

Chapter 2

Electrospun Nanofibers for Design and Fabrication of Electrocatalysts and Electrolyte Membranes for Fuel cells

Zhan Lin, Yingfang Yao, and Xiangwu Zhang

Abstract In the past decades, in response to the energy needs of modern society and emerging ecological concerns, the pursuit of novel, low-cost, and environmentally friendly energy conversion and storage systems has raised significant interest. Among these systems, fuel cells have gained much attention for their high efficiency and high power density, with low greenhouse gas emission. As one of the most promising and versatile fabrication methods for one-dimensional mesostructured nanomaterials composed of organic, inorganic, metallic, or hybrid components prepared as randomly or orientedly arranged continuous nanofibrous mats with possibilities of ordered internal morphologies such as core-sheath, hollow, or porous fibers, or even multichanneled microtubes, electrospinning has been widely investigated to fabricate electrocatalysts and electrolyte materials applied in fuel cells because of their dimensional, directional, and compositional flexibility. In this chapter, the application of electrospun nanofibers for the specific design and fabrication of different components is reviewed in detail. Particular progresses with the use of electrospun nanofibers on improved fuel cell performance, such as power density, ionic conductivity, interfacial resistance, and chemical stability, as well as mechanical strength are emphasized, which, as we hope, can trigger further development and evolution of fuel cells as one potential energy conversion device and system.

Zhan Lin and Yingfang Yao contributed equally to this chapter.

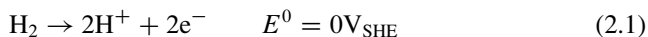
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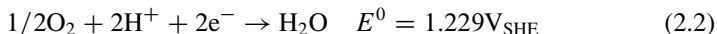
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2.1 Introduction

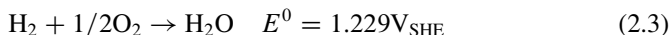
Fuel cells are electrochemical cells where the chemical energy of the fuel was converted into electricity for power generation with high efficiency [1, 2]. Industrial purified hydrogen and air are often used in fuel cells to eliminate any pollution or emission, which is known as proton exchange membrane fuel cells (PEMFCs). In a typical PEMFC, a stream of hydrogen is delivered to the anode side of the membrane electrode assembly (MEA) [3, 4]. At the anode, it is catalyzed by platinum (Pt) and split into protons and electrons. This oxidation half-cell reaction is represented as follows:



The protons formed in this reaction permeate through the proton exchange membrane (PEM). However, the electrons travel along an external load circuit to the cathode side of the MEA and provide electric power along the way. At the cathode, a stream of oxygen is meanwhile delivered, and the oxygen molecules react with the protons permeating through the PEM and the electrons arriving through the external circuit to form water molecules. The reduction half-cell reaction is represented as follows:



The full-cell reaction is

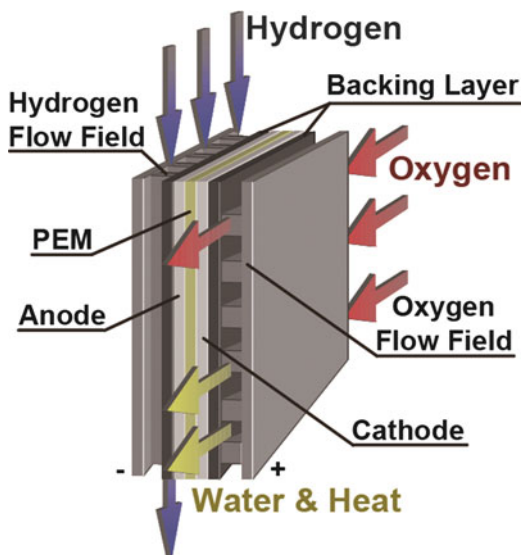


The scheme of a PEMFC can be seen in Fig. 2.1.:

Fuel cells can also use hydrocarbon as fuels although they are associated with local carbon dioxide emissions. There is great interest in direct methanol fuel cells (DMFCs) for portable electronic applications; however, the major development of fuel cells is focused on stationary and transportation usage. Over the past two decades, intense research and development endeavors were triggered by the need to integrate alternative energy carriers and thus energy conversion systems to improve energy sustainability, increase lifetime, and reduce cost [5, 6]. These efforts are currently dedicated to advanced performance and robustness, focusing on all components of membrane electrode assembly: electrocatalysts (lower catalyst loading, increase specific activity, and reduce cost), catalyst support materials (stabilize different support materials to redox reactions), and electrolyte membranes (increase conductivity at high temperature and low relative humidity, improve mechanical strength, and chemical stability) [7, 8].

As one of the versatile and widely spread technologies to produce 1-D nanofibers, electrospinning has been extensively investigated as the potential materials applied in both the catalyst materials and electrolyte membranes [9, 10]. With the properties

Fig. 2.1 The schematic diagram of a PEMFC



of high aspect ratio and wide material diversity, electrospun nanofibers generally exhibit high conductivity, large specific surface area, and excellent mechanical and chemical stability.

2.2 Electrospun Catalysts

Catalyst material is the key component in a fuel cell; and it facilitates electrode reactions [11]. Commercial fuel cells typically use Pt nanoparticles as the electrocatalyst; however, the Pt nanoparticle electrocatalyst suffers from low activity and poor durability. To address the problems, electrospun catalysts were developed with high activity, good poisoning resistance, and excellent stability. Table 2.1 shows the applications of various electrospun catalysts in fuel cells. The synthesis of catalytic electrospun nanofibers of PtRh and PtRu was first reported by Kim et al. [12]. As shown in Fig. 2.2, the diameter of the nanofibers was within 50 nm. The mass activity of PtRu nanofibers was better than that of highly dispersed PtRu nanoparticles on carbon. The enhanced electrical properties and pertinent interface formation with nanofiber catalysts are believed to contribute to the improved performance. The centimeter-long nanofibers of Pt by electrospinning were fabricated by Shui et al. [16]. These Pt nanofibers showed the diameter of 5–20 nm, with the fiber formation rather than beads dependent on the type of carrier polymer (e.g., PVP), which was removed during heat treatment. There was no need for a catalyst support in the fuel cell electrode by using these Pt nanofibers. Shui et al. continued to report Pt-Fe alloy nanofibers prepared by electrospinning and dealloying for oxygen reduction reaction [15]. The overall nanofiber diameter was

Table 2.1 Applications of electrospun catalysts in fuel cells

Fuel cells	Materials	Microstructure	Advantages	References
DMFC	PtRh and PtRu	D 50 nm, MA 355 and 449 mA mg ⁻¹	Electrocatalytic properties enhanced by 30 % relative to PtRu/C	[12]
	Pt	D 50–70 nm, MA 47 mA mg ⁻¹	Electrocatalytic properties on MOR	[13]
PEMFC	Pt	D 20–40 nm	Higher ORR activity by 50 %	[14]
	Pt-Fe	D 10–20 nm	2.3 times higher than that of conventional Pt/C catalysts	[15]
Others	Pt	D 5–20 nm	Freestanding Pt electrocatalysts	[16]
	Pd	MA 322 mA mg ⁻¹	Simple and cost-effective synthesis of nanofibers	[17]
	Pt and PtRh	D 25–35 nm	High power density	[18]

Microstructure descriptions include diameter (*D*) and/or mass activity (*MA*)

10–20 nm and the ligament diameter only 2–3 nm. These porous long nanowires interweaved to form a self-supporting network with a high specific activity, which was 2.3 times higher than that of conventional Pt/C catalysts. There are a few other reports on the electrospun catalysts; however, comparing to other methods such as chemical vapor deposition, an extremely fine fiber diameter (<10 nm) by electrospinning is difficult to achieve.

2.3 Electrospun Nanofiber-Supported Catalysts

The requirements of the support material for electrodes, such as high electronic conductivity, large specific surface area, and excellent electrochemical and chemical stability, are crucial for both the performance and durability of fuel cells. In addition, the metallic catalyst loading should be reduced due to the high cost of catalyst materials. The dispersion and size distribution of catalyst nanoparticles are optimized for maximum exploitation and rapid kinetics, which provide a way to decrease the metal loading. Table 2.2 summarizes electrospun nanofibers from carbon and other materials such as TiO₂ [24, 33] and conducting polymers [38, 39] as the supports for electrode catalysts in different fuel cells.

2.3.1 Carbon Nanofiber-Supported Catalysts

Carbon nanomaterials have been considered as suitable catalyst supports in fuel cells [40–45] because of their unique graphite properties combined with flexible

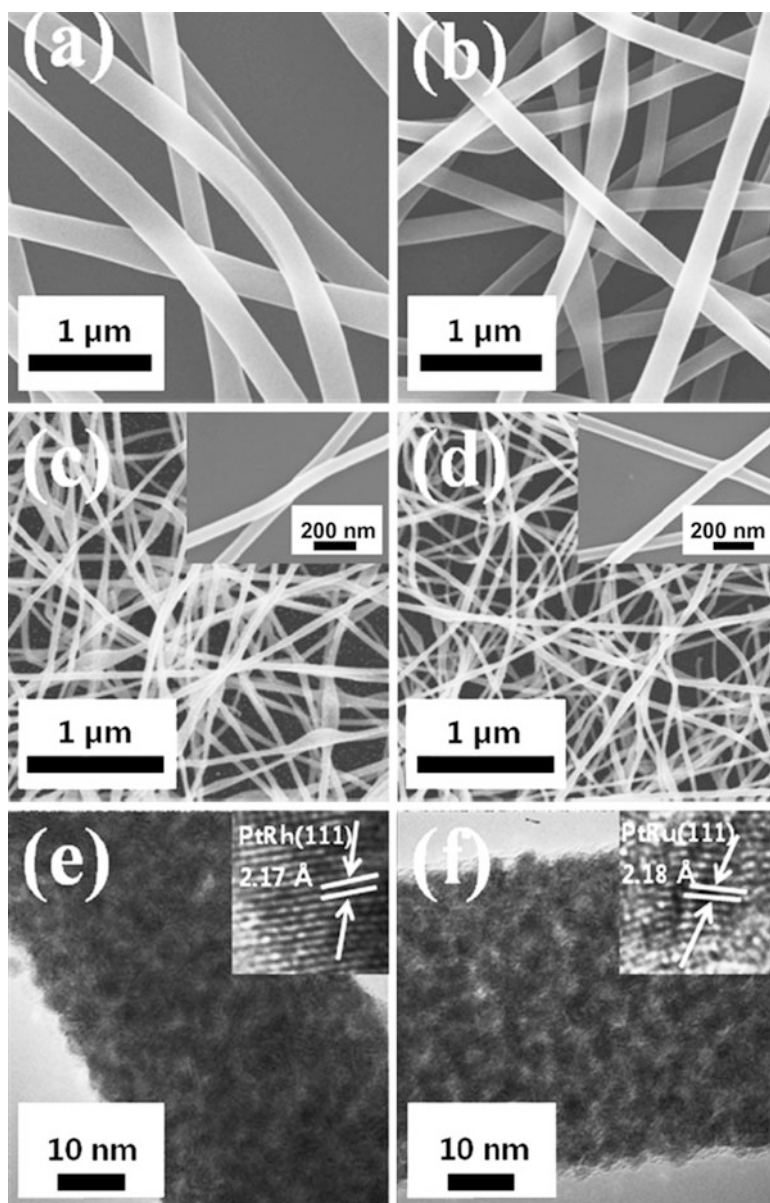


Fig. 2.2 FESEM images of as-spun (a) PtRh and (b) PtRu precursor/PVP and bimetallic nanofibers of (c) PtRh and (d) PtRu; *insets* of (c) and (d) show the diameter of bimetallic nanofibers. HRTEM images of (e) PtRh and (f) PtRu nanofibers; *insets* of (e) and (f) are inverse fast Fourier transform image of PtRh and PtRu nanofibers (Reprinted from Kim et al. [12], Copyright 2008, with permission from Elsevier)

Table 2.2 Electrospun nanofiber-supported catalysts for fuel cells

Fuel cells	Materials	Microstructure	Advantages	References
DMFC	Pt/CFM	FD $\sim$ 150 nm, PD 50–200 nm, MA 18.5 mA mg ⁻¹ Pt	Carbon fibrous mats improve the performance of catalyst	[19]
	Pt, Au/CFM	FD 740 nm, PD 7.5 and 4.2 nm, MA 450 mA mg ⁻¹ Pt	Better stability and smaller charge transfer resistance	[20]
	PtRu/1-aminopyrene-CNFs	FD 100–300 nm, PD 3.1–3.6 nm, MA 32.7 m ² g ⁻¹	High active surface area and improved performance	[21]
	Electrodeposited Pt/CNFs	FD 200–300 nm, PD 20 nm	Pt/CNFs with a Pt loading of 0.170 mg cm ⁻² has the highest activity	[22]
	Pt/CNFs	FD 150 nm, MA 98 mA cm ⁻²	Higher electrocatalytic activity, more stability, larger exchange current, and smaller charge transfer resistance	[23]
	Pt (NP and NW)/TiO ₂	FD 150–300 nm, PD $\sim$ 7 or 150 nm, MA 56.2 mA mg ⁻¹ Pt	The additional catalytic facets on the nanofibers can enhance both catalytic ability and robustness	[24]
	Pt/TiO ₂	FD 30–60 nm, PD $\sim$ 5 nm	Highly dispersed Pt nanoparticles without agglomeration	[25]
	PdO-CO ₃ O ₄	FD 300–500 nm	Nafion/PdO-CO ₃ O ₄ /GCE exhibits the greatest electrocatalytic activity toward methanol electrooxidation	[26]
	Pt-PAN fibers			
	Pt-anchored electrospun WO ₃	FD 200–400 nm	The peak current density of Pt nanotubes anchored to WO ₃ nanofibers is 4.5 times higher than that of their spherical counterparts	[27]

PEMFC	Pt/e-CNFs	FD 250 nm, PD ~2.6–2.9 nm, MA 302 mA mg ⁻¹ Pt	The performance of the MEA prepared by e-CNF was excellent, owing to the morphology and the enhanced electrical conductivity	[28]
	PtPd/CNFs	FD ~250 nm, PD 29–64 nm	Pt-Pd/CNFs possess good performance in the electrocatalytic reduction of oxygen	[29]
	Pt/Nb-doped TiO ₂	FD 50–100 nm, PD 5 nm, MA 17.1 m ² g ⁻¹	Nb-doped TiO ₂ retained 60 % of the electrochemically active surface area after 1,000 cycles	[30]
	CrN-Cr ₃ C ₂	FD 200–500 nm	Conductivity studies revealed that the fiber systems are suitable for electrochemical applications	[31]
Others	Pt/Nb-TiO ₂	FD 10 nm, PD ~3 nm	Excellent catalytic activity for oxygen reduction	[32]
	Pd layer/TiO ₂	FD 115 nm, PD ~60 nm	Promote glycerol electrooxidation in alkaline medium	[33]
	PtxAu100-x/CNF	FD 700 nm, PD ~120 nm	Highly efficient electrocatalytic oxidation of formic acid	[34]
	Ni/YSZ	FD 300 nm	The peak power density is twice of that with the conventional anode	[35]
	FeCo-CNF	FD 100–200 nm	FeCo-CNF catalysts possess the comparable electrocatalytic activity and better tolerance to ethanol crossover than Pt/C in the oxygen reduction	[36]
	CNF-based biofilms	FD ~1,000 nm	The bioelectrocatalytic anode current density is shown to reach values of up to 30 A m ⁻² , which represents the highest reported values for electroactive microbial biofilms	[37]

Microstructure descriptions include fiber diameter (FD), particle diameter (PD), and/or mass activity (MA)

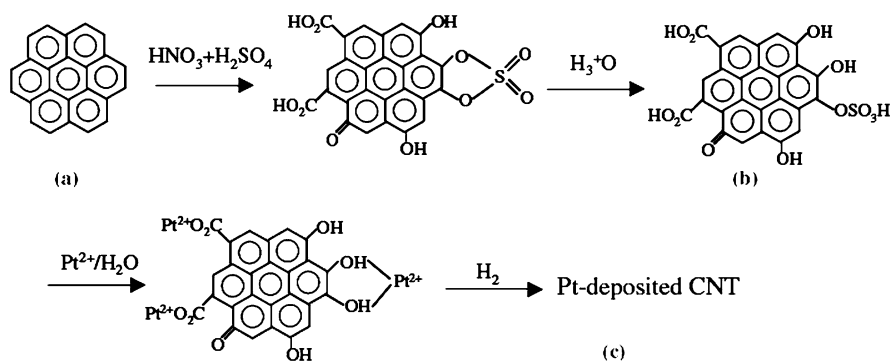


Fig. 2.3 Scheme of the mechanism of Pt deposition via the oxidation of $\text{HNO}_3 + \text{H}_2\text{SO}_4$ on CNFs (Reprinted with the permission from Yu et al. [51]. Copyright 1998 American Chemical Society)

structures. Among various carbon nanomaterials, electrospun carbon nanofibers (CNFs) are promising support materials for catalysts in fuel cells, due to their unique one-dimensional structure, high electronic and thermal conductivities, and good electrochemical stability [46–48]. However, CNFs are chemically inert and it is necessary to activate their graphitic surface because the deposition, distribution, and size of Pt or Pt alloy nanoparticles strongly depend on the surface properties of CNFs [49, 50]. Until now, many methods, such as electroless deposition and electrodeposition, have been carried out to prepare electrospun CNF-supported catalysts for the alcohol oxidation and oxygen reduction in fuel cells.

2.3.1.1 Electroless Deposition

Electroless deposition, also known as chemical deposition, is the most widely used method in preparing highly dispersed Pt nanoparticles on carbon supports for fuel cells. Figure 2.3 shows the typical preparation procedure of the chemical deposition method for Pt/CNF catalysts [51]. First, the aromatic conjugate ring structure of the CNFs was modified by an oxidation process of extremely aggressive reagents (HNO_3 or H_2SO_4 or their mixture). During that process, various surface functional groups such as quinoid ($=\text{O}$), hydroxy ($-\text{OH}$), and carboxyl ($-\text{COOH}$) were produced. These functional groups can supply defect sites for the Pt nanoparticle deposition. After adding Pt salt and a reductive agent such as H_2 , HCHO , or ethylene glycol, Pt^{2+} ions can be reduced and deposited on the defect sites created during the acid treatment.

This procedure was adopted by many scientists working on the preparation of electrospun nanofiber-supported catalysts. Steigerwalt et al. reported a multistep deposition and reactive decomposition of a precursor molecule containing 1 Pt and 1 Ru atom on herringbone graphitic carbon nanofibers (GCNFs) [52]. The resultant nanocomposites had a total metal content of 42 wt% with a bulk Pt/Ru atomic ratio of 1:1, and metal alloy nanoclusters had average particle sizes of 6–7 nm.

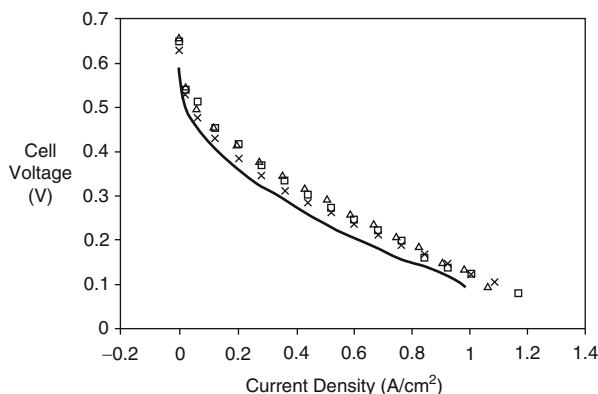


Fig. 2.4 *I-V* curves comparing the performance of Pt-Ru nanocomposites at a loading of 1.5 mg cm^{-2} with (triplicate) and without (solid line) CNF supports as anode catalysts in DMFCs (Reprinted from Guo et al. [53], Copyright 2006, with permission from Elsevier)

Comparative testing of those nanocomposites and unsupported Pt-Ru colloid with similar surface area and catalyst particle size revealed a 50 % increase in electrochemical performance for the Pt-Ru/GCNF nanocomposites. Guo et al. reported CNFs as supports to prepare highly dispersed Pt-Ru catalysts for DMFCs [53]. The results showed that the diameter of Pt-Ru nanoparticles was around 5 nm in Pt-Ru/CNF composites, and the CNF-supported catalysts gave better performance than commercial catalysts when the current density was higher than 50 mA cm^{-2} in spite of low methanol oxidation peak current density (Fig. 2.4). This improvement is ascribed to the large specific surface and unique structural properties of CNFs. More recently, a microwave-heated polyol process was employed to synthesize carbon-supported metal catalysts for DMFCs [54–56]. Unlike the conventional heating strategy, the microwave heating process can accelerate the reduction of the metal ions on the surface of carbon supports and reduce the temperature and concentration gradients in the solution, resulting in a more uniform environment for the nucleation and growth of metal particles [57]. Tsuji et al. prepared Pt-Ru alloy nanoparticles supported on CNFs within a few minutes by using a microwave-polyol method [58]. Three types of CNFs with very different surface structures, such as platelet, herringbone, and tubular ones, were used as carbon supports. The methanol fuel cell activities of Pt-Ru/CNF catalysts were in the order of platelet > tubular > herringbone, and the methanol fuel cell activities of PtRu/CNFs measured at 60°C were 1.7–3.0 times higher than those of a standard Pt-Ru catalyst loaded on carbon black Vulcan XC72R, which is shown in Fig. 2.5. Since CNF surfaces are always smooth and chemically inert, harsh oxidative methods are used to produce active sites to allow catalyst nanoparticles to be deposited on and anchored to the surface of CNFs. However, such treatments can potentially destroy the integrity of the CNFs, which result in their low electronic conductivity and poor cyclability. A method based on mild activation for electrospun CNFs and subsequent deposition can be utilized, that is, electrodeposition.

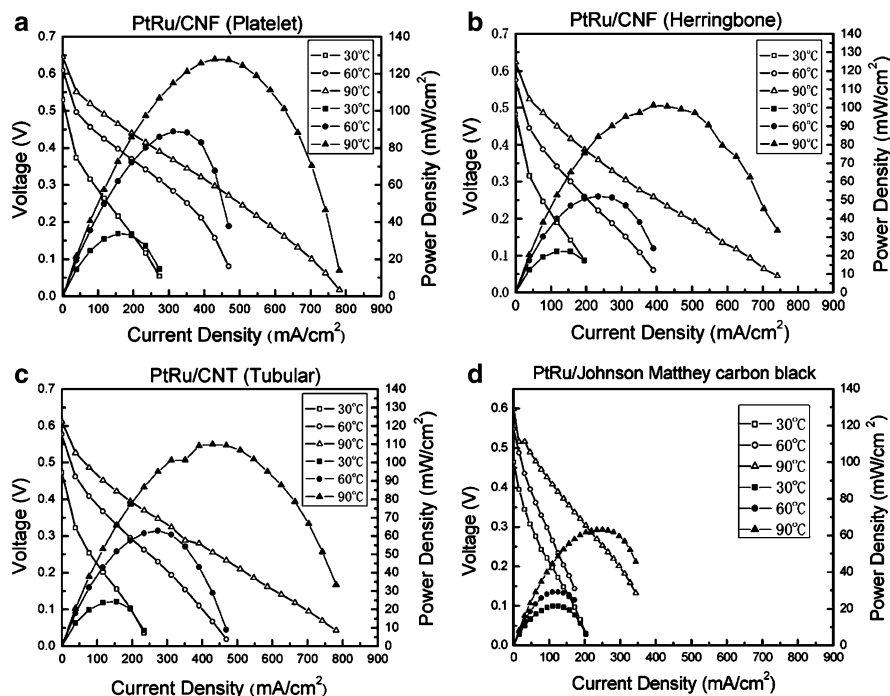


Fig. 2.5 Electrocatalytic activity of Pt-Ru catalysts loaded on platelet CNFs (a), herringbone CNFs (b), tubular CNFs (c), and carbon black Vulcan XC72R (d). Open and solid symbols represent voltage and power density, respectively (Reprinted with the permission from Tsuji et al. [58]. Copyright 2007 American Chemical Society)

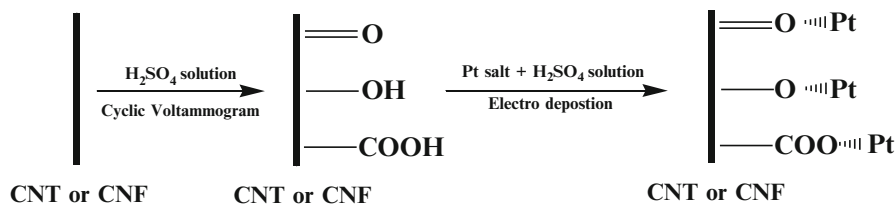
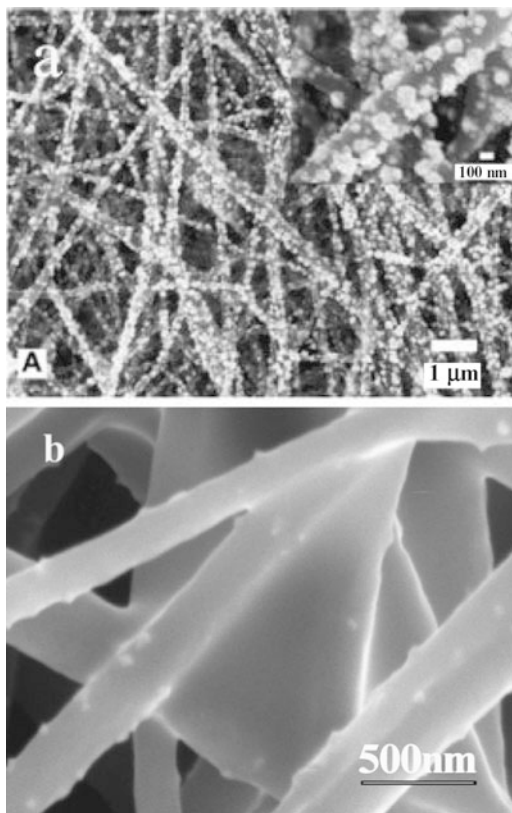


Fig. 2.6 Schematic diagram illustrating the procedure of electrodepositing Pt nanoparticles onto a CNT or CNF

2.3.1.2 Electrodeposition

Electrodeposition, which is used for attaining Pt particles onto the carbon supports, was developed by several research groups to improve the Pt utilization and reduce Pt loading [59–62]. The synthesis procedure for Pt/CNF catalysts using electrodeposition is shown in Fig. 2.6, which is similar to that used in the electroless deposition. In the electrodeposition, CNFs are first cycled in a sulfuric acid solution

Fig. 2.7 SEM images of as-prepared Pt/CNF electrode using multi-cycle CVs in 2.0 M H_2PtCl_6 + 0.5 M H_2SO_4 solutions (a) (Reprinted from Li et al. [19], Copyright 2008, with permission from Elsevier) and Pt/CNFs prepared with the electrodeposition potentials -0.2 V (vs. $\text{Ag}/\text{AgCl}/4.0$ M KCl) in 5.0 mM $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ + 1.0 M H_2SO_4 solutions (b) (Reprinted from Lin et al. [65], Copyright 2009, with permission from Elsevier)



between -0.7 and $+1.2$ V to oxidize the surface. During that process, various surface functional groups such as quinoid ($=\text{O}$), hydroxy ($-\text{OH}$), and carboxyl ($-\text{COOH}$) were produced, which can supply defect sites for the Pt nanoparticle deposition [63]. For instance, Wang et al. have successfully prepared Pt/CNT catalysts by electrodepositing Pt nanoparticles on CNTs in a $\text{H}_2\text{SO}_4 + \text{H}_2\text{PtCl}_6$ solution [64]. The results showed that although the Pt loading was 0.2 mg cm^{-2} on the CNT surface, the average diameter of the Pt particle was much larger (i.e., 25 nm) compared to the commercially available Pt/C catalysts, and the fuel cell performance was also lower than that of the conventional catalyst at a comparable Pt loading. Li et al. used the cyclic voltammogram method to deposit Pt particles onto CNFs, but the diameters of deposited Pt nanoclusters were too large (50–200 nm) for practical fuel cell applications (Fig. 2.7a) [19]. In comparison, Lin et al. reported the preparation and characterization of Pt/CNFs by the electrodeposition of smaller Pt nanoparticles (≤ 55 nm) onto electrospun CNFs under different potentials (Fig. 2.7b) [65]. The Pt/carbon composite nanofibers possessed the properties of high active surface area and fast electron transfer rate, which led to a good performance toward the electrocatalytic oxidation of methanol.

2.3.2 Other Nanofiber-Supported Catalysts

Except for carbon, polymers and other materials were also explored as alternatives for supporting catalysts in fuel cells. Electrospun polyaniline (PANI) nanofibers were fabricated by Liu et al. as the support for Pt. The diameter of the PANI nanofibers was 60–80 nm, which supplied a high surface area to disperse the nanoparticles [66]. These electrospun PANIs also exhibited a porous network for gas flow and good electrical conductivity, which made them an excellent support for electrode catalysts in fuel cells. The electrocatalytic activity of PANI/Pt was found to be much higher than that of bulk Pt electrodes; for example, the current density value was 24.7 versus 7.5 mA cm⁻² mg⁻¹ at 0.68 V. Xia et al. electrospun anatase TiO₂ nanofibers followed by the deposition of Pt nanoparticles with 2–5 nm in diameter [24]. The electrochemical activity and durability for anatase TiO₂ nanofiber-supported Pt nanostructures for direct methanol oxidation were much higher compared with those of commercial Pt/C catalysts. The improvement in catalytic activity and durability results from the synergistic effect of the underlying anatase surface and the Pt nanostructures with well-defined facets. Novel conductive or semiconductive oxides such as TiO_x [67, 68], SiO₂ [69], and MnO_x [70] were also electrospun as catalyst supports for fuel cell electrodes with enhancement in the catalytic performance. Metal oxides are superior to conventional catalyst supports due to their exceptional chemical stability and corrosion resistance at the potentials and pH in fuel cell operations. Such metal oxide-supported catalyst systems showed promising results in terms of catalyst performance and durability and also the tolerance to methanol, compared with conventional Pt/C electrodes [71, 72].

2.4 Electrospun Electrolyte Membranes

As a versatile technique for producing nanofibrous mats, electrospinning has been utilized for the development of composite fuel cell membranes for the purpose of modifying the proton exchange membranes and improving their performance. For example, non- or less-proton-conductive component, acting as mechanical reinforcement, can be incorporated into a porous matrix, generally Nafion®, for higher mechanical properties or lower methanol crossover. An overview on this type of studies was shown in Table 2.3.

Alternatively, electrospun functionalized nanofibers with high proton conductivity could also be incorporated into polymer matrices, in which perfluorosulfonated polymers, such as Nafion®, were selected as the matrix polymers. With the filled proton-conducting component fibers, the proton conductivity of composite membranes could be greatly enhanced. The relative reports are shown in Table 2.4.

There was a general thought that the proton conductivity is highly dependent on the concentration of the protonated groups or the ion-exchange capacity (IEC), that is, the volume fraction of the proton conductive component. For example, with the

Table 2.3 Electrospun non- or less-conductive component as mechanical reinforcements

Matrix polymer	Filler nanofibers	Remark	References
Nafion®	Polyvinyl alcohol	PVA was cross-linked with glutaraldehyde and had lower proton conductivity and lower methanol crossover	[73–76]
Nafion®	Polyvinylidene fluoride	17 wt% PVDF was electrospun with the solvent of 1:1 w/w acetone/dimethylacetamide. The composite membranes had lower conductivity but better properties of MEA performance and methanol crossover	[77]
Nafion®	Sulfonated poly(ether sulfone)	The composite membranes had a triple-layer structure of Nafion-SPES/Nafion-Nafion membrane. The composite membranes had a relative lower conductivity but better fuel cell performance and lower methanol crossover	[78]
Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO)	Cross-linked bromomethylated sulfonated polyphenylene oxide (BPPO)	The composite membranes had lower conductivity of 0.03–0.07 S/cm compared with SPPO of 0.09–0.15 S/cm but much lower water swelling ratio and improved fuel cell performance	[79, 80]
Perfluorosulfonic acid prepared in laboratory	Polyethersulfone loaded with CaCO ₃	The composite membranes had highly increased break strength and Young's modulus	[81]
660 EW perfluorosulfonic acid (PFSA) from 3 M Company	Polyphenylsulfone	The composite membrane with 70 vol% PFSA and 30 vol% polyphenylsulfone had lower conductivity but lower water swelling ratio	[82, 83]
Sulfonated poly(arylene ether sulfone) (SPAES)	Sulfonated silicate-nanocapsulated polyimide (sPI)	The composite membrane had relatively comparable conductivity with that of SPAES but better mechanical strength with SPAES	[84, 85]
PBI	Polybenzoxazine (PBz)-modified polybenzimidazole (PBI)	The composite membranes showed enhanced mechanical properties, twofold higher proton conductivity at 160 °C, and 34 % increased power density	[86]
Nafion®	SiO ₂ -coated polyetherimide	The composite membranes showed high mechanical properties, much lower water swelling, and lower proton conductivity	[39]
Nafion®	Poly(phenyl sulfone)	The composite membranes exhibited higher Young's modulus	[82, 83]

Table 2.4 Electrospun proton-conducting fiber fillers for PEM applications

Matrix polymer	Filler nanofibers	Proton conductivity (S/cm)	References
Poly(diallyldimethylammonium chloride) (PDDA), poly(styrene sulfonic acid, sodium salt) (PSS) LBL self-assembly	Sulfonated poly(flourenyl ether ketone) (SPFEK) and polyether sulfone (PES) co-electrospun fibers sandwiched with PES beaded nanofibers	0.06 (80 °C, 100 % RH), $E_a = 1.30$ KJ/mol	[87]
Norland Optical Adhesive (NOA63)	Perfluorosulfonic acid polymer (PFSA, 3 M Corporation)/poly(acrylic acid) (PAA)/sulfonated octaphenyl polyhedral silsesquioxane (sPOSS) with weight ratio of 65: 5: 35	0.498 (120 °C, 90 % RH)	[88]
UV-cured NOA63	Sulfonated poly(arylene ether sulfone)	~0.10 (25 °C, in water) for 80 vol% fibers	[88, 89]
Sulfonated poly(arylene ether sulfone)	Sulfonated polyhedral oligomeric silsesquioxane	0.094 (30 °C, 80 % RH)	[88, 89]
UV-cross-linked polyurethane (PU)	Sulfonated poly(arylene ether sulfone) (sPAES)/sulfonated polyhedral oligomeric silsesquioxane (sPOSS) (w/w = 60/40)	0.37 (80 °C, 80 % RH)	[90]
UV-cross-linked NOA63	Perfluorosulfonic acid polymers from 3 M Corporation (825 EW and 733 EW polymers)	~0.1 (80 °C, 80 % RH, 733 EW PFSA with 70 % fiber volume fraction)	[91]
Nafion®	SiO ₂ /sulfonated polyether ether ketone	0.077 (90 °C, 100 % RH)	[92]
N/A	Nafion® nanofibers	~0.12 (30 °C, 90 % RH)	[93–95]
N/A	Sulfonated poly(ether ether ketone ketone) (SPEKKK)	~0.08 (25 °C, 100 % RH)	[96]
Cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid)	Sulfated zirconia (S-ZrO ₂)	0.34 (100 °C, 80 % RH)	[97]
Nafion®	Sulfonated polystyrene (S-PS)	0.18 (80 °C, 100 % RH)	[98]
Nafion®	S-ZrO ₂	0.31 (80 °C, 100 % RH)	[99]
Lab-made sulfonated polyimide: NTDA-BDSA-r-APPF	NTDA-BDSA-r-APPF	1.3 (80 °C, 98 % RH, fiber axial direction) 0.036 (fiber perpendicular direction)	[100]

addition of cross-linked PVA nanofibers, the proton conductivity of Nafion/PVA composite membranes was reduced to 0.025 S/cm compared with 0.096 S/cm for Nafion 117. This value could be further reduced to around 0.01 S/cm with IEC value reduced from 0.58 to 0.33 meq/g, compared with the IEC value of 0.91 meq/g for Nafion 117 [73–76]. Similar phenomenon was evident with the use of Nafion/PVDF [77], Nafion/SiO₂-coated polyetherimide composite membranes [39], etc., as the proton exchange membranes. In addition, with the filling of long-range one-dimensional nanofibrous materials, a series of other properties of the membranes were significantly improved, such as the mechanical properties [73–76], hydrolytic stability [79], reduced methanol crossover [73–76], and so forth.

With the in-depth comprehension of the working principle of ion transport in proton exchange membranes, for example, Nafion[®], quantitative and qualitative modeling studies have been conducted for supporting the optimization of not only the composition of the membranes but also the operating conditions, thereby yielding higher efficiencies and power densities. In terms of microscopic models, there have been many models based on statistical mechanics, molecular dynamics, and macroscopic phenomena applied to the microscopic structure of the membranes. These models provide a fundamental understanding of processes like diffusion and conduction in the membranes on a microscopic scale including the effect of small perturbations, such as nonhomogeneity of pores, electric fields on transport, and the introduction of small-scale structural effects. The basis for all these models is the description of the microscopic structure of the polymer that was proposed in the early 1980s by Gierke and Hsu [101]. In their work, the authors correlated the experimental data through geometric and phenomenological relationships for the swelling of the polymer caused by the uptake of water and its effect on the diffusion coefficient of water in the membrane pores. The correlation evolved by analyzing the data taken under different operating conditions led to the formulation of a widely accepted description of the polymeric membranes in terms of an inverted micellar structure, in which the ion-exchange sites are separated from the fluorocarbon backbone, and thus forming spherical clusters (pores). These clusters are connected by short narrow channels. The model was hence termed as “cluster network” model. When the membrane is dry, an average cluster has a radius of about 1.8 nm and it contains about 26 $-\text{SO}_3^-$ groups distributed on the inner pore surface, as illustrated in Fig. 2.8a. In the swollen state, the diameter increases to about 4 nm and the number of fixed SO_3^- groups goes up to about 70. Under these conditions, each pore is filled with about 1,000 water molecules and the connecting channels have a diameter and a length of about 1 nm. According to this theory, there is a critical amount of water available in the membrane, below which proton transport is extremely difficult due to the absence of extended pathways. Above or near the threshold, the conductivity (σ) is as follows:

$$\sigma = \sigma_0(c - c_0)^n \quad (2.4)$$

where c is the volume fraction of the aqueous phase, c_0 the percolation threshold for the water content in the membrane, n a universal constant which depends on the

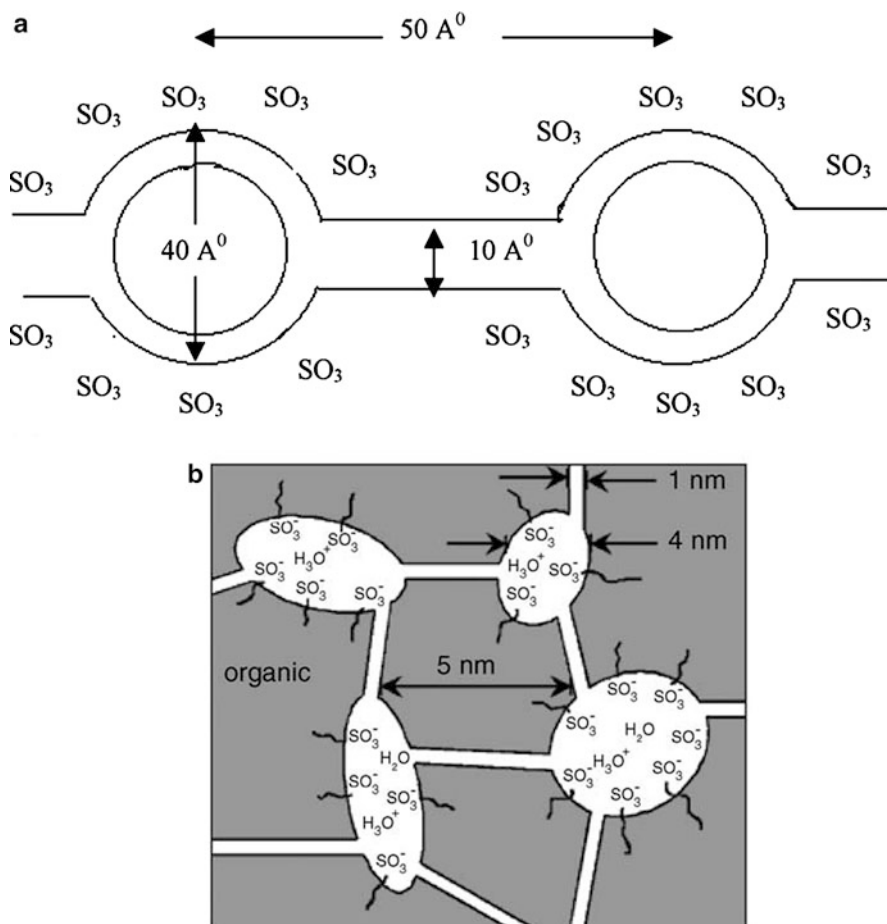


Fig. 2.8 Schematic diagrams of (a) cluster network model (Reprinted with the permission from Yeager and Eisenberg [101], Copyright 1982 American Chemical Society) and (b) random cluster network model (Reprinted with permission from Eikerling et al. [102], Copyright 1997 American Chemical Society)

dimensions of the system, and σ_0 a factor related to the molecular interactions that can only be computed from specific microscopic models. A comparison between experimental results and percolation theory showed a good agreement.

Based on the cluster network model, further studies propose an interpretation of the percolation properties of proton conductivity as a function of water content by using a "random network model" [102], which is a modification of the "cluster network model." This model includes an intermediate region wherein the side chains ending with pendant sulfonic acid groups, which are bonded to the perfluorinated backbones, tend to form cluster within the overall structure of the material resulting in the formation of hydrated regions. Unlike the "cluster network model," the

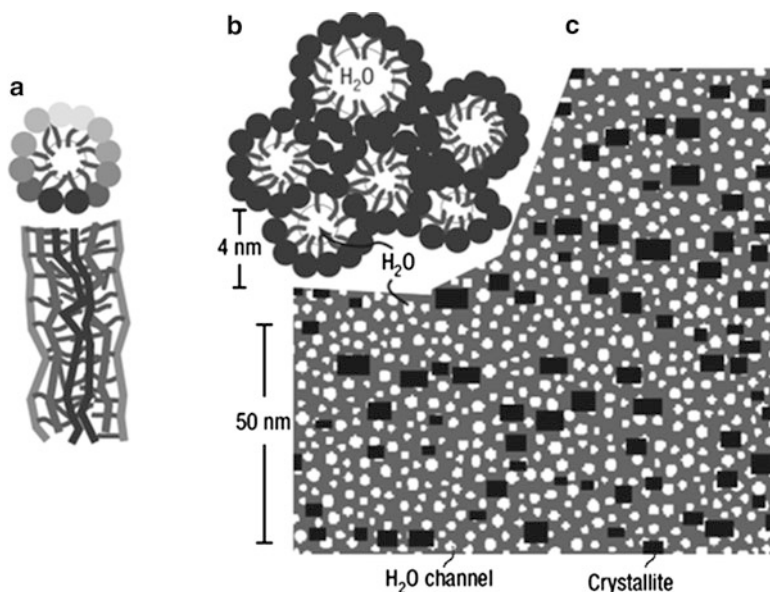
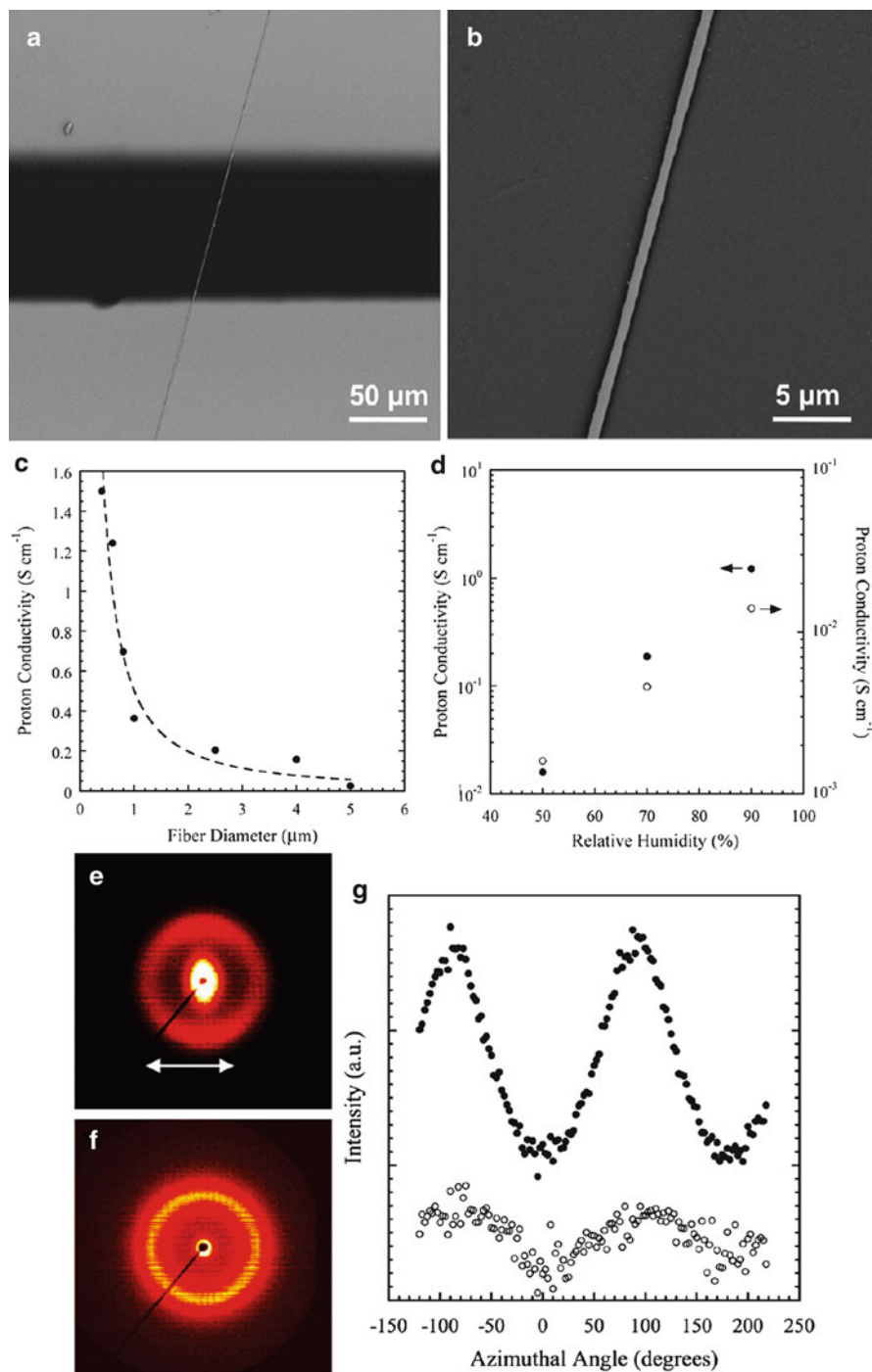


Fig. 2.9 (a) Two views of an inverted-micelle cylinder, with the polymer backbones on the outside and the ionic side groups lining the water channel. Shading is used to distinguish chains in front and in the back. (b) Schematic diagram of the approximately hexagonal packing of several inverted-micelle cylinders. (c) Cross sections through the cylindrical water channels (white) and the Nafion crystallites (black) in the noncrystalline Nafion matrix (dark gray) (From Schmidt-Rohr and Chen [105]. Reprinted by permission of Nature Publishing Group)

hydrated regions in this model are distributed randomly in the polymer matrix, which facilitates quicker transport of protons upon the rotation of these side chains. In this case, although the hydrated regions drift apart, the traverse motion of protons through the membranes is possible, as shown in Fig. 2.8b. Haubold et al. verified through small-angle X-ray scattering (SAXS) that the “random network model” could be applied to Nafion [103]. James et al. deployed the atomic force microscopy (AFM) technique and found the “random network model” to be generally acceptable on Nafion 117, which is a commonly available Nafion membrane, typically used in the region of 9–34 % RH [104]. Based on the recent model (inverted-micelle cylinder model) of Nafion (Fig. 2.9), the diameter of the ionic channel is 1.8–3.5 nm, with an average diameter of 2.4 nm, while the length of the channel is at the level of tens of nanometers, with the hydration degree of 20 vol% (11 wt%) water.

According to the modeling of proton exchange membranes, the transport of hydrated protons depends not only on the amount of protogenic functional groups but also on the effective phase separation and appropriate arrangement of ionic clusters in the membrane. Inspired by the ion channel structure, 1D nanomaterials should be one of the most promising candidates, including sulfonate single-wall carbon nanotubes [106, 107], sulfonate nano- or micro-channels [108–110], self-assembled nanomaterials [111], and electrospun nanofibers [82, 100, 112–114].



It was shown that even with inert polymer matrix, such as UV-cross-linked NOA63 or PU for mechanical reinforcement, the composite membranes with electrospun functionalized nanofibers could still offer a significantly higher in-plane proton conductivity than that of commercial Nafion membranes [77, 83, 114–116], which was possibly due to the continuous network of proton-conducting nanofibrous paths which span the membrane thickness. It was also reported that because of the high shear force and fast drying process during electrospinning, the electrospun Nafion nanofibers show obvious higher scattering maxima of $q \sim 1.65 \text{ nm}^{-1}$ on 2D X-ray patterns than that of 1.58 nm^{-1} for Nafion cast films, indicating the anisotropic alignment of ion aggregates in nanofibers and isotropic ion aggregates in cast films. The inner alignment of ionic structure can significantly improve proton conductivity. As shown in Fig. 2.10, with the fiber diameter reducing to 400 nm, the proton conductivity along the fiber axis can be as high as 1.5 S/cm [93–95]. Interestingly, when composite membranes were filled with well-aligned sulfonated nanofibers, the in-plane conductivity was different between the axial and perpendicular directions, verifying the uniaxial enhancement of proton transport in functionalized polymers [100].

Besides the electrospun functional polymers, ceramic nanofibers, such as solid superacid like S-ZrO₂, can also be used as the nanofibrous fillers. During the formation of hybrid membranes, hydrophilic attractions between the sulfate groups on S-ZrO₂ fibers and sulfonic acid groups in Nafion lead to the aggregation of ionic clusters onto the organic-inorganic interfaces. The increased amount of interfacial protogenic groups forms long-distance ionic pathways along the S-ZrO₂ fibers that ensure effective proton transport through the entire membranes, as shown schematically in Fig. 2.11. As a result, the in-plane proton conductivity can also be highly improved.

2.5 Summary and Outlook

Nanofibers for fuel cells can potentially play a key role in meeting global energy demands in the coming century due to their unique structures and high surface area to volume ratios [117, 118]. Among many nanofiber fabrication methods,



Fig. 2.10 Properties of electrospun Nafion nanofibers: (a) SEM image of a single high-purity Nafion nanofiber (99.9 wt% Nafion) bridging two electrodes; (b) enlarged image of (a); (c) proton conductivity (at 30 °C, 90 % RH) versus fiber diameter for high-purity Nafion nanofibers measured on individual nanofibers; (d) humidity-dependent proton conductivity (30 °C) of a single high-purity Nafion nanofiber (*solid symbols*) and a cast Nafion film (*open symbols*); 2D X-ray scattering patterns (at 86 % RH, 25 °C) of (e) macroscopically aligned high-purity Nafion nanofibers (*arrows* indicating longitudinal direction of fibers) and (f) Nafion cast film; (g) X-ray scattering intensity as a function of azimuthal angle for macroscopically aligned high-purity Nafion nanofibers (*solid symbols*) and a cast Nafion film (*open symbols*) (Reprinted with permission from Tamura and Kawakami [100]. Copyright 2010 American Chemical Society)

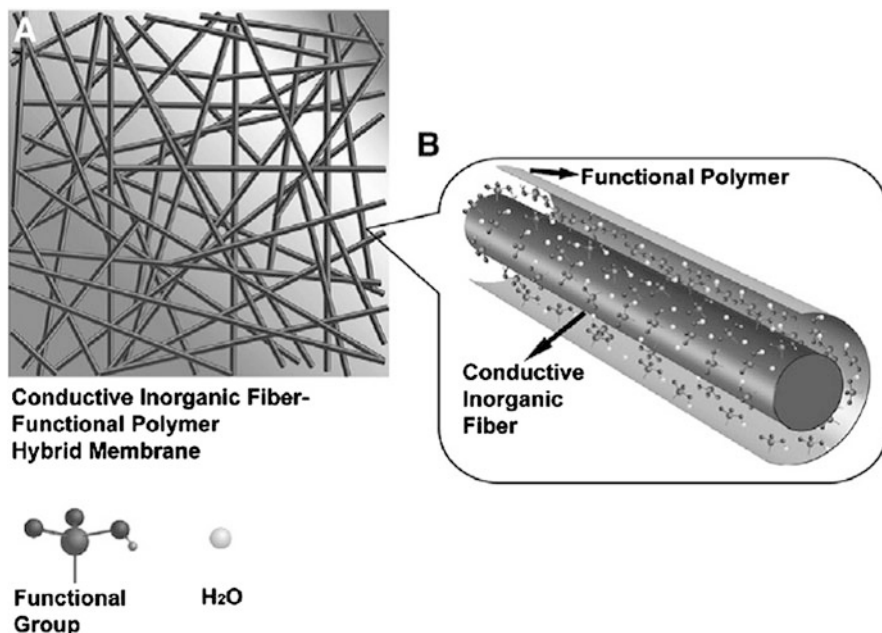


Fig. 2.11 Schematic diagrams of (a) conductive inorganic fiber/polymer hybrid membrane and (b) the long-range ionic channel between the conductive fiber and functional polymer matrix (Reprinted from Yao et al. [97], Copyright 2011, with permission from Elsevier)

electrospinning is arousing the most intense interest due to its comparative low cost and high production rate for practical energy-related applications. It is a relatively feasible method which provides great control over the fiber morphology, such as the homogeneity, porosity, and a variety of structures including core-shell, hollow, and aligned fibers [119].

There are still several challenges left to be overcome before the large-scale usage of electrospun materials in fuel cell applications. For nanofibrous applications in catalysts and supports, the developments are further needed to reduce fiber diameters and improve the diameter uniformity for higher electrocatalytic ability and lower cost. The process parameters affecting the electrospinning technique are still not fully understood; thus, there are still limitations on the types of catalysts and support materials synthesized by electrospinning. In the applications of composite membranes, nanofibers have been widely investigated as either mechanical or stability reinforcing component or proton conductor. With the further investigation of electrospinning technology, solutions with sufficient viscosity can be electrospun to nanofibrous networks [120]. Other fibrous structures composed of various materials, such as solutions of self-assembled small molecules, can also be electrospun to nanofibers and used as the filler of proton exchange membranes [121]. Furthermore, as the fiber mats generally lie in the composite membranes, while the in-plane proton conductivity increased, the through-plane conductivity was still on

a relatively low level, which however was the actual proton transporting direction. Further work on electrospun nanofibers used in proton exchange membranes needs to focus on the progress of through-plane proton conductivity and the improvement of fuel cell performance. Addressing these concerns requires dedicated, renewed, intense, and extensive research on nanofibers from electrospinning, which will make their scale-up become practical for fuel cells from an industrial perspective in the near future.

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