



ORIGINAL ARTICLE

Nano/micro-structural engineering of Nafion membranes for advanced electrochemical applications



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Abstract Nafion membranes are actively electrochemical devices such as fuel cells, conventional two compartments electrochemical cells, and photoassisted electrolyzer cells. It provides good selectivity of penetrating ions from one electrode compartment to another and accelerates the separation of the products. Though the conventional Nafion membrane has been widely applied, there are still some crucial challenges, such as the flow of ions transferred by fouling, charge gradient resistance, and mechanical instabilities in long-term applications. In particular, the charge transfer resistance of the membrane is a key characteristic to realize the efficient transfer of charges across the electrodes within the electrolyte. The researchers have tried cost-effective nano/micro-structural engineering strategies to produce high-quality Nafion membranes for improved electrochemical applications. The proper surface patterning and selective functionalization or hybrid formation of Nafion with specialized materials could improve the overall mechanical strength, charge sustaining and flow rate potentials of the parent Nafion. This manuscript provides a brief overview of Nafion based nano and microstructured membrane and their modification strategies for energy conversion devices. Two strategies are shortly overviewed with respective examples: (1) physical modification via nano/micropatterning and (2) nanocomposite formation with selective materials. The modified Nafion membranes by various structural engineering strategies propose new and effective pathways to enhance the performance of energy conversion devices, which are keys for solving current environmental issues.

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1. Introduction

For decades, fossil fuels have been a primary source of driving vehicles, industries, and domestic utilities. The excessive burning of carbon-based fuels has generated CO_x, NO_x, and SO_x-based toxic gases, which considerably challenges environmen-

tal sustainability and human health. Due to these facts, researchers are motivated to use greener energy generation techniques and are looking for alternative opportunities that are environmentally friendly as well as renewable. Hydrogen is regarded as zero-carbon fuel that offers an alternative way to produce greener energy. It has a low volumetric energy density, i.e. 1 kg hydrogen gas carries equivalent energy of 2.8 kg gasoline [1]. Water is an abundantly occurring compound that can produce hydrogen and oxygen by photocatalytic, photoelectrocatalytic, or electrocatalytic approaches [2]. These approaches have received substantial research interest due to their least environmental implications in recent decades. For overall water splitting, the separation of hydrogen and oxygen products is a key research challenge at the industrial scale. By fuel cells, produced hydrogen and oxygen recombine to produce electrical energy with water. In this case, the rate of combining hydrogen and oxygen should be well controlled to achieve maximum efficiency. Indeed, in these energy conversion devices, selective and controlled mass transfer is required to maximize the overall efficiencies. One way to accomplish these characteristics is to design a permeable membrane containing device. The separating membrane should have attributes of antifouling resistance, sustaining cross potential capability, high thermal, mechanical and chemical stabilities, and low cost. Nafion membrane satisfies most of the above requirements. Therefore, it has been one of the promising separating membranes for electrochemical energy conversion devices where hydrogen cations (H^+) are the primary transferring charged matter [3,4]. Typical electrochemical assemblies consist of ion exchange membrane (PEM), electrolyte, respective electrodes, and electrical energy supplier (potentiostat). At the same time, an artificial solar light source is supplied in photoelectrocatalytic or photocatalytic systems.

Numerous factors control the transport mechanism of ion exchange membrane. These factors include the membrane's selectivity towards specific ions (protons in the case of fuel cells), the potential difference across separating membrane, pH environment (alkaline or acidic), the diffusion capacity of transporting ions, the concentration and viscosity of electrolyte solution, etc. Usually, the more polarizability and potential difference lead to accelerated mass transportation across the membrane. However, the membrane fouling, and ion collision rate should be considered. Solution's pH essentially controls the generation of specific ions, e.g., more proton ions are favoured in highly acidic conditions (low pH) and vice versa. As a case study, the comparative analysis of NaOH and KOH electrolytes using Nafion-12 as separating membrane in a zinc-iron flow battery demonstrated that the Nafion membrane exhibited more phase separation and cluster radius within NaOH [5]. The improved membrane performance within NaOH electrolyte endowed a better ion conductivity than KOH solution due to high pH. Furthermore, density functional theory (DFT) simulations confirmed a facile adsorption/desorption between the Na^+ and the $-SO_3^-$ in Nafion than K^+ and the $-SO_3^-$. Moreover, the ions' diffusion capacity and radius size are equally important during the transportation across permeable membranes as fouling is favoured if the radii of ions and collision rates are not optimized.

Over the years, the research community and industry have used Nafion membrane-based devices to generate energy. However, the conventional Nafion still encounters serious discrepancies such as fouling, an immediate drop in charge con-

centration gradient across the membrane, and low thermal and mechanical stabilities. In large-scale applications, the high flow of anodic fuel crossover to the cathode side through conventional Nafion could lead to mixed potentials and cathode poisoning, declining the device performance [6]. These days, various modification strategies have been reported to advance the characteristics of the conventional Nafion. This review briefly introduces the potential properties and modification strategies of Nafion membrane that can lead to improved device performance.

2. Nafion based proton exchange membrane

Nafion-based proton exchange membrane (PEM) could play a vital role in the electrochemical reactions by selective proton permeability and product separation. A typical Nafion membrane has an interesting interpenetrating structure with the following distinct characteristics [7].

- 1) The hydrophobic perfluorocarbon regions offer excellent chemical, thermal resistance, and gas diffusivity with mechanical strength.
- 2) Water clusters surrounding the charged sulfonic acid-rich hydrophilic regions allow selective permeability towards proton transport.

The maximum entropy (MaxEnt) coupled mesoscale simulations and small-angle X-ray/neutron scattering (SAXS/SANS) experiments showed that the nanoscale ionic clustering in perfluorosulfonic acid (PFSA) ionomers are intimately linked to, but spatially separate from, the larger-scale organization of the fluorocarbon backbone (Fig. 1A). The high-density regions of fluorocarbon segments were ascribed to the regions of lower ionic clusters and vice versa (Fig. 1B) [8]. The combinational structure of hydrophobic and hydrophilic regions of Nafion allows effective ion exchange by separating the products from recombination and controlling the crossover of the fuel. Therefore, Nafion has been applied to typical H-cell and fuel cells as a promising separating membrane, as demonstrated in Fig. 1C. The purpose of Nafion can be distinct in different devices. For example, in the water-splitting process, the primary function of Nafion membrane is to separate the anodic and cathodic products while only allowing the proton transportation to overcome the recombination of the generated ions. Within proton exchange membrane (PEM) fuel cells, their fundamental function is to permit proton transportation and prevent electron conduction.

For about a decade, Nafion membranes have been optimized for long-term commercial uses and performance enhancements. A commercially optimized Nafion membrane has the following industrial advantages.

- 1) High permeability and selectivity: The hydrophobic and hydrophilic regions selectively determine the selectivity and permeability of Nafion membrane. These membranes are suitable for protons and related ions exchange having the same ion size and charge.
- 2) High ion conductivity: Nafion membrane offers temperature-dependent conductivity (0.083 S cm^{-1} at 23°C) to protons. It is determined that the conductivity increases with temperature in the case of proton exchange.

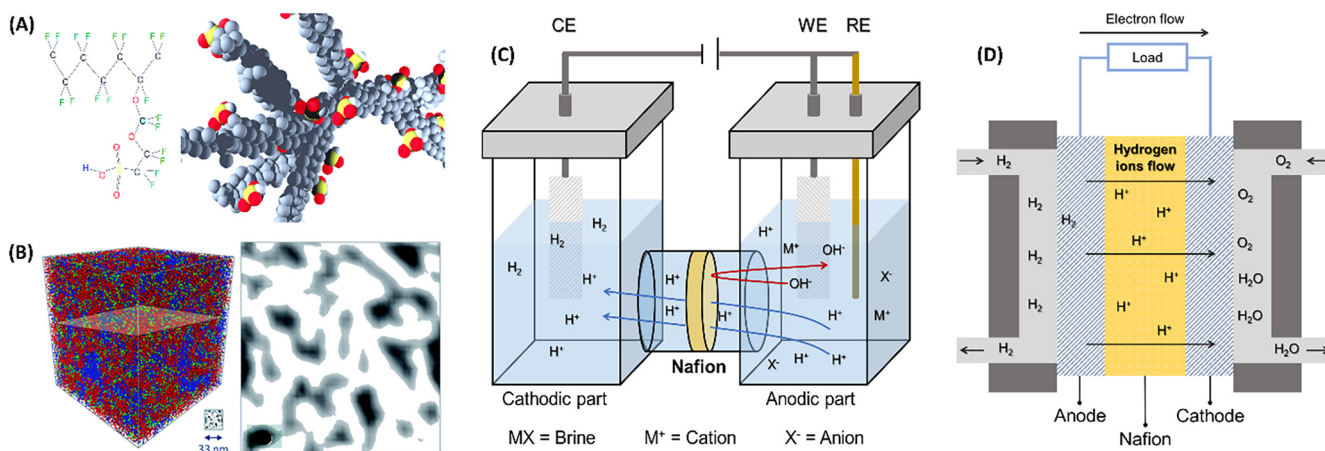


Fig. 1 (A) The chemical structure of conventional Nafion; grey spheres are hydrophobic Teflon backbone structure, red and yellow spheres are hydrophilic sulfonated clusters connected by an oxygen ion to the backbone chain [7], Copyright 2011, Springer Nature. (B) Simulated structure of Nafion, high-density regions of fluorocarbon segments showing the regions of lower ionic clusters and vice versa [8], Copyright 2011, The Royal Society of Chemistry. Schematic illustrations of (C) constructions of Nafion based H-Cell containing brine as an electrolyte, and (D) fuel cell with the mechanism of charge (current) generation by H^+ transportation.

- 3) Chemically stable. Nafion membrane exhibits good chemical stability among the existing membranes due to their tunable surface properties and chemical composition that can resist high oxidizing and corrosive environments during the reaction.
- 4) Thermally stable. Nafion membrane could sustain a suitable thermal environment, specifically in photocatalytic systems where solar irradiation could cause severe photocorrosion. The cage-like high molecular structure always offers a unique character to maintain an appropriate thermal environment.
- 5) Good mechanical properties. The improved tensile and strain properties of Nafion membrane due to the modifiable backbone are appealing towards highly stacked and stretchable devices.

Even though Nafion is a good material for PEM, there are still considerable potentials to be improved for better cell performances. With modern research protocols, structural and functional modifications of conventional Nafion membrane could lead to effective performance increase in terms of high separation efficiency and stability within the electrolytic systems. Here, we introduce the nano/micro patterning and composite forms of Nafion, which are the two widely reported techniques to improve the properties of Nafion membrane (Fig. 2).

3. Patterning of Nafion membrane

Earlier, Nafion membranes with relatively flat surfaces were utilized in electrolytic and fuel cell applications. However, it encounters issues like low ion exchange capacity, high resistance, and charge drop. The hydrophilic and hydrophobic characteristics of Nafion can be tuned by applying selective patterning. The patterning of Nafion offers a valuable role in proton transport, surface functionalization, water management, and optimization of the 3-phase boundary. Incorporation of patterned Nafion in the device enhances the stability,

reducing the cost as it boosts the activity of the electrode material and improves the separation of products which leads to higher current and power densities. In the case of fuel cells and other electrochemical systems, the pattern can improve the following mechanisms.

- 1) The patterning improves the interfacial characteristics and catalyst utilization by reducing the catalyst dead zone. The overall device performance is expected to increase due to high reaction rates and superior electrokinetics.
- 2) The asymmetric surface offers more surface area that can effectively enhance the electrolyte transport and proton conductivity properties within the electrolytic system.
- 3) The transport of materials can be directed in a particular direction by tuning the shape, size, and lengths by inducing patterns. For example, a prism-shaped pattern was found effective by collecting the water droplets at the bottom as it offered low resistance to water droplets in a particular direction [9].
- 4) The hydrophilic/hydrophobic regions of Nafion membrane can be selectively exposed by designing specific geometries and hence could be beneficial in controlling the wetting attributes of the device.

Considerable efforts have been made to selectively pattern Nafion membranes into nano, micro and multiscale patterns [8]. Various popular nanopatterning methods include lithographic techniques (soft lithography, electron-beam lithography), chemical synthesis, physical filling (pore-, swelling- and nanorod-filling), and ion-beam bombardment. As shown in Fig. 3(A), Choi et al. fabricated nanopatterned Nafion with high structural fidelity using a PDMS master mold [10]. The curing temperature was critical in controlling the growth of nanopatterns. At elevated temperature, the Nafion nanofeatures almost matched the master mold size, i.e., ridge and groove are ~ 800 nm, and depth is ~ 600 nm. For example, at

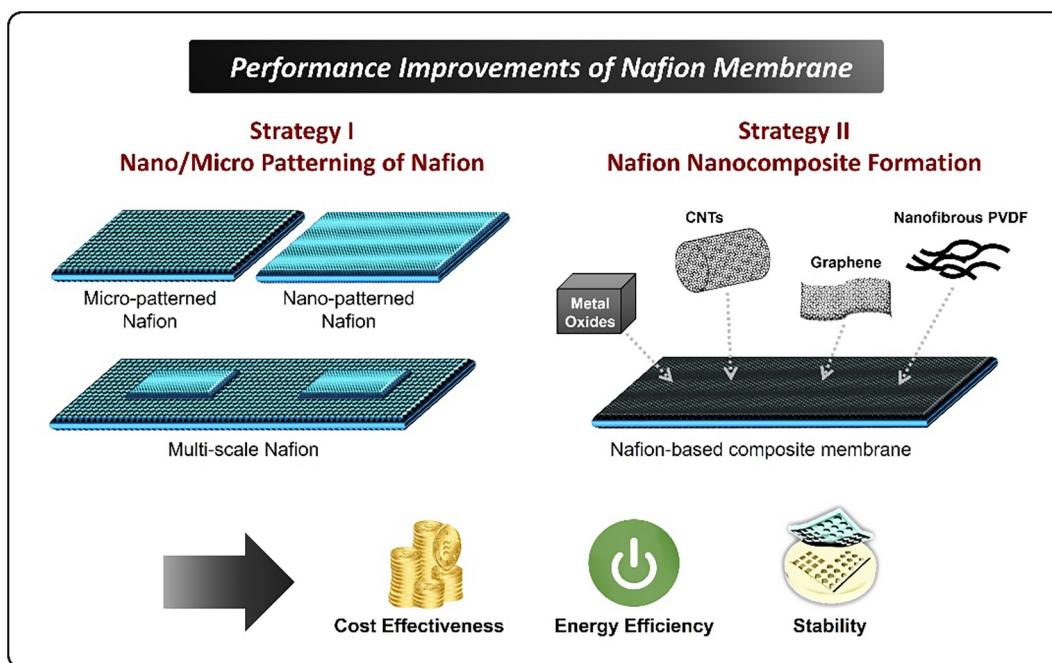


Fig. 2 A schematic representation of advantages and improvement strategies of Nafion.

105 °C and 20% Nafion concentration, the nanopatterned mold dimensions were ~ 532 nm (ridge), ~ 1008 nm (groove) and ~ 447 nm (depth). However, a further increase in temperature could lead to the bending of the master mold. Therefore, the curing temperature should be optimized. While at room temperature, the mold dimensions were ~ 270 nm (ridge), ~ 1291 nm (groove) and ~ 276 nm (depth). Since Nafion solution has sufficient time to swell the master mold at a lower temperature, considerable nanopattern deformation is caused.

Similarly, the microscale patterning of Nafion membranes could produce highly pore assembled and well-organized structures at the interface of Nafion. Like nanopatterning, micropatterning can be achieved by molding methods, plasma treatment, and electron beam lithography. For example, micropatterned Nafion membrane is fabricated over Au micro-electrode via combined photolithographic sputtering and lift-off techniques (Fig. 3B) [11]. A positive photoresist with disk-shaped holes patterns (200 μm diameter) was used in this process. After plasma treatment and spin-coating, the substrate was annealed, and the photoresist was dissolved with acetone to achieve the micropatterned Nafion modified electrode. The scanning ion conductance microscopy (SICM) shows approximately 80 and 290 nm thick Nafion films when using 1% and 2.5% Nafion solutions. The micropatterned Nafion-modified electrodes considerably enhanced the assaying signals of FcCH_2OH^+ as the patterned electrodes could accumulate more cations.

The more advanced, multiscale patterning of Nafion membrane is a relatively newer research area that can induce nano- and micro-scale features within the same membrane. The multiscale modifications lead to improved proton conductivity, transport efficiency, well-coupled interface, and desired fuel crossover. However, achieving a multiscale pattern is always considerably challenging due to the multiple assembling nature. Choi et al. have widely investigated the patterning of

Nafion specifically at a multiscale level for energy-related applications [12–16]. One of their studies reported LEGO-like integrations of microscale Nafion membranes by quantitatively controlling the oxygen inhibition (scavenging effects) of ultraviolet-curable materials. The different oxygen concentrations selectively caused various curing contrasts in the parent resin. The infiltrated oxygen within the PDMS blanket formed a grey zone that inhibited the radical induce polymerization of the polyurethane acrylate (PUA) resin. Under UV irradiation, slow curing of PUA occurred near the oxygen inhibition layer (OIL) and vice versa. Depending on the ratio of crosslinkers and the amount of infiltrated oxygen within the PUA resins, the curing can be controlled at specific regions, leading to multiscale patterning. The LEGO-like integrated pattern membrane showed robustness supported by mechanical stability within the PEM fuel cell. The complete fabrication strategy of designing multiscale patterned Nafion is provided in Fig. 3C. The multiscale design induced the combining effect of declined membrane resistance and enhanced electrochemical active surface area [13].

Table 1 lists employed techniques used to fabricate patterned Nafion at nano, micro and multiscale levels having desired properties.

4. Nafion-based composite membrane

Functionalization or hybrid formation of Nafion with a suitable material could achieve the goals of durability, facile transportation of products, and separation. Due to the organopolymer nature of Nafion, it is susceptible to various modifications. The carbon-based materials are extensively reported to be combined with Nafion. For example, single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) are equally employed to modify Nafion membrane for various purposes [23–27]. In an earlier

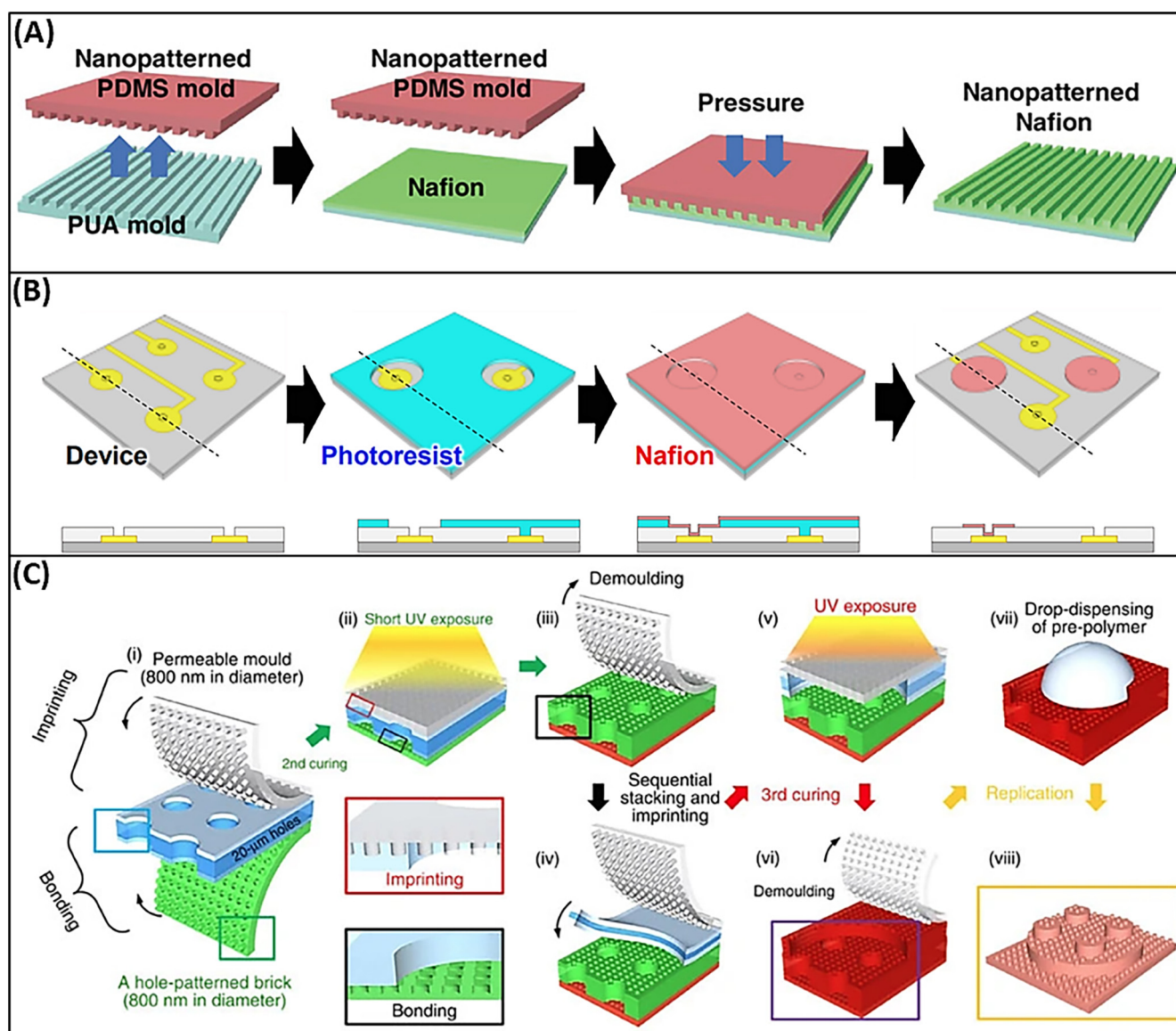


Fig. 3 Schematic illustrations of (A) Nanopatterned Nafion [10], Copyright 2020, Wiley. (B) Micropatterned Nafion [11], Copyright 2017, Chemistry Letters, CSJ. (C) Multiscale patterned Nafion [13], Copyright 2015, Nature.

study, SWCNTs/Nafion composite films were constructed over an interdigitated electrode [28]. Nafion acts as a matrix to give stable and homogeneous cast thin films. The role of Nafion as a binder is well explored in this study, which is helpful to retain the conductivity of the hybrid between SWCNTs and mesoporous silicon. The CNTs/Nafion composite films respond quickly to methanol concentration changes as the resistance boosts considerably with a rising concentration (0.5 M \rightarrow 4 M). Similarly, the histidine and imidazole functionalized CNTs/Nafion films showed appreciable proton transport properties by providing suitable hydrogen bonding sites (Fig. 3A) [6]. In a more recent study, SWCNTs/mesoporous silicon/Nafion hybrid has been designed for nonenzymatic glucose electrochemical sensing applications [29]. Graphene and its modified forms are also coupled with Nafion for improved electrochemical features. Polyoxometalate and phosphotungstic acid coupled graphene oxide–Nafion composite membrane was found

exceptionally efficient for proton conductivity at a relatively lower relative humidity (RH) (Fig. 4B). The power density for the hybrid reached 841 mW cm⁻², compared to 210 mW cm⁻² for pristine Nafion membrane at 80 °C under 20% RH. The 4-fold enhancement of the power density can be attributed to the lower ohmic resistance by enhanced hydrogen bonding with protons [30]. Polyvinylidene fluoride (PVDF) is another important organic conducting polymer. The PVDF-modified Nafion membranes are reported for improved fuel cell performance in the literature by various researchers [31–33]. More recently, Fan et al. demonstrated the simultaneous effect of unmodified and acetone modified PVDF on Nafion membrane [31]. The electrospinning technique was helpful in generating the fibrous morphology (Fig. 4C). The nanofibrous composite Nafion membranes were employed in a hydrogen/bromine regenerative fuel cell. Dual nanofiber mats (made of Nafion perfluorosulfonic acid (PFSA) ionomer and PVDF

Table 1 Nano/micro patterning techniques for generating patterned Nafion membranes.

Materials	Pattern shape/fabrication strategy	Favourable properties	Ref.
N-211, PDMS as a moulding material	Spatially microhole arrayed pattern/soft lithography	High mechanical stability by the nonetched surface around a hole pattern providing sufficient mechanical support, and improved maximum power density by low resistance	[12]
N-212 Perfluoropolyether (PFPE) as a moulding material	Prism shaped micropatterned membrane/soft lithography	Water management, good catalyst utilization, enhanced interfacial properties with low resistance	[17]
N-212, Stainless steel as a moulding material	250, 500, and 635 meshed microchannels/soft lithography	Extended three phases boundary and large surface area	[18]
N-212	Multiscale Nafion/soft lithography	Low membrane resistance, large electrochemical surface area, good stress-strain, and stress distribution	[13]
N-117	Nano pillar pattern(500–1000 nm)/soft lithography	Facilitate protons transportation by enhancing the catalyst utilization and high pattern fidelity	[19]
N-212	Nano lines pattern (300 nm)/electron beam lithography-dry etching	Facilitated proton transportation and high pattern fidelity	[20]
N-212	Lawn-like nanopattern(20–200 nm)/ion beam bombardment	Low membrane resistance requires low catalyst loading with enhanced catalytic activity	[21]
N-212	Grass-like microstructure patterns/plasma treatment	Plasma treated membranes possessed reduced ohmic resistances and superior transport chemistry	[22]
N-212	Blind micropores with a critical dimension of 2 μm and 5 μm pitch/electron beam lithography	Exhibited significant methanol crossover with lower ohmic resistance and Tafel slope for better performance	[3]
N-212	Micropatterns overlaid on the nanopatterns/creep-assisted sequential imprinting	10% higher performance than the conventional one attributed to low resistance in mass transport due to unique cone-shape morphology by creep-recovery effects and improved interfacial surface area	[14,15]

were utilized for this purpose. The electrospinning method was used to achieve the fibrous morphology of the desired component. The PFSA served as a proton transporter while the PVDF reinforced the mechanical properties, as an electrospinning carrier polymer for PFSA and a hydrophobic chargeless component to control PFSA swelling. The matrix of Nafion and PVDF were mixed in various volume fractions (ranging from 0.30 to 0.65). The fibrous Nafion embedded PVDF (N(fibres)/PVDF) demonstrated efficient $\text{Br}_2/\text{Br}_3^-$ barrier characteristics, e.g., the N(fibres)/PVDF product with 40 vol% Nafion having 48 μm thickness had comparable area-specific resistance to Nafion-115 (0.13 $\Omega\text{ cm}^2$). However, the steady-state $\text{Br}_2/\text{Br}_3^-$ crossover flux was low (3.0 times almost) than Nafion-115 [32,33]. These modifications lead to superior water adsorption of almost 12%, which improved the overall electrochemical performance of the device as indicated by the electrochemical impedance spectroscopy. The modified membrane demonstrated a steady output voltage above 0.21 V (96.3% improved) compared to the unmodified membrane setup. The chemical oxygen demand (COD) removal rate for molasses wastewater was 66.7% (75.1% improved). Moreover, the stability of the cell is also enhanced due to the robust mechanical characteristics of the PVDF.

Likewise, based on the type of application, Nafion can be modified with inorganic nanoparticles. For example, a TiO_2 /Nafion composite membrane was engineered by transporting the layer of TiO_2 from the porous TiO_2/Si wafer to Nafion membrane using the spin coating technique. A controlled thermal imprinting step follows this. This method is found useful in minimizing the filler agglomeration, which usually occurs in conventional drop-casting and solvent evaporating techniques. Thus, water is retained within the hygroscopic TiO_2 -

layers. In the next step, the composite membrane was subjected to patterning into prism shape, which enhanced the interfacial surface area of these membranes (steps are given in Fig. 4D). These modifications improve the fuel generation efficiency of Nafion-211 membrane-based fuel cells under low humidity and higher temperature [16]. The summary of the synthesis, membrane fabrication and improved features of Nafion based composites is provided in Table 2.

5. Conclusion and future perspectives

In this review, we have explained the strategies to enhance the performance of Nafion membrane within energy generating systems. We have aimed at two primary approaches. At first, a more physical treatment that focused on nano and micropatterning through plasma treatment, electron beam, lithograph soft lithography, and creep-assisted sequential imprinting were discussed with examples. The nano and micropatterning are widely reported in the literature. However, multiscale patterning is quite challenging due to the co-existence of complex geometries that lead to various energy barriers between microscale and nanoscale patterns and high costs. Secondly, composite formations with various materials, such as graphene and their oxides, CNTs, PVDF, and TiO_2 , were explained with respective examples. The modification with various composite materials imparts characteristics such as enhanced chemical, thermal and mechanical stability, and improved conductivity. With improved features, the modified Nafion can be utilized in long term commercial applications to generate energy. The latest PEM fuel and electrolyzer cells employ Nafion membranes to effectively control the proton exchange across and improve the device's overall efficiency.

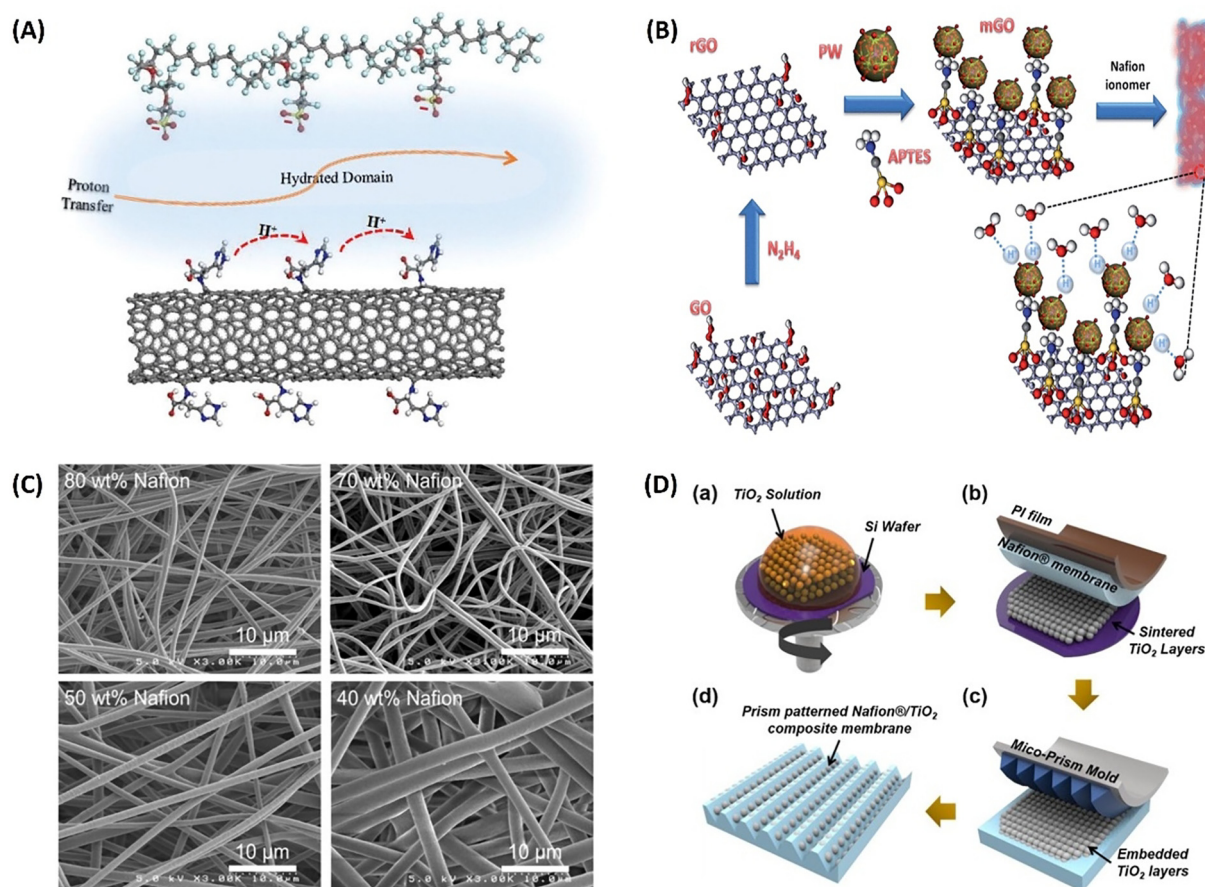


Fig. 4 Schematics of (A) the H⁺ transfer in CNT–Nafion membrane via hydrated domain (Blue circle: N, yellow circle: S, red circle: O, grey circle: C, and white circle: H) [6]. Copyright 2017, Taylor & Francis Group. (B) Fabrication of the phosphotungstic acid coupled with a covalently modified reduced graphene oxide with 3-aminopropyl-triethoxysilane (APTES) and Nafion composite membrane [30]. Copyright 2015, The Royal Society of Chemistry. (C) SEM images of nanofibrous PVDF loaded Nafion electrospun mats [32]. Copyright 2017, Elsevier. (D) A fabrication method of prism-shaped TiO₂/Nafion composite membrane composite (a–d) [16]. Copyright 2020, Elsevier.

Although substantial advancements have been realized in modifying Nafion membranes for energy-related applications, few critical recommendations are worthy of careful consideration. The formation of strong oxidizing and reacting peroxides, superoxides, OH species, and reactive metal ions (Fe⁺² and Cu⁺² etc.) within the electrolytic medium could deteriorate the Nafion structural and chemical integrity. The active ions and free radicals could attack active C–F, C–O and C–S bonds of Nafion and impart decay [36]. Due to these reactions, the gas permeability and proton conductivity characteristics of the device are severely affected. Therefore, strategies should be designed to improve the mechanical as well as chemical properties of Nafion. Multiscale patterning is one way to induce robustness. However, multiscale patterning is always a considerable challenge as multi-steps are involved, and improper patterning could cause mechanical errors in the structure of Nafion such as creep, wrinkles, cracks (pinholes) and delamination. This will result in the mechanical degradation of Nafion membrane that negatively impacts the device performance. Therefore, various parameters should be carefully optimized in these cases, such as selecting a suitable struc-

tural design (mold) and avoiding uneven compression, temperature, and humidity changes.

Although the active surface area of Nafion-based membranes is already improved to a fair level, the proton transport (at a relatively lower humidity) requires further improvement. One solution to this issue is to select suitably conducting and large surface area materials such as metal–organic frameworks (MOFs). The MOFs can offer multi functionalities to enhance the adsorption/desorption, transport, and proton conductivity properties of Nafion to an improved level. The ease of functionalizing MOFs can efficiently improve the proton conductivity, as also reported by Wang et al [37]. They determined that NH₃ modified Zn-MOFs offered 5 times more proton conductivity than unmodified Nafion due to collaborative host/guest hydrogen bonding aptitude within H₂/O₂ fuel cell. Similarly, ZIF-8 and polyacrylate carboxyl microspheres (PCMs) embedded in Nafion matrix endorsed the proton conductivity to 0.24 S cm⁻¹. The enhancement is attributed to the 3D microsphere morphology of NPs that increase their dispersion within the Nafion matrix and improve the conductivity [38].

Table 2 Fabrication techniques for generating hybrid Nafion structures.

Nafion based modified materials	Fabrication methods	Membrane fabrication details	Favourable properties	Ref.
Histidine functionalized CNTs/Nafion	Dry cast method	Imidazole functionalized 0.5 wt% CNTs were suspended in DI water and was added to 5 wt% Nafion solution. The resultant mixtures were cast in Petri dishes, and membranes were obtained after drying at 70 °C for 12 h. In the sulfonation step, the membranes were boiled in 3 vol% hydrogen peroxide and 0.5 M sulfuric acid, followed by washing and drying.	The proton conductivity properties of the fabricated membranes improved as the power density of the imidazole-CNTs/Nafion membranes was 3-times more than pristine Nafion membranes. Also, the conductivity of Nafion/Im-CNTs remained at a nearly constant value until 120 °C.	[6]
SWCNTs/Nafion-117 composite films	Photolithography methods	The interdigitated electrode was produced by e-beam evaporating 200 nm Pt on a layer of silicon dioxide thermally grown on top of a silicon wafer. The dispersion of the SWCNTs was conducted using purified SWCNTs powder in a 0.5 wt% Nafion-117 solvent solution.	Nafion functioned as a matrix to give stable and homogeneous cast thin film. The resistance boosts considerably with a rising methanol concentration (0.5 M → 4 M).	[28]
MWCNTs/Nafion magnetic aligned sulfonated MWCNTs/Nafion composite membranes	Ultrasonic assisted wet chemistry synthesis	1, 3, 5 wt% of sulfanilic acid group-functionalized MWCNTs within 5 wt% Nafion solution having a suitable anisotropy and in-plane magnetic field	Enhanced anisotropic mechanical and proton conductive properties, a reduced water absorption capacity. The magnetic behaviour and sulfonic groups assist the proton conduction.	[34]
Polyoxometalate coupled graphene oxide–Nafion composite membrane	Ultrasonic mixing and casting	PW-mGO or mGO was impregnated into Nafion ionomer with a mass ratio of 1%. The composite membranes were prepared in a glass Petri dish and dried at 120 °C for 5 h.	The composite membrane was found efficient for proton conductivity at a lower RH. The power density for the hybrid reached 841 mW cm ⁻² at 80 °C under 20% RH showing 4-folds enhancement due to lower ohmic resistance.	[30]
Monolayer graphene-Nafion-212 sandwich membrane	Spin-coating deposition	Nafion ionomer was spin-coated on the graphene/copper foil surface. The deposited copper foil was dissolved in FeCl ₃ containing solution, which released Nafion ionomers/graphene film. In the next step, the film was transferred onto Nafion-212 membrane. Finally, another Nafion-212 membrane was hot-pressed onto the Nafion/graphene film to obtain the sandwich.	The methanol crossover is reduced by 68%. The proton conductivity is only compromised by 7% after modification. Graphene provided exceptional mechanical support to Nafion.	[35]
Electrospun Nafion/PVDF single-fibre blended membranes	Electrospinning	Dual nanofiber mats (made of Nafion perfluorosulfonic acid (PFSA) ionomer and PVDF) were used in electrospinning to achieve fibrous morphology. The matrix of Nafion and PVDF were mixed in various volume fractions (ranging from 0.30 to 0.65).	The PFSA served as a proton transporter while the PVDF reinforced the mechanical properties. The fibrous Nafion embedded PVDF showed good Br ₂ /Br ₃ barrier characteristics. The product with 40 vol% Nafion having possessed comparable area-specific resistance to Nafion-115.	[32,33].
TiO ₂ /Nafion-211 composite membrane	Layer transfer method followed by patterning	Commercial TiO ₂ pastes were diluted in ethanol at weight ratios of 1:1 and 2:1 (ethanol:TiO ₂ paste), and the prepared TiO ₂ solution was sonicated for 20 min to obtain a uniform dispersion of TiO ₂ NPs and polymer binders in ethanol. The Si wafer is used as a support for layer formation. This layer is then transferred to Nafion-211.	The synthesis method is valuable to minimize the filler agglomeration. The water is retained within the hygroscopic TiO ₂ layers. The prism shape patterning enhances the interfacial surface area of the hybrid membrane. Modifications lead to improved fuel generation efficiency of Nafion-211 membrane-based fuel cell under low humidity and elevated temperature.	[16]

Add to the above, the operating conditions of the device should be selected at an optimized scale to lengthen the Nafion life for long term applications. For example, under typical automotive operating conditions, high humidity fluctuation could lead to high residual tensile stress that causes strong mechanical failure [39]. Therefore, controlling the humidity cycle fluctuation is a very important parameter to enhance the life cycle of Nafion and the device. Electrode selection is always critical in devising electrochemical cells. Usually, those electrodes should be avoided, which can corrode quickly and generate active ions such as Fe^{+2} and Cu^{+2} . Similarly, halide-based electrolytes are known for etching the surfaces, so they should be avoided to protect the Nafion membrane surface. Lastly, a more challenging task is the existence of the exact module and precise theory that could explain the in-depth structure of Nafion membranes after various modifications are still missing. Therefore, the first principle and advanced molecular dynamics calculations should be applied to such systems to identify various parameters. Computational analyses will help us estimate optimized structures even at the multiscale level. Massive efforts are still needed to understand the mass transport mechanisms in modified Nafion systems as various modifications lead to immense structural and functional changes in the Nafion membrane.

CRedit authorship contribution statement

Ibrahim Khan: Methodology, Validation, Figure drafting, Literature survey, Writing - original draft. **Ju Hyun Lee:** Figure drafting, Literature survey, Figure permissions. **Junyong Park:** Figure drafting, Literature survey, Figure permissions. **Sanghyuk Wooh:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing - review & editing.

Conflict of interest

The contributing authors disclosed no conflict of interest.

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