A review on ion-exchange nanofiber membranes: properties, structure and application in electrochemical (waste)water treatment

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CONFLICT OF INTEREST

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GRAPHICAL ABSTRACT



ABSTRACT

In view of today's challenges in clean water depletion and wastewater management, electrochemical water treatment processes are increasingly applied for e.g. desalination of brackish water, recovery of resources and energy production from waste streams, and disinfection of wastewater. These electrochemical processes typically make use of an ion-exchange membrane in between the anode and cathode. The choice of material for this membrane is crucial for the performance of the cell and often its performance is the key bottleneck. Over the last decade, research has been focused on the production

of ion-exchange nanofibers as membrane material due to their outstanding ionic properties as a result of their specific morphology. Nanofiber membranes are known to have a large specific surface area, flexibility, high porosity and interconnected pores. Different strategies are applied for the production and structural design of these ion-exchange nanofiber membranes, which are discussed in this review. Nanofibers with an ion-exchange functionality can be produced by either pre- or post-functionalization methods, combined with electrospinning. Depending on the application, these nanofiber mats can be used as such, or further membrane processing is possible to improve the dimensional stability, typically by adding a pore-filling matrix in between the nanofibers. Eventually, the current state of research on ion-exchange nanofibers in electrochemical separation and degradation applications is discussed. The many examples highlighted in this review prove the potential of nanofibers as ion-exchangers and provide insights for future research in this area.

KEYWORDS

lon-exchange membranes, nanofibers, electrospinning, electrochemical separation, wastewater treatment

1. Introduction

The availability of clean drinking water and the safe disposal of wastewater are major concerns in today's society. Globally, over 2 billion people resort to contaminated drinking water sources, resulting in the transmission of many diseases [1]. This contaminated water is often a result of the direct disposal of wastewater in fresh water bodies, especially in third world countries. Furthermore, due to the increasing population and water demands, it is estimated that by 2025 half of the world's population will be living in water-stressed areas [2]. To tackle these problems, membrane separation processes such as ultrafiltration and reverse osmosis are extensively used in water filtration and purification applications due to their high efficiency and flexibility [3]. However, increasing environmental awareness and strict demands towards water quality have required the development of more advanced technologies such as electrochemical water treatment processes [4]–[7].

These processes find their use in applications such as desalination of brackish water, chemical oxidation/disinfection of wastewater and recovery of resources from waste streams [8], [9]. The use of electrochemical processes in water treatment extends towards energy applications as well, for example for the production of energy from organic pollutants in wastewater, which is called a microbial fuel cell [10]. All these processes commonly make use of an ion-exchange membrane as semi-permeable separation barrier and the performance of this membrane is crucial for the process efficiency [11]–[13].

These ion-functionalized materials should be permeable towards counter ions but impermeable towards co-ions, thus creating a permselectivity [14]–[16]. Ion-exchange membranes can typically be divided into two categories, depending on their ion selectivity. Cation exchange membranes (CEM) contain negatively charged functional groups such as $-SO_3^-$, $-COO^-$, $-PO_3^{2-}$, and allow passage of cations while rejecting anions. Anion exchange membranes (AEM), on the other hand, contain positively charged functional groups such as $-NR_3^+$, $-NR_2H^+$, and allow passage of anions while rejecting cations (Figure 1) [11], [17], [18].



Figure 1: The use of an ion-exchange membrane in electrochemical setups: a) CEM with negatively charged groups allowing passage of cations, b) AEM with positively charged groups allowing passage of anions.

Depending on the application, the ion-exchange membrane needs to possess several specific properties. For desalination applications, the membrane should have a high selectivity, excellent mechanical properties and good chemical resistance [19]. For fuel cell applications, on the other hand, the membrane should act as a physical barrier with high dimensional stability, low permeability and high selective proton conductivity [20]. The application of ion-exchange membranes goes beyond electrochemical processes as well. For example, they can be used for heavy metal ion removal from wastewater streams. In this case the membrane should have a high selectivity and good adsorption/desorption efficiency with fast ion-exchange rates [19]. Over the last few years, ion-exchange membranes are being considered in biomedical applications as well, such as drug delivery and wound healing [21], [22]. It is clear that the ion-exchange membrane should be designed in such a way that it has excellent properties in ion-exchange performance as well as physical performance dedicated to each application.

Research on the development of ion-exchange membranes dates back to 1890 with the work of Ostwald (Figure 2). The first large-scale use of an ion-exchange membrane was mentioned in the late 1950s for the desalination of brackish water [23]–[25]. The following decades, much research has been performed into the improvement of these membranes. A large breakthrough was made through the development of DuPont's CEM Nafion® in the 1970s [26], [27]. Nafion® is a perfluorosulfonic acid (PFSA) based membrane and is used extensively in a wide range of electrochemical applications [28], [29]. The phase-separated morphology of the hydrophobic fluorocarbon backbone and hydrophilic ionic side chains results in excellent mechanical properties and high chemical resistance combined with superior ion-exchange properties [30], [31]. These characteristics form the basis of its popularity in commercial use. Despite these interesting properties of Nafion®, the biggest disadvantage of the material is the high cost and reduced performance at lower humidity, which is mainly a significant problem for proton exchange membrane hydrogen fuel cells (PEMFC) [32]. Furthermore, classical ion-exchange membranes used in electrochemical wastewater processes typically suffer from scaling and fouling due to their dense structure [33]–[36]. Additionally, many membranes also show significant degradation over time, which reduces their performance [37]–[42].



Figure 2: Time line of ion-exchange membrane and ion-exchange nanofiber development.

Much research on new ion-exchange membranes has been done the last few decades to further improve the ionic and physical properties [26], [43]. A recent promising alternative, which has gained increased attention over the last years, is the use of ion-exchange nanofibers (Figure 2, Figure 3). Nanofibers are a class of fiber materials with diameters ranging from 50-500 nm and a length of several km [44]–[46]. Nanofibers have distinct properties such as high molecular orientation, high surface to volume ratio, high porosity and interconnected three-dimensional structure, which are beneficial for the ion-exchange performance [47]–[49]. Furthermore, by the electrospinning process, nanofibers are deposited into a non-woven membrane consisting of nanofibers within which an uniaxial alignment of the polymer chains is present [50]. This provides enhanced mechanical strength and interconnected ion conductive channels which facilitates ion conductivity [51]–[53]. Improved fouling resistance of nanofibers in wastewater treatment applications has been reported as well [54]–[59].



Figure 3: Ion-exchange nanofibers produced by the electrospinning process. For further mechanical enhancement, the nanofibers are often processed by densification or incorporated in a matrix material. In case of the latter, the nanofibers can be used as reinforcement, as ion-exchangers or as both. These ion-exchange nanofiber membranes show high potential in advanced electrochemical separation applications.

Research on ion-exchange nanofibers has been progressively done over the last years also in the context of electrochemical separations to tackle the current clean water shortage problems. Classical ion-exchange membranes are often not suitable for these applications, due to their high resistance, excessive fouling and often poor stability. Nanofibers show many benefits in these applications, such as improved selectivity, higher conductivity, higher Coulombic efficiency and anti-scaling properties. In this review, a critical assessment is given about the production, properties and structure of ion-exchange nanofiber based membranes (Figure 3). The ionic groups can be introduced on the nanofibers by pre-functionalization, before electrospinning the polymer, or by post-functionalization, after electrospinning the polymer. The current state of research on ion-exchange nanofibers is focused on two distinct membrane processing types: stand-alone ion-exchange nanofibers in the form of a non-woven web or embedded nanofibers in a matrix. Current research on stand-alone nanofibers is mostly focused on applications where a high surface area and/or porosity is required, such as heavy metal ion removal from water streams. These processes benefit from an enhanced volumetric productivity resulting from

the porosity of the membranes and improved ion uptake due to the high surface area of the nanofibers [60], [61]. Embedding the nanofibers in a pore-filling matrix to obtain a composite ion-exchange membrane has originally been encouraged by the need of more physically and ionically stable membranes in PEMFC applications but can also show significant benefits in electrochemical water treatment applications [51]. In this case the nanofibers can function as reinforcement and/or as ion-exchanger. In this review, a critical assessment is given on both processing types. Additionally, the current state and future potential of ion-exchange nanofibers in important advanced electrochemical separation applications is discussed [51].

2. Ion-exchange nanofibers

2.1 Production methods

Due to its simplicity, versatility and easy upscaling, continuous solvent electrospinning is the most common technique used in the industry to produce nanofibers from numerous materials including organic polymers, ceramics, metals and composites [62]–[64]. With this process, the nanofibers are typically deposited as a non-woven membrane with high porosity, high surface area and interconnected pores [65]–[68].

The solvent electrospinning process makes use of the electrostatic repulsion of surface charges in the polymer solution in order to uniaxially elongate a viscoelastic jet [69]. The electrospinning setup consists of three major components (Figure 4): the high-voltage power supply, the spinneret with a needle containing the polymer solution and a grounded collector [69]. A syringe pump feeds the polymer solution at a controllable rate through the needle, which is connected to the high voltage power source. By applying a high voltage (~kV), the solution gets charged and experiences two types of electrostatic forces: electrostatic repulsion between surface charges and Coulombic forces due to the external electric field. These forces result in the distortion of the liquid into a so-called Taylor cone at the tip of the needle. When the electrostatic forces overcome the surface tension of the polymer solution, a jet is formed and ejected from the solution. This jet undergoes stretching and whipping while the solvent evaporates, resulting in an elongated thread with a significantly reduced diameter. This thread is then collected on the grounded collector as a randomly oriented nanofibrous membrane [67], [69]–[72]. A stable electrospinning process is highly dependent on several parameters such as polymer concentration and viscosity, applied voltage, flow rate, distance between needle and collector,...



Figure 4: a) Electrospinning setup. Applying a high voltage supply results in the elongation of the polymer solution resulting in the formation of nanofibers on the collector [69]. b) SEM image of a typical nanofibrous membrane.

As introduced before, ion-exchange nanofibers can be produced in two different ways: by directly electrospinning of an ion-functionalized polymer solution (pre-functionalization) or by electrospinning of a neutral polymer solution which is post-functionalized to obtain ionic groups.

2.1.1 Pre-functionalization

Even though the electrospinning of neutral polymer solutions is studied extensively, electrospinning of charged nanofibers is more novel and difficult [73]. Electrospun polyelectrolyte nanofibers commonly have a significantly lower fiber diameter compared to their neutral opponent [74], [75]. Furthermore, due to the polymer chains containing similarly charged groups, charge repulsion can take place, resulting in insufficient macromolecular entanglements [76]. This leads to instable electrospinning with formation of droplets and beads instead of nanofibers [52]. One example is the electrospinning of PFSAs such as Nafion®, which have been given a lot of attention in the literature [77]-[81]. Many researchers have tried to electrospin PFSAs into nanofibers but with limited success. An overview of the solution properties for stable electrospinning of PFSAs reported in literature is given in Table 1, with the obtained fiber diameter and ionic conductivity of the material after electrospinning as well. Due to hydrophobic interactions of the perfluorocarbon backbone and ionic interactions of the side chains, PFSA solutions form aggregates. These aggregates limit chain entanglements which inhibit electrospinning [52]. One way to overcome this is by the addition of a high molecular weight polymer which serves as a carrier and breaks these aggregates. For example, Bajon et al. produced Nafion® nanofibers with the aid of different carrier polymers such as poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP). They found that the addition of PVP mixed with alcohol to the Nafion solution resulted in the most optimal electrospinning process [79]. Poly(acrylic acid) (PAA) has also been reported as carrier polymer, but high concentrations are needed to obtain a stable electrospinning process [78]. Generally, due to the addition of a carrier polymer during electrospinning, the fraction of ion conductive material is reduced within the nanofiber. While the ion conductivity of bulk Nafion® films is 0.1 S cm⁻¹, the reported conductivity is lower for most Nafion® nanofibers (Table 1) [82]. One exception is reported by Dong et al. who obtained super proton conductive high purity Nafion® nanofibers with the addition of only 0.1% carrier polymer [83]. An ion conductivity as high as 1.5 S cm⁻¹ is reported, resulting from the absence of high amounts of carrier polymer.

Perfluoro- sulfonic acid	Concentration (wt%)	Carrier polymer	Concentration (wt%)	Solvent carrier polymer	Fiber diameter (nm)	lon conductivity (S cm ⁻¹)	Ref
Nafion®	10	PVA	5	Water	-	-	[79]
Nafion®	10	PVP	10	Alcohol	-	-	[79]
Nafion®	5	PAA	≥12	3/1 Isopropylalcohol/water	90-600	-	[78]
Flemion	8.3	PVA	9	Water/DMAc	183-436	-	[81]
Aquivion	10 20	PEO	1 0.75	DMAc	250-300	0.097 (95%RH, 80°C)	[84]
Fumion	10 20 40	PEO	2 2 2	DMAc	350-600	0.058 (95%RH, 80°C)	[84]
Nafion®	5-25	PEO	1	2/1 propanol/water	161-730	-	[85]
Nafion®	5	PVA	2	-	80-140	0.01 (water, RT)	[86]
Nafion®	5	PEO	1	-	80-180	0.0059 (water, RT)	[86]
Nafion®	5	PVA	10	Water	68-163	-	[87]
Nafion®	5	PEO	0.1	Methanol	400	1.5 (90%RH, 30°C)	[83]

Table 1: Solution parameters of stable perfluorosulfonic acid electrospinning processes.

In view of the search of more ecological alternatives, the pre-functionalization method is often applied for other polymers as well, such as sulfonated polystyrene (PS) and sulfonated poly(ether ether ketone) (SPEEK), but in general, much attention needs to be given to optimize the solvent system and electrospinning conditions [52], [74], [88].

2.1.2 Post-functionalization

Post-functionalization is usually done when a high ion loading on the surface of the fibers is required, for example for adsorption/desorption of metal ions from a waste solution. The amount of ionic groups present in an ion-exchange membrane is typically indicated by the ion-exchange capacity (IEC). With post-functionalization methods, a high IEC can be obtained by maximizing the degree of functionalization, and overall the IEC of the membrane can more easily be tuned. This is also a consequence of the high surface-to-volume ratio in nanofibrous membranes, which allows for many available sites for post-functionalization.

Polymer	lonic group	Functionalization method	Functionalization time (min)	IEC (mmol g ⁻¹)	Ref
PS	$-SO_{3}^{-}$	98% H ₂ SO ₄ + Ag ₂ SO ₄ (RT)	30	3.74	[89]
PS	$-S0_{3}^{-}$	80% H ₂ SO ₄ (60°C)	120	1.34	[90]
P4VP	$-\mathrm{NH}_3^+$	40 wt% dibromopropane/ n-hexane	0.5	0.78	[90]
PS	$-S0_{3}^{-}$	1) 7.5 wt% Divinylbenzene (90°C) 2) 95% H ₂ SO ₄ (60°C)	2) 200	2.53	[91]
PS	$-S0_{3}^{-}$	1) 98% H ₂ SO ₄ /formaldehyde + Ag ₂ SO ₄ 2) 98% H ₂ SO ₄ + Ag ₂ SO ₄ (70°C)	1) 10 2) 30	2.86	[92]
PAN	-C00-	2N KOH (70°C)	30	2.39	[93]
Carbon	$-S0_{3}^{-}$	Fuming H_2SO_4 (15 wt% SO_3) (90°C)	600	2.94	[94]

Table 2: Overview of post-functionalization methods described in literature to obtain ion-exchange nanofibers.The reported methods and values are based on the optimal IEC obtained.

An overview of reported ion-exchange nanofibers produced by the post-functionalization method is shown in Table 2. The conditions are based on the maximum IEC that was obtained in all cases. Most ion-exchange nanofibers, produced by post-functionalization methods, are limited to carbon, poly(4-vinylpyridine) (P4VP), poly(styrene) (PS) and poly(acrylonitrile) (PAN) because they allow an easy and straightforward functionalization method [89]–[91], [93], [95]. However, post-functionalization processes might damage the fiber structure. For example, An *et al.* investigated the effect of sulfonation time on the IEC of PS nanofibers [89]. A maximum IEC of 3.74 mmol g⁻¹ was reached after 30 min of sulfonation, however, the IEC decreased again for longer sulfonation times due to shrinking and dissolving of the fibers. The IEC was slightly higher for the PS nanofiber compared to a sulfonated PS coated glass microfiber (3.61 mmol g⁻¹) [95]. To improve the mechanical stability of the nanofibers, crosslinking is often performed [91], [92]. However, at high crosslinking levels, the IEC can decrease significantly due to the limited availability of sites for sulfonation as a result of the crosslinking. The main challenge for post-functionalization methods is thus to find the right conditions in order to obtain the optimal values for both IEC and mechanical stability of the fibers.



Figure 5: Advantages and disadvantages of both pre- and post-functionalization methods for producting ionic nanofiber membranes.

Generally, both pre- and post-functionalization methods are often applied and the choice of method is mainly determined by the type of polymer that is used and its ease of electrospinning. However, this choice is often made arbitrary, as many ionic polymers have proven to be producible into nanofibers by both pre- and post-functionalization methods. An overview of the general advantages and disadvantages of both methods is illustrated in Figure 5. Overall, the main advantages of using the pre-functionalization method is the reduction in steps during production and the creation of interconnected ionic pathways along the fiber length as a result of electrospinning [83]. However, the difficulty of electrospinning ionic polymers remains a major issue, often demanding the need of additional carrier polymers, which in their turn reduce the ionic conductivity of the electrospun nanofibers. Post-functionalization methods eliminate this issue, making it a very interesting production method with often very high IEC values. However, the post-functionalization steps are often very harsh for the nanofibers, resulting in damaged fibers and reduced membrane robustness. In conclusion, more research should be performed on searching the optimal conditions to bring the production of ion-exchange nanofibers to its maturity.

2.2 Ion-exchange properties

The size effect of ion-exchange nanofibers has been studied by several researchers. It is generally observed that properties such as ion-exchange capacity and ionic conductivity are enhanced with decreasing fiber diameter. Imaizumi et al. studied the influence of nanosize on the ion-exchange capacity for sulfonic acid post-functionalized carbon nanofibers [94]. Carbon nanofibers with varying diameter were prepared and sulfonated using the same conditions for all fibers and the resulting IEC was measured. With reducing fiber diameter, the IEC increases exponentially due to the surface area effect of the nanofibers: more surface sites are available for functionalization, thus increasing the overall amount of ion-exchange groups. For comparison, the IEC of a commercial Nafion® film is ±0.9 mmol g⁻ ¹ while a nanofiber with diameter 80 nm had an IEC of 2.94 mmol g⁻¹ [82], [94]. Furthermore, the ionic conductivity also increases significantly within a single fiber at lower diameter. This was studied by Dong et al. on a high purity Nafion® nanofiber with only 0.1 wt% added carrier polymer: a conductivity of 1.5 S cm⁻¹ was observed for a fiber with a diameter of 400 nm (Figure 6) [83]. The preferential nanoscale alignment of interconnected ionic domains along the fiber length results in ion conductive channels which are more pronounced at lower fiber diameter, thus enhancing the ion conductivity of the fiber. This superior behavior of nanofibers is generally observed for other materials and/or production techniques as well [96]-[102].



Figure 6: Influence of fiber diameter on proton conductivity in high-purity Nafion® nanofibers. Reprinted with permission from [83]. Copyright 2022 American Chemical Society.

These observations lead to the conclusion that ion-exchange properties, such as IEC and ion conductivity, are improved significantly by the use of nanofibers, both produced by pre- or post-functionalization methods. These improvements compared to bulk ion-exchange materials are a direct result of the high specific surface area (resulting in high IEC) and high orientation of ionic domains along the fiber axis (resulting in a high ion conductivity).

The ion-exchange properties observed in nanofibers are extremely important and beneficial for electrochemical separation applications. A higher ion conductivity means that the membrane exhibits

lower internal resistance, resulting in a high process efficiency. Nevertheless, several other properties such as mechanical stability, chemical stability and fouling resistance are of extreme importance as well. Therefore, the type of material should be chosen with care. Generally, polymeric ion-exchange nanofibers have been studied extensively due to their ease of production and often good mechanical properties [16]. However, they have a low thermal resistance and are susceptible to degradation in aggressive chemical conditions [37], [103]. The use of ceramic nanofibers can offer some interesting advantages such as increased thermal resistance and excellent chemical resistance, which is one of the key requirements in electrochemical separation cells [104]–[106].

Overall, the electrospun nanofibers are produced into a porous membrane, which has a loose, porous structure with insufficient mechanical stability for the envisaged end applications. Therefore, additional processing steps are usually necessary to enable application in e.g. fuel cells and electrochemical water treatment, which often require very low fuel and water cross-over, respectively.

3. Processing of nanofibers into robust ion-exchange membranes

3.1 The road to nanofiber membranes

The high cost, high ecological impact, low thermal resistance and reduced performance at low humidity of the commercial Nafion® ion-exchange membrane are the main motives for research on new, nonfluorinated polymer membranes such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(arylene ether sulfone) (SPAES), sulfonated poly(imide),... [47], [107], [108]. They have the advantages of low cost, more ecological production and good mechanical and thermal properties [28]. However, in these polymer structures the sulfonic ionic domains are distributed closer along the backbone, resulting in poor phase separation between the hydrophobic backbone and hydrophilic side chains, with the creation of dead-end proton conductive channels [109], [110]. As a consequence, the ionic conductivity of these non-fluorinated polymers is typically much lower than for PFSAs. In order to achieve a higher ion conductivity, polymers with a high degree of functionalization (thus high IEC) are aimed at. However, these polymers are highly hydrophilic, resulting in a high water uptake. The presence of water in the membrane is beneficial for the ion conductivity but, on the other hand, extreme water uptake leads to excessive swelling of the membrane [110]-[112]. This in turn results in deteriorated mechanical stability [113]. Therefore, it is clear that in non-fluorinated polymers there is a trade-off between IEC and mechanical stability as a result of the high hydrophilicity of the membranes and their excessive swelling. Lowering the IEC reduces the hydrophilicity and consequently the swelling. This trade-off has been the limiting factor of these materials for commercial use, especially in electrochemical applications where membrane stability is extremely important. As a result, new research focuses on the elimination of this trade-off.

Nanofibers offer an excellent choice of material because of their superior ion-exchange properties (Figure 6) and enhanced mechanical properties due to chain alignment within the fibers. These nanofibers can be used as a non-woven mat, which offers a high porosity and surface-to-volume ratio. In applications where as many ionic sites as possible need to be reached for efficient interchange and/or adsorption of ions, this non-woven mat structure is greatly beneficial [114], [115]. On the other hand, the nanofibers can be embedded in a matrix, creating a composite ion-exchange nanofiber membrane consisting of two different phases (Figure 3). In this case the trade-off between IEC and mechanical properties can be further improved: one phase is responsible for the IEC while the other retains the water swelling and provides mechanical stability [28], [116]. Nanofibers can be used both as ion-exchange phase or as reinforcement phase because they offer many benefits for both parameters. In general, for applications where dimensional stability is important and the membrane needs to act as a physical barrier with high ion conductivity, nanofiber composite membranes are an interesting choice of material.

3.2 Nanofiber mats as ion-exchange membranes

Generally, the use of non-woven electrospun mats in electrochemical applications is limited due to their low dimensional stability and loose structure, often resulting in an undesired cross-over of fuel (in fuel cells) or water [117]–[119]. Usually, efforts are made to improve this by implementing various processing steps to convert the nanofibrous mat into a more dense film structure. Crosslinking is often done to enhance the stability of the nanofibers in water [120], [121]. This is needed to obtain a dimensionally

stable membrane with a high IEC. However, little is mentioned in literature about the fuel and or water permeability through these nanofiber mats, which is an important parameter in electrochemical cells. This densification can also be achieved by hot-pressing or compacting the nanofibers to obtain a denser structure, and as such reducing the cross-over of fuel or water [122], [123]. Alternatively, the addition of graphene oxide (GO) nanoparticles on the nanofibers has been studied by some researchers and proved to be very effective in improving the dimensional, thermal and mechanical stability of the nanofibers while also enhancing the ion conductivity [124], [125]. This has been ascribed to the water retention ability of the GO nanoparticles. However, more research should be performed to substantiate this.

Porous ion-exchange nanofiber mats have a high potential in non-electrochemical applications, for example in biomedical applications such as drug delivery, wound healing and bone tissue engineering. This is a direct consequence of the high surface area and high porosity of the nanofiber membrane. This allows for a more efficient drug loading and fast and efficient performance [22], [126]–[129]. Additionally, ion-exchange nanofiber mats can be beneficial for the use in ion chromatography. The classical packed bed chromatography requires a very low flow rate of the feed solution and long residence times to achieve high binding levels, which both reduce the performance efficiency [130]. Both these drawbacks can easily be overcome by using ion-exchange nanofibers with their high surface area, high porosity and high adsorption capacities as a result of a high IEC [131]–[133]. Common materials such as ionfunctionalized cellulose, cellulose acetate, PAN, PS and chitosan nanofibers have already proven to be very effective in the adsorption of certain proteins, enzymes, bacteria and viruses [130], [131], [142], [134]–[141]. These, and other ion-exchange polymers also find their use in nanofiber membranes for the removal of dyes and heavy metal ions from waste streams (Figure 7) [60], [61], [114], [143]–[149], [150]–[157].



Figure 7: Heavy metal ion removal by polypyrrole functionalized PAN nanofibers. a) The adsorption mechanism relies on anion-exchange between the metal ion and Cl-, followed by reduction of the metal ion. b) Adsorption tests showed that most ions in solution were removed by the nanofiber membrane. Figure taken with permission from [146].

Overall ion-exchange nanofiber mats show interesting properties which allow them to be used in several advanced applications. They always result in improved efficiency compared to conventional ion-exchange membranes. However, for electrochemical separation applications, further enhancement is needed to assure dimensional stability and low cross-over. Therefore, the use of ion-exchange nanofiber composites is often considered.

3.3 Nanofiber composites as ion-exchange membranes

Generally, ion-exchange nanofiber composites can be divided into two categories: composites with nanofibers that act as reinforcement, in this case the matrix contains ionic functional groups for ion-exchange, and composites with nanofibers that act as ion-exchangers, in this case the matrix can act as both inert uncharged phase for mechanical stability or as charged phase (Figure 8) [158].



- Ionic functional group
- Figure 8: Different compositions of nanofiber composites as ion-exchangers (blue zone = matrix): nanofibers as reinforcement and nanofibers as ion-exchangers with a) an uncharged matrix or b) a charged matrix.

In all cases, the aim of research on nanofiber composites as ion-exchangers for electrochemical applications is to achieve a high ionic conductivity while maintaining dimensional stability. For comparison, Nafion® has an IEC of 0.9 mmol g⁻¹, an ion conductivity of 0.13 S cm⁻¹ (in water, 100°C) and a tensile strength of 20-40 MPa with a Young's modulus of around 250 MPa (50%RH, 23°C) [82], [159]. The ion conductivity of ion-exchange materials is commonly investigated as a function of temperature and humidity. The maximum ion conductivity of Nafion® is obtained in its hydrated state. Lowering the humidity sharply decreases the conductivity to ~10⁻⁴ S cm⁻¹ [160]. Research on nanofiber composites as ion-exchange membranes has been extensively done in the field of fuel cell technology, but could provide insights for future research in the field of electrochemical water treatment as well.

3.3.1 Nanofibers as reinforcement

The presence of nanofibers embedded in an ionic pore filling matrix can enhance the mechanical and dimensional stability of the ion-exchange membrane. The three dimensional interconnected nanofiber structure suppresses the expansion of the membrane when in contact with water by holding together tightly (Figure 9) [161], [162].



Figure 9: Improved dimensional stability of a composite ion-exchange membrane. The interconnected nanofibers suppress the swelling of the matrix. Figure adapted from [162].

This mechanical stability is only possible if a good compatibility between matrix and nanofibers is present. This compatibility can be achieved by using nanofibers with a similar hydrophilicity as the matrix, by incorporating very thin nanofibers, by using a dual electrospinning technique or by introducing ionic interactions [161], [163], [164]. Table 3 lists the mechanical and ion-exchange properties of nanofiber reinforced ion-exchange membranes currently found in literature. Even though many

researchers claim to be able to improve the dimensional and mechanical properties by using nanofibers, often a thorough investigation on these properties is missing.

Table 3: Overview of mechanical and ion-exchange properties of nanofiber reinforced composite ion-exchange membranes. The non-conductive nanofibers act as support in the charged matrix. *Dependent on thickness

Nanofibers	Matrix	lonic group	IEC (mmol/g)	Water uptake (%)	lon conductivity (S cm ⁻¹) (%RH,°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Ref
Polyimide	SPAES	$-SO_{3}^{-}$	2.3±0.3	35±3	0.17-0.20 (95,80)	>40	-	-	[161]
Polyimide	SPEEK	$-SO_{3}^{-}$	-	24±5	-	41±3	-	-	[165]
Polyimide	SPFEK	$-SO_{3}^{-}$	-	16-24	0.15 (100,80)	35.1 (wet)	32	-	[166]
PAN	SPAES	$-SO_{3}^{-}$	1.7	51	0.16 (water,80)	13.8±0.1	-	692±39	[162]
Cellulose	SPES	$-SO_{3}^{-}$	-	10-40	0.13 (-,80)	35-40	-	-	[167]
PSU	Aquivion	$-SO_{3}^{-}$	1.0	48	±0.20 (95,110)	18±1	59±19	385±14	[168]
PPS	Nafion	$-SO_{3}^{-}$	-	12-35	0.02-0.08 (water,RT)	16-23	-	444-624	[164]
PPS	Nafion	$-SO_{3}^{-}$	1.2	15	0.17 (80,80)	-	-	-	[169]
PVDF	Nafion	$-SO_{3}^{-}$	-	-	0.002 (-,65)	-	-	-	[170]
PVDF	Nafion	$-SO_{3}^{-}$	-	-	0.03-0.06 (water,25)	-	-	-	[171]
PVA	Nafion	$-S0_{3}^{-}$	-	-	0.03-0.06 (95,90)*	34.8-53.5	5.8-10.2	559-1198	[172]
PVA	Nafion	$-SO_{3}^{-}$	-	-	0.01 (95,70)	-	-	-	[173]
Pd-SiO ₂	Nafion	$-SO_{3}^{-}$	0.9	±45	0.13 (water,-)	-	-	-	[174]
CeO ₂	Nafion	$-S0_{3}^{-}$	-	23-27~	0.10-0.11 (100,80)~	-	-	-	[175]
PVDF	PS	$-SO_{3}^{-}$	1.5-2.0	100-550	-	-	-	-	[176]
PPO	SPPO	$-SO_{3}^{-}$	1.1-2.0**	30-70**	0.03-0.08 (-,RT)	-	-	-	[177]
Poly(trimethyl hexamethylene terephtalamide)	Poly(diallyl dimethyl ammonium chloride)/ sulfonated poly(2,6 dimethyl 1,4 phenylene oxide)	-S0 ₃	-	-	0.01 (water,-)	1.7-6.5 (100%RH)	70-90 (100%RH)	52-198 (100%RH)	[178]
TiO ₂	SPEEK	$-S0_{3}^{-}$	1.7	45	0.09-0.10 (water,70)	37-40	74-116	-	[179]

** Dependent on degree of functionalisation ~ Dependent on fiber volume fraction

Polyimide is known to have great mechanical properties and is, therefore, a good candidate for reinforcement [161], [165], [166]. Additionally, it has been reported by Lee *et al.* that the presence of polyimide nanofibers can enhance dimensional stability as well. Area swelling ratios (ASR) of ±5% and 7.5% were reported for polyimide reinforced SPEEK and SPAES membranes with water uptake (WU) of 24% and 35%, respectively, while pure SPEEK had an ASR of at least 30% [161], [165]. Furthermore, the polyimide reinforced SPAES had a maximum proton conductivity of 0.17-0.20 S cm⁻¹ (95%RH, 80°C). These results indicate that the introduction of nanofibers in a sulfonated matrix can enhance the dimensional stability of the sulfonated polymer while maintaining high proton conductivity, thus breaking the trade-off that is inherently present in non-fluorinated polymers. However, a comparison of the proton conductivity between the reinforced and non-reinforced membranes was missing. In most cases, the presence of the non-conductive reinforcement fibers reduces the ion conductivity compared to the pure conductive matrix material [162], [164], [166], [168], [170]–[173]. An exception has been reported by Xu *et al.* by using cellulose nanofibers in a sulfonated poly(ether sulfone) (SPES) matrix (Figure 8) [167]. First of all, the dimensional stability was improved compared to pure SPES with a minimum swelling

ratio of 5-10% obtained at 2% cellulose. Furthermore, the proton conductivity was enhanced as well with the introduction of cellulose nanofibers, with a maximum of 0.13 S cm⁻¹ (80°C) at 5% cellulose. This is 1.6 times higher than pure SPES. This increased proton conductivity can be described to the hydrophilic behaviour of the cellulose nanofibers: the hydroxyl groups on cellulose react with the sulfonic acid groups on SPES, resulting in an improved distribution of sulfonic acid groups along the nanofiber length and thus the creation of proton conductive channels (Figure 10). Additionally, a lower methanol cross-over was observed with increasing fiber content.



Figure 10: Cellulose nanofiber reinforced SPES ion-exchange membrane. a) The interactions between the hydroxyl groups on the cellulose and the sulfonic acid groups of the matrix result in ionic pathways for protons. b) The introduction of cellulose nanofibers resulted in decreased swelling ratio. c) The proton conductivity increases due to the addition of cellulose nanofibers, compared to pure SPES. Figure taken and adapted with permission from [163].

Alternatively, Thiam *et al.* investigated Pd-supported SiO₂ nanofiber reinforced Nafion® membranes [174]. The addition of hygroscopic compounds such as silica is known to aid in water retention, which facilitates proton mobility. As a result, their nanofiber reinforced membrane had a similar proton conductivity as Nafion® (0.13 S cm⁻¹ in water) even though the volume fraction of conductive material was reduced due to the presence of the fibers. Furthermore, a reduction in methanol permeability was also observed and ascribed to the interactions between the nanofiber and matrix with the formation of a swelling blockade, leading to a reduced electro-osmosic drag. The influence of the water retention behaviour of the SiO₂ nanofibers on the dimensional stability of the membrane was absent, however.

As mentioned before, the presence of non-conducting nanofibers often reduces the ion conductivity of the composite membrane, and in many cases the trade-off between ionic conductivity and mechanical stability remains an issue. Therefore, research on nanofibers as reinforcement in composite ion-exchange membranes is limited and more attention is given to ion-conducting nanofibers due to the interesting ion-exchange properties of nanofibers.

3.3.2 Nanofibers as ion-exchangers

Nanofibers in uncharged matrix

As detailed before, the morphology of nanofibers results in much higher IECs compared to their bulk material. This is advantageous for ion-exchange applications, and therefore, the use of ion-exchange nanofibers is investigated extensively. However, the full potential of nanofibers cannot be exploited because these extremely high IECs lead to excessive swelling of the material in water with poor mechanical properties as a result, even in nanofiber structures. The use of an inert uncharged matrix in which the nanofibers are embedded can control the swelling and can provide overall mechanical strength, allowing the ion-exchange nanofibers to have higher IECs than possible in homogeneous polymer membranes [85]. An overview of reported nanofiber composite ion-exchange membranes with an inert matrix polymer is given in Table 4.

 Table 4: Overview of mechanical and ion-exchange properties of charged nanofiber composite ion-exchange membranes. The matrix consists of an inert polymer.

* Dependent on fiber volume fraction

Nanofibers	Matrix	lonic group	IEC (mmol/g)	Water uptake (%)	lon conductivity (S cm ^{.1}) (%RH,°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Ref
Nafion	PPS	$-S0_{3}^{-}$	-	2-32*	0.008-0.065 (water,RT)*	21-29	-	566-852	[164]
Nafion	PPS	$-SO_{3}^{-}$	-	20-35	0.055-0.06 (water,25)	-	-	-	[180]
Nafion	PVDF	$-S0_{3}^{-}$	-	-	0.03-0.06 (water,25)	-	-	-	[171]
PS	PPS	$-NR_3^+$	1.3-1.6**	50-148**	0.007-0.04 (water,23)**	17 (dry) 22 (wet)	3 (dry) 5 (wet)	-	[181]
Crosslinked PS	PPS	$-NR_3^+$	1.7/2.0~	108/144~	0.0057/0.0065 (water,23)~	42-45 (dry) 14-17 (wet)	15 (dry) 45 (wet)	-	[182]
Crosslinked PS	PPS	-NR ₃ +/ Imidazo- lium	1.6-2.0~	130-200~	0.035-0.057 (water,23)~	40-45 (dry) 13-17 (wet)	8-11 (dry) 25-29 (wet)	-	[183]
PPO	PPS	$-NR_3^+$	1.2-2.8*,~	50-250*,~	0.02-0.068 (water,23)*,~	20-40 (dry) 3-15 (wet)	5-15 (dry) 10-25 (wet)	-	[184]
SPEEK	NOA 63	$-S0_{3}^{-}$	1.3-2.0**	52	0.049 (water,25)	-	-	-	[185]
SPAES	NOA 63	$-S0_{3}^{-}$	0.3-2.0*	20-180*	0.01-0.12 (-,25)*	28	-	-	[47]
SPAES/SP OSS	NOA 63	$-SO_{3}^{-}$	2.1	90	0.1 (95,30)	-	-	-	[186]
Nafion	NOA 63	$-S0_{3}^{-}$	0.9	10-20*	0.06-0.08 (water,RT)*	15-20	38-40	300-500	[85]
PFSA	NOA 63	$-S0_{3}^{-}$	-	10-50*	0.007-0.16 (80,80)*	10-12	20-50	162-271	[187]
PFSA/SPO SS	NOA 63	-S0 ₃ ⁻	-	-	0.498 (90,120)	-	-	-	[188]
PPO	PVA	$-NR_3^+$	0.4-1.4*	43-92*	11-89 (-,80)*	20 (wet)	15-130*	-	[189]

** Dependent on degree of functionalisation

~ Dependent on the degree of crosslinking

The uncharged matrix commonly exists of a hydrophobic inert polymer which acts as a physical barrier for swelling, similarly to reinforcement nanofibers discussed in 3.3.1. This physical barrier is only efficient when there is good compatibility between the two phases. Ballengee and Pintauro reported in 2011 a novel, simple and robust production scheme for compatible nanofiber composite membranes (Figure 11) [164], [180]. Starting from dual nanofiber mats produced by simultaneous electrospinning both ion-exchange material and inert matrix, the matrix phase is allowed to soften and fill the interfiber void space. They started from an electrospun mat of both Nafion® and PPS fibers. Applying pressure and a thermal annealing process led to the softening of the Nafion® fibers, resulting in a PPS nanofiber reinforced Nafion® membrane, which is an ion-exchange membrane with non-conductive nanofibers as mentioned in 3.3.1. On the other hand, by applying pressure, exposure to chloroform vapor and thermal annealing, the PPS phase softened and filled the voids in between the Nafion® fibers, resulting in a Nafion® nanofiber composite membrane with PPS as an inert polymer matrix. Thus, altering the processing steps, different membrane morphologies could be obtained (see also Figure 8). A schematic representation is shown in Figure 9. Compacting of the nanofiber mats was typically done to increase the fiber volume fraction in the composite membrane.



Membrane with ion-exchange nanofibers

Membrane with reinforced nanofibers

Figure 11: Production of nanofiber composite ion-exchange membranes starting from an electrospun dual fiber mat of Nafion and PPS. Dependent on the applied treatment, an different membrane configuration was achieved. Figure adapted from [164].

This production method can be applied to other polymer systems as well, as shown by their further research which mainly focused on the production of anion-exchange nanofiber composite membranes [181]. Promising results for dimensional stability were obtained. By crosslinking the nanofibers, the mechanical performance of the membranes can even be further enhanced. In this case, the nanofibers act as both ion-exchangers and reinforcement [182]. This allows to employ nanofibers with an even higher degree of functionalization (and thus IEC), without losing mechanical and dimensional stability. However, it was noticed that for higher IECs, the membrane stability did still inherently reduce, albeit in a lesser extent. Overall, their results prove the potential of the dual electrospinning method, often resulting in membranes with low permeability, but enhancement of the proton conductivity should be aimed at in future work (Table 4).

Material	Relative mat density (-)	Proton conductivity (S cm ⁻¹) (water,25°C)
1) Initial electrospun mat	0.15	0.008
2) Densified mat	0.45	0.016
3) Welded mat	0.74	0.041
4) Composite membrane	0.74	0.049
Homogeneous solid membrane (reference)	1	0.061

Table 5: Relative mat density and proton conductivity at different points in the four-step procedure [185].

A completely different approach of producing nanofiber network ion-exchange membranes was proposed by Choi *et al.* in 2007, using a four-step procedure (Table 5): 1) electrospinning of an ion-functionalized polymer, 2) compacting the nanofibrous mat to increase the volume density in the final membrane, 3) polymer welding between intersecting fibers to create an interconnected three dimensional network, 4) filling the interfiber void space with an inert polymer NOA 63 [185]. Going through step 1 to 4 of the procedure, the fiber volume fraction increases and the proton conductivity of the composite membrane is enhanced as well (Table 5), proving the benefits of the four-step procedure. Even higher proton conductivities could be reached by adding sulfonated polyhedral oligomeric silsesquioxane (SPOSS) nanoparticles which work as water retaining compounds and conductivity enhancers [186]. A proton conductivity of no less than 0.498 S cm⁻¹ (90%RH, 120°C) was reported for PFSA/SPOSS nanofibers in NOA 63 [188]. However, after a period of 12h, almost all SPOSS present in the membrane was lost, which limits its use in applications. Further stabilization is thus needed. The role of the inert NOA 63 matrix was studied as well and proved to have a positive influence on the mechanical and dimensional stability of the nanofiber composite membranes [47], [185], [187], [188].

Both tensile strength and Young's modulus is enhanced with increasing NOA 63 content while the inplane swelling decreases. Overall, however, proton conductivity decreases fast with increasing NOA 63 content. Therefore, an optimal value of fiber volume fraction should be aimed at with a balance between desired mechanical/dimensional stability and proton conductivity. Furthermore, their research focused mainly on the production and characterization of these nanofiber membranes. Thorough testing of the membranes should be aimed at in the future to investigate the cell performance of the nanofiber membranes.

The fiber volume fraction in the composite membrane has an influence on both conductivity and mechanical properties. With increasing fiber volume fraction, the ion conductivity enhances while the mechanical robustness and dimensional stability decrease. The inert matrix improves the stability of the membrane already significantly compared to homogeneous membranes, however only limited amount of matrix material can be added. It can be concluded that the trade-off between conductivity and mechanical properties often remains an issue in the case of ion-exchange nanofiber composites with an inert matrix.

Nanofibers in a charged matrix

To improve the ion-exchange properties of nanofiber composite membranes, preference is often given to the incorporation of ion-exchange nanofibers in an ion-exchange matrix. Depending on the materials that are used, reinforcement and dimensional stability can be given by both nanofiber or matrix phase. Furthermore, due to the ionic interactions, the ion conductivity can be improved and the compatibility between the two phases is enhanced [190]. This compatibility between nanofibers and pore filling matrix is important and can help in minimizing the trade-off between conductivity and mechanical stability [191]. Due to this increased compatibility for ion-exchange nanofibers in a charged matrix, this processing method is often the preferred choice amongst researchers. An overview of the reported ion-exchange nanofiber composites is given in Table 6.

 Table 6: Overview of mechanical and ion-exchange properties of charged nanofiber composite ion-exchange membranes. The matrix consists of a charged polymer.

Nanofibers	Matrix	Ionic group	IEC (mmol/g)	Water uptake (%)	lon conductivity (S cm ⁻¹) (%RH,°C)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Ref
Carbon	PEEK	$-S0_{3}^{-}$	1.8-2.0*	17-26*	0.10-0.13 (water,60)*	60-75	10-20	-	[192]
PEEK	Chitosan	-S0 ₃ ⁻ /-NH ⁻	0.5-0.9**	60-85**	0.08-0.12 (water,25)**	39.5-46.5	5-17	-	[193]
PVDF	Chitosan	-P00 ⁻	-	-	0.02 (water,RT)	-	-	-	[194]
PAES	VBTC	$-NRH_2^+$	-	20-30*	0.07-0.10 (water,70)*	-	-	-	[195]
PEEK/PVB	PEEK/ PVA	$-SO_{3}^{-}$	0.2-0.6**	34-192**	0.003-0.01 (-,60)	47	16	1200	[196]
Cellulose	PSU	-SO ₃ ⁻ /-NH ⁻	1.2-1.3	35-65	0.08-0.26 (water,80)	-	-	-	[197]
Cellulose	PSU	$-SO_{3}^{-}/-NH^{-}$	1.2	22.4	0.196 (100,80)	-	-	-	[198]
PAN	PSU	-S03 -C00-	1.2-1.3	35-60	0.10-0.22	25-40	13-18	-	[199]
PEEK	Chitosan	-S0 ₃ ⁻ /-NH ⁻	0.5	-	0.46 (water,90)	-	-	-	[200]
PVA/PEI	PEEK	-SO ₃ / -NRH ₂ ⁺	1.3	44-65	0.40-0.60 (water,80)	-	-	-	[201]
PEEK	Chitosan	-SO ₃ ⁻ /-NH ⁻	0.8-1.1	80-100	1.0 (water, 95)	-	-	-	[202]
SiO ₂ -PVDF	Chitosan	$-NR_3^+$	5.7	130-140	0.04 (water,80)	25	100	-	[203]
PS	PS	$-NRH_2^+$	1.0-1.8**	70-250**	0.03-0.07 (water,60)**	13.4-30.4	60-80	-	[204]

^t Dependent on fiber volume or weight fraction ** Dependent on degree of functionalisation

PPEK	PEKK	$-SO_{3}^{-}$	1.6-2.0**	35-160**	0.07-0.21 (water,80)**	12.6-15.9	17.6-26.4	-	[191]
PAES	PAES	$-NR_3^+$	1.5	104	0.08 (water,30)	50	34	1700	[205]
PAES	PAES	$-NR_3^+$	3.3	55-78*	0.066 (water, 20-25)	55-58*	20-23*	1485-1596*	[206]
PI	PI	$-SO_{3}^{-}$	1.4	22-29*	0.03-0.10 (98,80)*	-	-	-	[207]
PI	PI	$-SO_{3}^{-}$	1.6	38-42	0.20-0.30 (98,90)*	-	-	-	[208]
PPEK	PPEK	$-SO_{3}^{-}$	1.8	30	0.16 (water,80)	19.3	10.1	-	[209]
PVA/ chitosan	PVA/ chitosan	$-NR_3^+$	-	60-160	0.01-0.02 (KOH,25)	-	-	-	[210]
PEEK	Aquivion	$-SO_{3}^{-}$	1.8-2.6*	76-96*	0.1 (90,80)*	10-16	7.8-18.6	268-440	[211]
PAN	Nafion	-S0 ₃ ⁻ /-NH ⁻	1.1-1.2	38-55	0.1-0.263 (water,80)	30-35	13-17		[212]
PMIA	Nafion	-S0 ⁻ ₃ /-NH ⁻	1.0-1.2	40-55	0.26 (water,80)	25-35	17-19	-	[213]
Nylon 6,6	Nafion	-P00 ⁻ -S0 ₃	-	5	0.11 (100,30)	16.5-17.6	23.4-24.3	-	[214]
PI	Nafion	$-SO_{3}^{-}$	0.96	17	0.1 (95,80)	19.8	15.4	400	[190]
PBI	Nafion	$-SO_{3}^{-}$	0.79	18	0.13 (95,80)	35	19	-	[215]
PVA	Nafion	$-SO_{3}^{-}$	1.0-1.1	40-44	0.053-0.063 (HCl,25)	23-25	10-17	520-660	[216]
Carbon	Nafion	$-SO_{3}^{-}$	1.12	36	-	-	-	-	[217]
Carbon	Nafion	$-SO_{3}^{-}$	0.8	26	0.127 (100,90)	32.9	10	-	[218]
PEK	Nafion	$-SO_{3}^{-}$	1.8	-	-	-	-	-	[219]
PVDF	Nafion	$-SO_{3}^{-}$	-	36	0.1 (-,95)	-	-	-	[220]
PES	Nafion	$-SO_{3}^{-}$	-	-	0.15 (water,90)	-	-	-	[221]
PES	Nafion	$-SO_{3}^{-}$	-	-	0.15 (95,90)	-	-	-	[222]
PEEK	Nafion	$-SO_{3}^{-}$	-	20-40*	0.09 (100,20)	28-32	-	-	[223]
PVA	Nafion	$-SO_3^-$	0.3-0.6	19-36	0.025 (water,95)	-	-	-	[224]
PVDF	Nafion	$-SO_{3}^{-}$	-	27	0.06 (-,20)	12±0.7	230±23	1840±220	[225]
PVDF- TrFE/SiO ₂	Nafion	$-SO_{3}^{-}$		30-34**	0.43-0.69 (100,RT)	6-8	8-17	135-250	[226]
PEEK/SiO ₂	Nafion	$-SO_{3}^{-}$	2.0	26	0.077 (water,90)	-	-	-	[227]
SiO ₂	Nafion	-C00 ⁻	-	38-80	0.16-0.24 (water,80)	-	-	-	[228]
ZrO ₂	Nafion	$-S0_{3}^{-}$	0.8	18	0.3 (water,80)	-	-	-	[229]
ZrO_2	PAMPS	-S0 ₃	2-2.7*	47-107*	0.34 (water,100)	-	-	-	[230]

For example, Liu *et al.* investigated the production of sulfonated carbon nanofibers in a SPEEK matrix [192]. The influence of the improved compatibility between fiber and matrix phase on the physical and ionic properties was studied. It was reported that the addition of 1 wt% of carbon short nanofibers resulted in a proton conductivity of 0.13 S cm⁻¹ (water,60°C), compared to 0.096 S cm⁻¹ for pure SPEEK. Furthermore, the mechanical properties were enhanced as well due to the additional interactions in the membrane structure. The trade-off between ion conductivity and mechanical stability was proven to be non-existing for these high IEC, non-fluorinated nanofiber composite membranes. The importance of fiber-matrix compatibility was also proven by Wang *et al.* who investigated the properties of electrospun SPEEK nanofibers in a chitosan matrix [193]. The -SO₃H groups on SPEEK interact with the -NH₂ groups on chitosan to form acid-base pairs along the nanofiber surface. These interactions result in the inhibition of chain movement, which leads to enhanced structural and thermal stabilities. Additionally, these

interactions contribute to the enrichment of proton-hopping sites along the fiber length and a low-energy barrier for proton transport due to the Grotthuss mechanism, resulting in enhanced proton conductivity (Figure 12) [193]. This extraordinary behaviour is generally observed for other acid-base nanofiber structures as well. For example, Zhao *et al.* used different bio-based molecules as basic carriers and reported membrane performances that greatly exceeded the one of Nafion® (Table 6) [197], [199], [212], [213]. Further improvement is possible by creating ordered and interconnected nanochannels in the acid-base pairs, resulting in an ion conductivity as high as 1 S cm⁻¹ [200], [202].



Figure 12: Schematic of the production of a SPEEK/chitosan nanofiber composite membrane. Proton-hopping sites are available at the fiber/matrix interface. Figure taken with permission from [193].

Another option to enhance fiber/matrix compatibility is by using the same IEC polymer material for both phases. Excellent interfacial compatibility and better microphase aggregations are obtained, resulting in an improved conductivity [204]. Zhang et al. studied the properties of sulfonated poly(phtalazinone ether sulfone ketone) (SPPESK) nanofibers filled with a SPPESK matrix [191]. The fibers contribute to the aggregation of ionic clusters and improve the swelling resistance significantly. By using fibers with a higher IEC than the filler material, the beneficial ion-exchange properties of the nanofibers could be fully exploited while maintaining dimensional stability. Further enhancement of mechanical properties and conductivity is possible with the implementation of aligned nanofibers. Tamura et al. studied the properties of aligned sulfonated polyimide (PI) nanofibers in a sulfonated PI filler material [207]. The proton conductivity was larger in the fiber direction compared to the perpendicular direction and increasing with increasing fiber fraction. Furthermore, for five-membered ring PI, the conductivity in the fiber direction even reached a value of 0.3 S cm⁻¹ (98%,90°C) for the membrane with the lowest fiber diameter and highest fiber fraction [208]. However, the aligned nanofibers were not directed along the thickness of the membrane but rather in-plane, thus the effective conductivity through the membrane was significantly lower. For future applications, the production of through thickness aligned nanofibers would be needed. Gong et al., for example, produced proton exchange membranes with through thickness aligned SPPESK nanofibers with a SPPEK filler [209]. Both in-plane and through-plane proton conductivity values were reported. However, because the widely used characterization method of membrane proton conductive properties is via measuring in-plane conductivity, the values of throughplane conductivity cannot be compared to other reports mentioned here, and the values mentioned in Table 6 for SPPEK show the in-plane conductivity as well [231]. Nevertheless, the through-plane proton conductivity was significantly enhanced for through thickness aligned nanofibers compared to surface aligned nanofibers and cast membranes, as expected. The extensive production method to obtain through plane aligned nanofibers forms, however, a significant limitation for large-scale use.

The use of inorganic nanofibers is interesting to improve the thermal stability and ion-exchange properties of the membranes [232]. Inorganic substances are known to have enhanced water retention properties [51], [106], [233]. Up until now, research on inorganic ion-exchange nanofibers is still limited, but the available research shows extraordinary results. Wang *et al.* studied the properties of biofunctional SiO₂ nanofibers in a Nafion membrane [228]. The fibers were functionalized with amino acids to incorporate ion-exchange groups (Figure 13). Due to the hygroscopic behaviour of SiO₂, the

membranes showed a much higher WU compared to Nafion® at temperatures between 20°C and 80°C. A high WU is beneficial for proton transport but is usually accompanied by a low dimensional stability. Remarkably, in this case the swelling ratio for all modified SiO₂ nanofiber composite membranes is lower than for Nafion® (20-80°C), proving the enhanced dimensional stability. Furthermore, a maximum proton conductivity of 0.24 S cm⁻¹ was observed (80°C), which is twice as high as for pure Nafion®, combined with a significant decrease in undesired methanol permeability (Figure 13).



Figure 13: Modification of Nafion membrane with biofunctional SiO2 nanofibers. a) Improved conductivity was observed for all cases, compared to pure Nafion®. b) The methanol permeability was reduced for all cases compared to pure Nafion®. Figure taken and adapted with permission from [228].

These highly promising characteristics were also investigated by Yao *et al.* on superacidic sulfonated ZrO_2 nanofibers incorporated in a Nafion matrix [229]. Due to the extraordinary conductive properties of the inorganic nanofibers, the proton conductivity increased significantly with increasing fiber volume fraction. Furthermore, lowering the fiber diameter results in a substantial improvement of the proton conductivity of the membranes. A maximum conductivity of no less than 0.3 S cm⁻¹ (100%RH, 80°C) was reported. The membranes were tested for prolonged time (9 days) with changing temperature (20-120°C) and humidity (20-100%) and their mechanical stability remained unaltered over this time period. This excellent behavior of inorganic ZrO_2 nanofibers was further validated in other work where they used an organic fiber filler of poly(2-acrylamido-2-meathylpropane-sulfonic acid) (PAMPS) [230]. It can be concluded that functionalized inorganic nanofibers in an organic matrix show a high potential as ion-exchangers due to their water retention properties, thermal stability and mechanical integrity, leading to ion conductivity values that greatly exceed those of pure Nafion®.

4. Ion-exchange nanofibers in electrochemical water treatment and energy harvest from waste streams

A broad range of electrochemical technologies apply to water treatment and energy production from wastewater [4], [234]. Over the last years, membrane-based processes have shown many benefits and

are often preferred over membrane-free processes [235]. The use of ion-exchange membranes exclude undesired side reactions in the electrolyte, improve the process efficiency and offer enhanced selectivity and resource recovery by forming a physical barrier between anode and cathode [11], [236]. The economic gain of these membrane-based processes is mainly dominated by the operating costs such as energy consumption, which is, in its turn, significantly determined by the membrane performance [16]. Due to the superior ionic properties of ion-exchange nanofibers (Figure 6), they are being increasingly considered in various electrochemical processes. Over the last decades, their potential has been extensively researched as ion-exchange membrane in PEMFCs and methanol fuel cell applications for the production of electricity. Recently, research on ion-exchange nanofibers has also increased for different electrochemical water treatments, such as bioelectrochemical systems, electrodialysis and diffusion dialysis, and offer many advantages for both resource recovery and energy production from waste streams (Table 7). Current research on nanofiber membranes for these different techniques is discussed, both for water treatment applications such as desalination and acid/base production/recovery as well as for energy harvest from wastewater by means of microbial fuel cells and microbial electrolysis cells.

Table 7: Overview	of nanofiber usage	and advantages for	or different electrochemical	water treatment techniques.
	<u> </u>	<u> </u>		

Technique	Application	IEM Nanofiber material	Advantages nanofibers	Ref							
		PEEK	Selective transport of monovalent ions	[237]							
		Carbon/PVC nanofiber composite	Enhanced hydrophilicity, potential, transport number, permselectivity and ionic conductivity	[238]							
		PVDF	Improved ion transmission due to higher water uptake and lower membrane resistance	[239]							
		РРТА	Selective separation of monovalent cations in organic solvents + high temperature resistance	[240]							
	Desalination of brackish water									РРТА	Selective separation of monovalent anions in brackish organic solvents
Electrodialysis (ED)		PVDF	Many ion transmission pathways + low membrane resistance + good ion selection	[242]							
		BPPO/SPPO nanofiber composite	Improved dimensional stability + ion flux + high current density + selective transport of monovalent ions	[243]							
		PVC based	More favourable ion- exchange properties for reverse ED	[244]							
			Kevlar based	Exceptional desalination, Li selectivity, anti-scaling properties	[245]						
		Kevlar based	High desalination performance, organic solvent resistance, high cation-exchange capacity	[246]							
		Kevlar based	High IEC, excellent separation, high mechanical strength	[247]							

		PS P4VP	Enhanced water splitting for high surface area nanofibers	[115]
		PPO	Lower potential drop	[122]
	Acid/base production (bipolar	PVA	Enhanced water splitting	[248]
	membrane)	PEEK + PPO	Increased interfacial area minimizes water depletion + enables high current operation	[249]
		PS PPO	Enhanced water splitting Lower potential drop	[250]
Diffusion dialysis (DD)	Acid or base recovery	PPO	Higher hydroxide permeability + higher separation factor for base recovery	[251]
	,	PPO-SiO ₂	Higher acid permeability + higher separation factor for acid recovery	[252]
		PVDF/Nafion nanofiber composite	Improved thermal stability + power generation	[253]
	Microbial fuel cell (MFC)	Carbon/Nafion nanofiber composite	Higher Coulombic efficiency + higher power production + decreased fouling	[254]
Bio-		PVDF/PFSA nanofiber composite	Higher power density + lower membrane resistance	[255]
electrochemical systems (BES)		PVA/Nafion or PEEK/PVA nanofiber composite	Higher power density + lower internal resistance + low oxygen permeability	[256]
	Microbial electrolysis cell	PI/PAES nanofiber composite	Improved hydrogen production + selective proton transport + reinforcement	[165]
		PI/PAES nanofiber composite	Improved hydrogen production + dimensional stability	[161]

4.1 Electrodialysis (ED)

4.1.1 Desalination of brackish water

Electrodialysis (ED) is one of the most widely used techniques in desalination due to its economic feasibility, high efficiency, easy scale-up and stable effluent quality [238]. ED is competing directly with reverse osmosis (RO) for desalination and has proven to be beneficial in a certain range of feed water salt concentration (<10.000 mg L⁻¹) [257], [258]. An ED setup consists of several AEMs and CEMs that are placed in an alternating way in between the two electrodes (Figure 14). An electrolyte solution is passed through the electrode compartments, while the feed solution (brackish water) is passed through the other compartments. When an electrical potential is applied, reduction reactions take place at the cathode resulting in the production of hydroxide ions. To assure electro-neutrality, a cation/anion should pass the CEM/AEM next to the cathodic department. Similarly, at the anodic department oxidation reactions take place, resulting in the production of protons. To compensate, a cation/anion should pass the CEM/AEM next to the anodic department. Which process will take place is dependent on the stacking of the ion-exchange membranes. In a setup with multiple AEMs and CEMs that alternate each other, the electro-neutrality driving force will eventually lead to the alternating depletion of salts in the dilute departments and the concentration of salts in the other departments (Figure 14) [257]–[260].



Figure 14: Electrodialysis cell for desalination application. Figure adapted from [259].

The production of potable water from brackish water via ED is a very promising technique to solve the lack of availability of fresh drinking water in many areas in the world [261]. This requires that the presence of both monovalent and divalent ions are within acceptable ranges. Depending on the source of the brackish water and the utilization of the treated water, selective separation of monovalent or divalent ions are needed. Conventional membranes used in ED have only slight differences in selectivity for different ions, and commonly the sedimentation of divalent ions leads to membrane fouling, so the use of monovalent selective AEMs or CEMs is desired [262]. However, they typically have a high cost and low separation performance. To improve the flux and permeability of monovalent/divalent selective membranes. ion-exchange nanofibrous membranes are often considered [237]-[239], [242], [243], [263]. Electrospun ED membranes show many advantages such as high porosity, high ion flux and the presence of ion conductive channels, all resulting in reduced membrane resistance [244]. Sulfonated PEEK nanofibers have proven to be very effective in the selective removal of Na⁺ ions compared to Ca²⁺ and Mg²⁺ (Figure 15) [237]. The separation factor (ratio of flux between 0.1 mol L⁻¹ Na⁺ and Ca²⁺ or Mg²⁺) was more than twice as high compared to cast sulfonated PEEK membranes, and independent on the applied potential. Furthermore, the permselectivity of the electrospun SPEEK membrane was 0.9 for a NaCl electrolyte vs. 0.12-0.19 for a MgCl₂ or CaCl₂ electrolyte, proving the high selectivity for Na⁺.



Figure 15: a) Flux of different cations for both SPEEK and electrospun SPEEK (ESPEEK) at 2 V cm⁻¹. b) Flux of different cations for ESPEEK at different potential gradients. The ESPEEK membrane shows an increased selectivity of cations. Figure taken with permission from [237].

Jiang and Zheng *et al.* reported the production of electrospun sulfonated PVDF nanofibrous membranes for ED by a novel multi-jet electrospinning technique in which sheath gas was added to improve the

productivity of a uniform membrane [239], [242]. The desalination ratio of NaCl reached more than 50% in about 30 min. The IEC and selectivity increased with decreasing thickness while the membrane resistance decreased, resulting in improved performance. However, thinner membranes also resulted in reduced mechanical strength (only 2.3 MPa), thus limiting their application in ED. To improve the dimensional and mechanical stability, the nanofibers are often incorporated in a pore filling matrix (3.3.2). Typically, the fibers are oppositely charged compared to the matrix, which enhances the ion selectivity [238], [264]. While most applications of ED occur in aqueous media, more attention is being given to organic media as well [265]. Zhao *et al.* expanded the development of ED membranes to the treatment of waste organic streams [240], [241], [245], [247]. Their ED membranes are based on poly(paraphenylene terephthalamide) nanofibers, which are characterized by their organic solvent resistance, high strength and outstanding thermal stability. Excellent desalination performance at both high temperature and in organic solvent environments was reported. The cation desalting efficiencies for (NH₄)⁺, Na⁺, Li⁺ and Mg²⁺ were 99.99%, 99.7%, 89.1% and 56.2%, respectively.

A disadvantage of membrane-based processes is the occurrence of membrane fouling due to the formation of deposits on the membrane surface or even in the membrane [266], [267]. This causes an increase in internal resistance and a decrease in permselectivity and IEC [36]. Fouling of inorganic salts, known as scaling, often occurs in cation-exchange membranes in desalination applications by ED [34], [268]–[270]. Scaling products typically consist of crystallized salts containing Mg and Ca, present from the treated water, and is inevitable. Porous ion-exchange membranes containing functionalized nanofibers can reduce the effect of fouling/scaling [57], [245], [271]. However, this effect is never completely avoidable. Therefore, cleaning of the ion-exchange membranes is needed, which is typically done in acidic solutions [272]–[276]. This can deteriorate the membrane structure, and as a result highly chemical resistant ion-exchange membranes are desirable [39], [40], [277]. Nanofibers made from inorganic materials such as silica or zirconia could offer a highly beneficial solution. They have proven to be very effective as ion-exchange membranes due to their typically high ion conductivity and moreover, they have an excellent chemical resistance [228]–[230].

Alternative methods for desalination of streams, such as membrane capacitive deinoization (MCDI) exist as well [278]. The use of nanofibers has also been extensively investigated for MCDI, albeit with focus on developing efficient electrode materials, rather than ion-exchange membranes [279], [280]. The current available research on ion-exchange nanofibers for desalination via ED could however be extended towards MCDI applications as well.

Overall, nanofiber membranes often show beneficial performances compared to cast membranes in desalination properties, with a higher selectivity and permeability. However, little is mentioned about their osmotic drag. When ions pass through an ion-exchange membrane, they are typically accompanied by their hydration shell, which size and strength is dependent on the type of ion [281], [282]. This results in a water flux through the membrane and should be minimized as much as possible. More research is needed to investigate the influence of nanofiber membranes on the osmotic water flow.

4.1.2 Acid/base production

Ion-exchange nanofibers have proven to be very effective as an interlayer in bipolar membranes for electrochemical acid/base production from waste streams via ED. Bipolar membranes consist of both an AEM layer and a CEM layer and induce the splitting of water in protons and hydroxide ions [283]. These ions then react with salts from the feed waste solution to form the corresponding acids and bases with the aid of an additional AEM and CEM (similar as Figure 14) [122]. By implementing an AEM and/or CEM nanofiber interlayer in the bipolar membrane, a 3D junction is created with a high interfacial area which enhances the interaction with water molecules compared to flat cast membranes [115], [248], [249]. The ion-exchange nanofibers act as a catalytic layer and increase the water splitting efficiency (Figure 16) [249]. Additionally, the presence of the nanofibers also enhances the mechanical robustness of the bipolar membrane. More specifically, the interlocking of cationic and anionic fibers improves resistance to delamination.



Figure 16: a) Bipolar membrane with anion-exchange polymer (AEP) and cation-exchange polymer (CEP). b) Bipolar membrane with a nanofiber interlayer in between the AEP and CEP resulting in increased interaction. Figure taken with permission from [249].

Alternatively, all three layers in the bipolar membrane can be made from electrospun nanofibers [122], [250]. Pan *et al.* reported the production of a bipolar membrane consisting of sulfonated PPO as cation-exchange layer (CEL), polyethylene glycol (PEG) as interlayer and quaternized PPO as anion-exchange layer (AEL) [122]. The membrane was produced by electrospinning the different layers on top of each other and hot-pressing them. This membrane morphology resulted in a reduced voltage drop (3.5 times lower than cast membranes at 100 mA cm²) across the bipolar membrane and thus a better performance. Additionally, both dimensional and mechanical properties of the nanofibrous bipolar membranes were similar as for the cast bipolar membranes. Similar results were found by Modarresi *et al.* who used graphene as interfacial layer for phosphate recovery [250].

Overall, research on ion-exchange nanofibers in bipolar membranes is relatively new and has only been studied over the last few years. The use of inorganic compounds is known to have a positive effect on the efficiency of water-splitting [284]–[286]. Therefore, inorganic nanofibers could show significant potential in bipolar membranes. However, it is known that enhanced water-splitting also induces membrane fouling, which might be a significant limitation for the application of inorganic compounds as bipolar membranes [284].

4.2 Diffusion dialysis (DD)

Diffusion dialysis (DD) is a separation process driven by a concentration gradient, which makes use of an ion-exchange membrane. As this process is a thermodynamically favourable process, the energy consumption is typically very low and results in a high efficiency for wastewater treatment [287]. This technique is mainly used for the recovery of acids or alkali from waste streams in industry (Figure 17). For the recovery of acids, the DD setup consists of an AEM that allows passage of anions such as Cl⁻, SO_4^{2-} while rejecting the metal cations. The H⁺ ions, however, can also diffuse through the AEM due to their smaller size, lower valence state and higher mobility. This diffusion of protons is driven by the requirement of electrical neutrality and is crucial in DD processes [287], [288]. The recovery of alkali works similarly and uses a CEM that rejects anions while allowing passage of cations and small OH⁻ molecules for electrical neutrality [287], [289].



Figure 17: Example of a diffusion dialysis setup with an AEM for the recovery of acids.

Conventional cast membranes typically suffer from low H⁺ or OH⁻ permeability due to their dense structure. Ion-exchange nanofibers show an improved permeability of H⁺ or OH⁻ through the membrane but this is typically accompanied by a high permeability of the undesired cations (in an AEM) or anions (in a CEM) as well, and as such reducing the overall selectivity. Pan *et al.*, however, studied the effect of heat treated ion-exchange nanofibers on the performance in diffusion dialysis for both acid and alkali recovery [251], [252]. The heat treatment led to the densification of the loose nanofiber structure and resulted in a reduced permeability for the undesired co-ions, while the structure was still loose enough to allow H⁺ or OH⁻ permeation. The separation factor (ratio of the dialysis coefficient of OH⁻/H⁺ to A⁻/C⁺, with A⁻/C⁺ the undesired co-ion) for heat treated nanofibers was 36 and 68, for alkali and acid recovery, respectively, compared to 22 and 49.5 for cast membranes. Overall, only limited research has been performed on the use of nanofibers for diffusion dialysis and thus more research is needed to further elaborate on their potential and shortcomings.

4.3 Bioelectrochemical systems (BES)

Generally speaking, BES are systems that use biocatalysts to induce oxidation and reduction reactions [290]–[292]. The most common applications of BES are microbial fuel cells for the production of energy and microbial electrolysis cells that uses energy for the recovery of resources from wastewater [293]–[295]. The biggest advantage of using BES is the reduced greenhouse gas emission compared to conventional techniques [291].

4.3.1 Microbial fuel cell (MFC)

Renewable energy generation sources have a great importance in the global energy crisis. Microorganisms, such as bacteria, can generate electricity from the organic matter and biodegradable substances in wastewater by oxidizing them at the anode, while simultaneously treating the wastewater [296], [297]. MFC is a technique that utilizes the chemical bonds in these organic compounds as energy source [298]–[300]. The anodic and cathodic chamber are typically divided by an ion-exchange membrane that allows passage of protons (Figure 18a).



Figure 18: a) A microbial fuel cell consisting of an anodic and cathodic chamber separated by a proton-exchange membrane. b) A microbial electrolysis cell for the production of hydrogen gas from wastewater, separated by a proton-exchange membrane. Figure adapted from [296] and [301].

The efficiency of the MFC is highly dependent on the ion-exchange membrane properties. The biggest issues in MFCs are the oxygen permeability through the membrane, membrane fouling and low power generation [35], [36], [256], [302]. High performance materials such as nanofibers have been studied to overcome these issues. In order to maintain the physical barrier between anode and cathode, the porous nanofiber membranes are typically filled with a pore-filling matrix, making them dimensionally stable. The use of nanofibers has resulted in increased power generation compared to Nafion® cast membranes in all cases [253]–[256]. For example, Ghasemi *et al.* studied the effect of carbon nanofibers in a Nafion matrix on the performance of the membrane [254]. The Coulombic efficiency of the system increased to 18.3% compared to 5% for pure Nafion®, meaning that the addition of carbon nanofibers in the membrane resulted in an increased process efficiency. They ascribed this to the increased surface area and porosity, which decreased fouling and enhanced proton transfer.

Even though research on ion-exchange nanofiber membranes in MFCs is limited, they have been studied abundantly in PEMFCs and direct methanol fuel cells (Table 3, 4 and 6). These nanofibers showed promising results that can provide insights for future MFC applications as well.

4.3.2 Microbial electrolysis cell (MEC)

Microbial electrolysis cells (MEC) use electricity to produce specific compounds in an electrochemical cell with the aid of microorganisms [11], [303]-[305]. An ion-exchange membrane is typically used to separate the anodic and cathodic compartments, and to prevent undesired side reactions [306]. One interesting application is microbial hydrogen production from wastewater. In this case, active bacteria oxidize organic matter from the wastewater at the anode and produce CO₂, electrons and protons. These electrons and protons can then combine to form hydrogen gas, with the aid of an external power supply (Figure 18b) [301], [307]. The proton exchange membrane makes sure that the hydrogen produced at the cathode does not intermix with the gases created at the anode [161]. For an efficient process, it is important that only protons pass through the ion-exchange membrane, while other cations remain in the anodic compartment. Especially in microbial electrolysis cells, the cation concentration is much higher than the proton concentration, resulting in competition. Conventional membranes, such as Nafion®, suffer from a low proton selectivity, high biofouling and high gas crossover [308], [309]. Alternative membranes containing sulfonated hydrocarbon based polymers have proven to show enhanced properties, but lack mechanical robustness. Therefore, nanofibers are often added as reinforcement, but can reduce the overall proton conductivity, as explained in 3.3.1. However, Chae et al. have shown that the addition of polyimide nanofibers to a SPEEK matrix does not only improve the dimensional stability of the membrane, but also maintains the conductivity, and more importantly, the proton selectivity of the membrane [165]. The proton transfer number was slightly higher than for Nafion® (0.95 vs. 0.93), while the sodium transfer number was slightly lower (0.91 vs. 0.93). Furthermore, the gas permeability was reduced as well. Similar results were obtained for their other work, in which polyimide nanofibers were incorporated in a SPAES matrix [161].

5. Future outlook

Despite the many examples of the superior performance of ion-exchange nanofiber membranes in comparison with conventional membranes, challenges exist to bring these membranes to maturity. While current research on ion-exchange nanofibers focuses mainly on fuel cell applications, they have a high potential in a broad range of other electrochemical applications as well. However, these techniques typically have strict requirements in regard of membrane properties. In view of future research on ion-exchange nanofibers, one can either focus on the necessary improvements of the new generation of ion-exchange nanofibers, or on the development of ion-exchange nanofiber membranes to improve other electrochemical separation processes (Figure 19).



Figure 19: Future research on ion-exchange nanofibers can be divided into two categories: research on necessary material improvements of current nanofiber membranes to tackle their shortcomings or research on potentially relevant electrochemical processes to broaden the application field of the ion-exchange nanofibers.

5.1 Necessary material improvements

- A constantly recurring issue of ion-exchange nanofiber membranes is the trade-off between IEC and mechanical stability, which should be given more attention in future research if they want to be considered in a broad range of applications.
- The use of ion-exchange nanofiber composite membranes are currently most extensively studied due to their enhanced dimensional and mechanical stability. However, the presence of a pore-filling matrix often reduces the ionic properties. Future research should focus on the development of ion-exchange nanofiber mats with improved mechanical and dimensional stability that can be used as stand-alone membranes.
- Nanofiber membranes typically have a very porous and loose structure and additional processing steps are needed to improve their separation properties, which are often cumbersome. This makes their potential of upscaling on an industrial level challenging. Producing nanofibers from materials which intrinsically contain water-repellent functional groups and with an excellent mechanical stability could be a solution, as this would reduce the additional processing steps significantly. This would substantially increase their industrial potential.
- Current research mentions little about the osmotic properties of ion-exchange nanofiber membranes. More attention should be given to this property, as this can have a significant impact on the performance of the electrochemical treatment.
- The treatment of water often occurs in highly acidic or alkaline environments with many deteriorating chemical compounds, thus needing membranes with a high chemical resistance such as inorganic nanofibers. These inorganic ion-exchange nanofiber membranes have already shown superior performance in fuel cell applications, but should still be studied in view

of electrochemical water treatment to determine and/or improve their mechanical, ionic and resistivity properties.

• Fouling/scaling is an important issue of membranes in electrochemical techniques, which limits their application. Development of scaling resistant membranes or membranes that allow easy removal of precipitates are needed, especially for electrochemical desalination or water softening applications [310], [311].

5.2 Improvement of electrochemical processes by nanofiber ion-exchange membranes

There are many different techniques in electrochemical water treatment based on membrane-free systems. The use of membranes in these processes has been avoided due to the loss in conductivity imposed by the membranes and consequently the increase in energy consumption. However, some of these techniques can benefit from the presence of a membrane, if the decrease in the conductivity is not too big. This is why the use of nanofiber ion-exchange membranes can bring improvement for a large number of electrochemical processes, principally related to the treatment of low conductivity solutions.

One example of treatments is the disinfection of wastewater by in-situ redox reactions [234], [312]. This process has gained a lot of attention the last few years, driven by the need of cheap, reliable and efficient methods of disinfecting toilet water in a localized way, for example by the use of a solar-powered mobile toilet that electrochemically cleans and disinfects the disposed water for reuse (Figure 20). This benefits hygiene in countries with limited access to decentralized sanitation, and can eliminate many diseases in these areas.



Figure 20:Schematic of a solar-powered mobile toilet for the electrochemical disinfection of toilet wastewater [313].

Electrochemical disinfection processes are able to adjust to variations in influent, using compact systems and do not require additional chemicals [314], [315]. They rely on the anodic production of hydroxyl radicals or reactive chlorine species formed from naturally present chloride in the wastewater [234], [316]. The presence of an ion-exchange membrane between anode and cathode chamber has proven to be beneficial [317], [318].

• With the use of a membrane the anodic chamber becomes acidic while the cathodic chamber becomes alkaline [235], [236]. These acidic conditions are beneficial for the production of reactive chlorine and the destruction of microorganisms [234], [319]. This pH difference is feasible due to the membrane presence. Yang *et al.* reported a removal of 85% of parasitic

helminth eggs in membrane-divided systems, compared to 15% for membrane-free systems, due to the low pH and in-situ chlorine formation [236].

- By-products formation is one of the biggest issues in membrane-free systems [6], [313], [320]– [322]. Yang *et al.* reported a reduction of 92% of chlorinated by-products for a membrane-divided system compared to a membrane-free system [236].
- At the cathode chamber high-purity hydrogen gas is formed and can be captured for usage as energy source to maintain the system, leading to an overall energy cost reduction of at least 20% [207]. In membrane-free systems the hydrogen gas would be mixed with oxygen, nitrogen,... [323].
- The energy investment of membrane systems, certainly in combination with pretreatments such as vertical flow wetlands, is considerably lower than membrane-less systems. For example, Talekar *et al.* reported an energy investment down to 11 kWh m⁻³ wastewater treated and disinfected which is several times lower than membrane-less systems [319].

Another example of a treatment that could be improved with nanofiber ion-exchange membranes is the electrochemical advanced oxidation process (EAOPs). EAOPs have caused increasing interest because of the ability for the remediation of waters containing persistent organic pollutants [324], [325]. These technologies are based on the electrochemical generation of strong oxidants such as hydroxyl radicals (radical OH*) and the direct oxidation of the pollutant in the anode surface.

- The use of a membrane can avoid by-product formation and the reduction of the oxidized pollutants on the cathode surface [6], [322].
- A high permeation flux and treatment efficiency is obtained by the presence of the membrane, while the fouling of the membrane is reduced due to the synergetic effect of the electrochemical process [326], [327].

The presence of an ion-exchange membrane in electrochemical disinfection and advanced oxidation processes clearly improves the removal efficiencies. However, the membrane inherently increases the internal resistance of the cell, leading to increased cell voltages and cost [328]. Further energy consumption reduction can be achieved by implementing superior ion conductive membranes such as nanofibers. To avoid water transport between anode and cathode chamber, a non-porous nanofiber composite ion-exchange membrane or dense nanofiber structure should be considered. Furthermore, functionalized nanofibers have been developed with improved fouling and scaling resistance, better chlorine resistance and better acidic resistance during cleaning [329], [330]. These research results can aid in the development of superior ion-exchange nanofiber membranes for electrochemical wastewater treatment.

6. Conclusions

It is clear that nanofibers are promising materials for ion-exchange membranes. Solvent electrospinning is a straightforward and upscalable technique to produce these nanofiber membranes with several interesting properties such as high porosity, high surface area and interconnected pores. The high surface area creates many available sites for post-functionalization with ion-exchange groups, resulting in nanofibers with extremely high IECs compared to cast membranes. Alternatively, pre-functionalization methods can also be applied in which an ion-functionalized polymer is directly electrospun. Due to the uniaxial alignment of the polymer chains along the fiber length, ion conductive channels are created which lead to superior ion conductivity and enhanced mechanical properties. However, the membrane structures are very porous and loose, therefore for application in electrochemical separation, further membrane processing is always performed to obtain a membrane with good separation properties while maintaining the advantages of the nanofibers on the ionic properties. On the one hand, the functionalized nanofiber mat can be densified by heat treatment, crosslinking and/or hot-pressing. On the other hand, a pore-filling matrix can be added to the nanofibers, resulting in a nanofiber composite membrane. This latter technique is the most occurring membrane processing type, and finds its origin in the need for stronger and better performing non-fluorinated polymer membranes for fuel cell applications. Non-functionalized nanofibers are sometimes added to an ion-exchange matrix where the sole purpose of the nanofibers is to enhance the dimensional stability of the membranes in water, which is a recurring problem for non-fluorinated polymer membranes with high IECs. However, the introduction of the non-functionalized nanofibers often reduces the overall ion conductivity. To make use of the superior ionic properties of the nanofibers, in most cases ion-functionalized nanofibers are embedded in a pore-filling matrix. In this case, a non-functionalized matrix can act as reinforcement, or the nanofibers can act as reinforcement of the functionalized matrix while also improving the ionic properties of the membrane. Much research has been performed on different types of polymers and the performance of these ion-exchange nanofibers in electrochemical applications. Some interesting outcomes are the use of acid-base pairs between the nanofibers and matrix which facilitates ion hopping, and inorganic nanofibers that show very promising ionic properties while containing superior thermal and chemical resistance.

Overall, the use of ion-exchange nanofibers has been studied extensively as ion-exchange membrane for fuel cell applications, but they have recently found their way to electrochemical water treatment applications as well. These applications are based on different techniques, such as ED, DD and BES, and each technique requires different membrane properties. These strict membrane requirements have formed a challenging aspect for researchers in the development of new, better performing, materials. Nanofibers have already shown many advantages in some applications, but research is still mostly limited. More research should be performed on the cell performance of the nanofiber membranes and their large-scale potential should be improved. This review provides new insights in the potential of ion-exchange nanofibers, which can open doors for future research on membrane-based electrochemical water treatment.

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