-functionalized $BaTiO_3$ NPs and PVDF, (c) at 1% $BaTiO_3$ FESEM images, and (d) initial and final output voltage during the stability test. The image is reproduced with permission from Elsevier Pandey *et al.*, Nano Energy **107**, 108134 (2023). Copyright 2022 Elsevier Ltd. All rights reserved.

inorganic fillers has the potential to be a game-changer in wastewater treatment and energy harvesting.

V. FUTURE SCOPE

The future applicability of Nafion electrospun nanostructures is quite broad and promising, with the possibility of applications in energy, water, and biomedicine. A widely known application is fuel cells; Nafion is often used as a proton exchange membrane (PEM) because it has exceptional proton conductivity. The creation of electrospun Nafion nanostructures might produce PEMs with superior performance characteristics, such as excellent proton conductivity, enhanced mechanical qualities, reduced swelling, and increased durability. These improvements can potentially contribute to the broad use of fuel cell technology to generate clean energy. Furthermore, due to hydrophilic and sulfonic groups, Nafion nanostructures can detect gases, ions, biomolecules, environmental contaminants, and heavy metal ions from wastewater and air filtering. Electrospun Nafion has a large surface area and ion exchange capability, making it ideal for absorbing and eliminating environmental pollutants and becoming more effective with increased porosity and selectivity.

VI. SUMMARY AND CONCLUSIONS

The most recent research offers a glimpse into the ongoing activities that are taking place regarding the utilization of Nafion nanofibers that are filled with carrier polymers and nanofillers for energy generation and sensor application. This Review summarizes the efforts that have been made in developing, characterizing, and progressing the electrospinning possibilities of Nafion material for water treatment and energy harvesting. The incorporation of carrier polymers into the framework of the Nafion solution has resulted in an improvement in the electrochemical and mechanical properties, which are very advantageous for the harvesting of energy. The resulting nanofibers could also perform wastewater treatment because of their promising hydrophilic and hydrophobic structures, electric properties, and porosity. Despite this, a significant amount of research still has to be done to produce and characterize the Nafion composite nanofiber structure for various applications. In addition, the authors highlight the difficulties related to the electrospinning process and the potential solutions that could be used to overcome these difficulties. This Review concludes that Nafion nanofibers have tremendous promise when applied to various disciplines such as fuel cells, actuators, shape memory, biomedical, metal ion detection, and energy harvesting, despite encouraging development in Nafion employing electrospun nanofibers. The main obstacles in energy conversion, storage, and water treatment are solution compositions and microstructures. Most electrospinning studies are lab-scale. Scaling production is crucial for real-world use and commercial application. Finally, this work emphasizes the interdisciplinary character of Nafion polymer and its composites, connecting materials science and the intricate issues presented by various sectors.

ACKNOWLEDGMENTS

The authors extend their appreciation to King Saud University for funding this work through Researchers Supporting Project No. RSP2024R164, King Saud University, Riyadh, Saudi Arabia. The authors felt sincere gratitude to Kalasalingam Academy of Research and Education (Deemed to be University), to perform all the investigations. This article was co-funded by the European Union under the REFRESH – Research Excellence For Region Sustainability and High-tech Industries, project number CZ.10.03.01/00/22_003/0000048, via the Operational Programme Just Transition and has been done in connection with the Students Grant Competition, project no. SP2024/087. Specific Research of Sustainable Manufacturing Technologies were financed by the Ministry of Education, Youth and Sports and Faculty of Mechanical Engineering VŠB-TUO.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Venkata Dinesh Avvari: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **P. S. Rama Sreekanth**: Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal). **Raghavanantham Shanmugam**: Data curation (equal); Investigation (equal); Methodology (equal); Resources (equal). **Sachin Salunkhe**: Funding acquisition (equal); Investigation (equal); Project administration (equal); Resources (equal). **Robert Cep**: Funding acquisition (equal); Investigation (equal); Methodology (equal). **Emad Abouel Nasr**: Funding acquisition (equal); Investigation (equal); Methodology (equal). **D. Kimmer**: Data curation (equal); Project administration (equal); Resources (equal).

DATA AVAILABILITY

The data that support the findings of this study are available, upon request.

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