

Chapter 2

Organic/TiO₂ Nanocomposite Membranes: Recent Developments

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Abstract Fuel cells may become a key energy management, but technical and economic feasibility still need to be sensibly improved. Many studies in order to overcome the limits of the technology are nowadays in progress. A promising and interesting development solution appears to be the improvement of the membrane properties used in fuel cells by nanotechnologies. In this book chapter, a review on the recent developments about organic/TiO₂ nanocomposite membranes will be presented, and the results obtained in the recent years will be discussed. As a main issue, polymer composites containing a small amount of inorganic materials lead to a significant increment in the interfacial area of the organic–inorganic phases, enhancing a considerable volume fraction of the interfacial polymer. Moreover, these composite systems may be capable to provide unique combination of organic properties, such as electrical property and processability, together with inorganic, comprising thermal and chemical stability and minor fuel permeability. To sum up, the organic–inorganic composite systems might also provide improved chemical and mechanical stability, as well as high proton conductivity at high temperatures.

Keywords Fuel cells · Nanocomposite membranes · Titanium dioxide · Novel energy technology · Polymer electrolyte membranes

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1 Introduction

Fuel cells are nowadays being intensely investigated as novel energy source. Briefly explained, fuel cells are electrochemical devices in which an electrocatalytic process leads to a direct transformation of chemical energy of the fuel to electricity.

The high efficiency and the fact that fuel cells do not emit pollutants such as SO_x , NO_x and CO_2 , compared to coal combustion engines, makes fuel cell a very promising technology. On the other hand, the high costs involved with the commercialization of fuel cells make imperative to carry on further investigation to cope with them, mainly focusing on the development of new materials and optimization of prior or novel fabrication processes.

In particular, among the various fuel cell system types available nowadays, polymer electrolyte membrane fuel cells (PEMFC) appears to be promising, since they satisfy technical and economical requirements and results to be very versatile, and can be used for a wide range of small-scale applications such as automotive, stationary equipment and portable power generation, among others Kim et al. [1].

In PEMFCs, the power-generating system consists of an electrochemical reaction which involves gases such as hydrogen, methanol and ethanol. The main reactions are briefly summarized below:

On the anode: $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$

On the cathode: $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$

Resulting in the overall reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

A scheme of the operating mechanism of polymer electrolyte membrane fuel cell presented is in Fig. 1. The key component of PEMFCs is the polymer electrolyte membrane (PEM). This PEM behaves as a semipermeable barrier and thus provides a barrier for the passage of the electrons and fuel whereas functions as an electrolyte to transfer the protons from the anode to the cathode. Hydrogen ions (H^+) at the anode move to the cathode through the PEM, which produces as a consequence the electrical current and water as a by-product Jang and Hang [2].

In the 1970s, DuPont developed the first cation-exchange membranes based on polymer fluorosulfonic acid ionomers, named Nafion[®] series. Nafion[®] PEM was chosen as a standard for polymeric electrolyte fuel cells owing to thermal and chemical stability and high ionic conductivity (0.1 S cm^{-1} at fully hydrated condition). However, Nafion[®] membranes associated with several drawbacks, mainly a decrease in the ionic conductivity and low humidity at high temperatures, which poses a barrier for their definite commercialization according to expected cost-efficiency.

For these reasons, intensive research on novel proton-conducting membranes has been performed recently to improve the performance of the existing fuel cells. During the past few years, a plethora of researchers have focused on the development of reliable, high performance PEMs which could be able to provide high proton conductivity and, at the same time, ensure a series of key features comprising mainly:

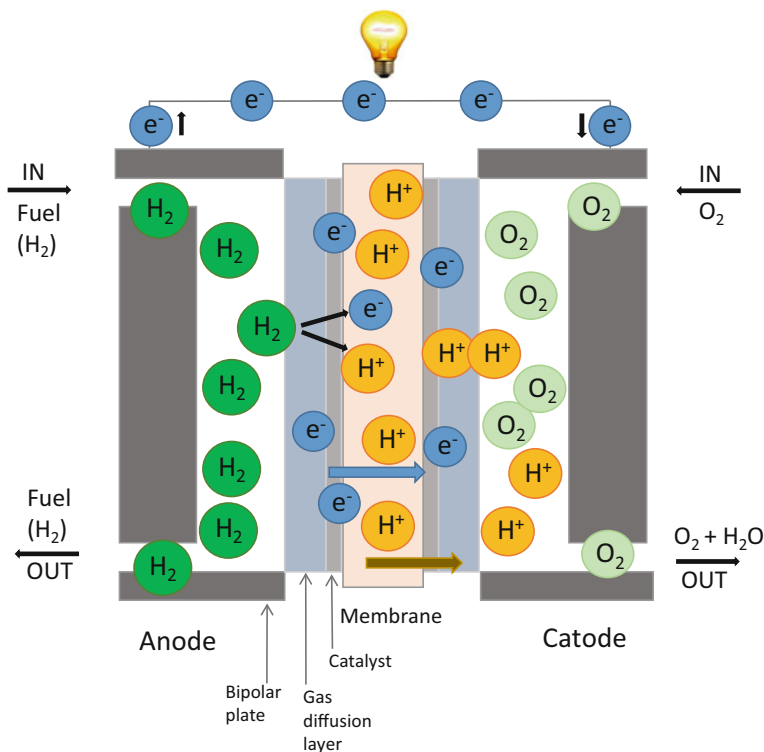


Fig. 1 Polymer electrolyte membrane fuel cell operating mechanism scheme

- low fuel permeability,
- high oxidative stability,
- good mechanical stability,
- low membrane electrolyte and assembly fabrication costs.

An interesting review on new polymer options for their implementation in these electrolyte membranes for fuel cells was published by Lee et al. [3]. For example, modified Nafion[®] and several hydrocarbon-based polymers such as sulfonated aromatic polymers based on poly(ether ketone) (PEEK), poly(ether sulfone) (PES), and polybenzimidazole (PBI) have attracted interest for use in PEMFCs in the recent years.

An illustrative summary of the principal polymers used in the fabrication of polymer electrolyte membrane fuel cells is given in Fig. 2.

In addition to this, it is especially relevant to highlight the role that inorganic–organic composite membranes have recently gained for these purposes, which is the main focus of the present chapter. Inorganic–organic composite membranes have drawn much attention for the development of new proton-conducting electrolytes in fuel cell applications in order to overcome such existing drawbacks.

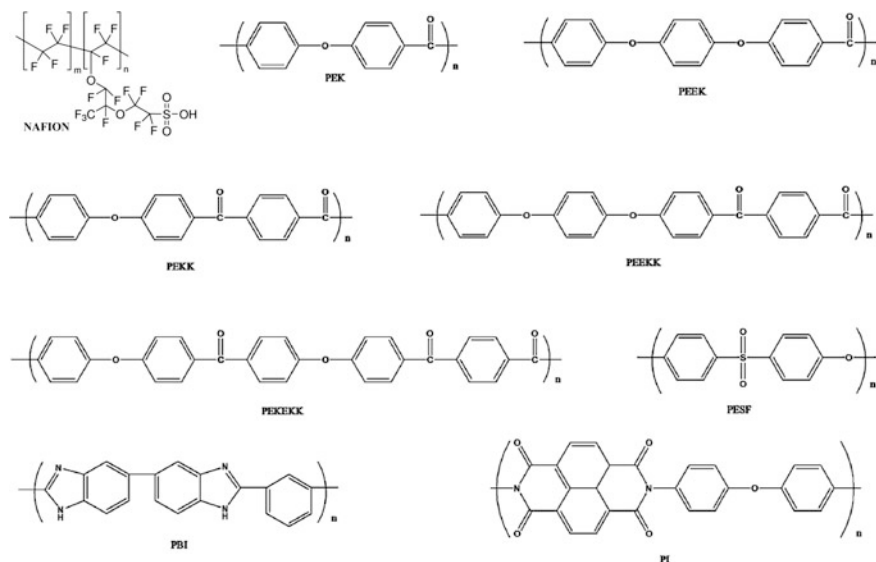


Fig. 2 Main polymers used in the fabrication of polymer electrolyte membrane fuel cells

Despite the advances accomplished on composite membranes research during the past few years, technical and economic challenges in the commercialization of fuel cells still hold on. Moreover, composite membranes can be prepared in various forms such as precursors and particles. There is a wide range of different materials and modification methods available to develop composite membranes. The most typical materials used extensively in recent research for composite fabrication include solid acids, silica and clays [4, 5], metals [6, 7] and blends using a second polymer because of unique properties and surface chemistry as well as excellent mechanical strength for long term use. The most widely used techniques to modify the inorganic particles by adding functional ionic sites, to improve the electronic properties, are chemical synthesis, sol-gel method and the doping or infiltration of inorganic nanoparticles and precursors [8].

In this book chapter, a review on the recent developments about organic/TiO₂ nanocomposite membranes will be presented, and the results obtained in the recent years will be discussed. As a main issue, polymer composites containing a small amount of inorganic materials lead to a significant increment in the interfacial area of the organic-inorganic phases, enhancing a considerable volume fraction of the interfacial polymer. Moreover, these composite systems may be able to provide a unique combination of organic properties, such as electrical property and processability, together with inorganic, comprising thermal and chemical stability and minor fuel permeability. To sum up, the organic-inorganic composite systems might also provide improved chemical and mechanical stabilities, as well as high proton conductivity at high temperatures.

2 TiO₂-Polymer Electrolyte Membranes (PEMs)

In polymer electrolyte membrane (PEM), methanol is converted into CO₂ by moving to the cathode, such that reduction of functional methanol results in the formation of a multiple potential at the cathode.

Also, composite materials formed by polymers as alternative to Nafion[®] such as polyethersulfone (PES), poly(etheretherketone) (SPEEK), and chitosan (CS) and inorganic fillers such as Fe₃O₄, TiO₂, montmorillonite (MMT), carbon nanofiber (CNF), and activated carbon nanofiber (ACNF), as well as carbon nanotubes (CNT) have been investigated for use as microbial fuel cells (MFC) membranes with promising results. The cost of these composite membranes is lower than that of Nafion[®]. Furthermore, the addition of inorganic fillers to the polymer electrolyte membrane in MFCs helps to reduce the substrate oxygen crossover and improves the performance of the membrane during the microbial fuel cell (MFC) operation. Incorporation of a variety of nanosized materials may produce synergistic effects.

A brief summary of the main organic–inorganic nanocomposite TiO₂ polymer electrolyte membrane (PEMs) systems proposed for PEMFCs up to the date is given in Table 1. Liccocia et al. [9] carried out the synthesis of nanocrystalline ceramic oxides added to Nafion[®] in order to achieve the goal of operating at temperatures above 120 °C. Commercial Nafion[®] 115 and Nafion[®]/TiO₂ composite membranes were tested in polymer electrolyte fuel cells, both for direct hydrogen (DH-PEFC) between 80 and 130 °C. The best performance was with Nafion[®]/TiO₂ composite membranes in whole range, obtaining a power density of up to 0.514 mW cm⁻² for the composite membrane versus 0.354 mW cm⁻² obtained with Nafion[®] 115 at 0.56 V and 110 °C. The stability of the composite membrane above 130 °C was the fascinating part of this report, reaching a power density of 0.254 mW cm⁻² at 0.5 V.

In a similar way Slade et al. [10] tested a series of cation-exchange membranes made with Nafion[®] modified with inert filler particles (SiO₂, ZrO₂ or TiO₂; 5–20 wt%). Results showed improvement in ion-exchange capacity/equivalent weight, water take-up, thickness change on hydration and ionic and electrical conductivity.

2.1 Perfluorinated Organic–Inorganic Nanocomposite Polymer Electrolyte Membranes (PEMs)

Although perfluorinated polymers present some advantages, they also exhibit a series of drawbacks, mainly due to the loss of fuel and proton conductivity at high temperatures given by their relative low water content. As a consequence, extensive research has been performed in the recent past towards the development and fabrication of high performance alternative membranes. A comprehensive summary of the perfluorinated organic–inorganic nanocomposite PEMs is presented in Table 2.

Table 1 Main organic–inorganic nanocomposite TiO₂ polymer electrolyte membranes (PEMs) used for PEMFC

Membrane type	Membranes synthesized
Perfluorinated organic–inorganic nanocomposite PEMs	TiO ₂ /PVDF-HFP, TiO ₂ /Nafion [®] , TiO ₂ -RSO ₃ H/Nafion [®] and TiO ₂ aerogels/Nafion [®] doped with Nb, Ta and V
Acid–base polymer complex-based organic–inorganic PEMs	TiO ₂ /SO ₃ H/Nafion [®] , F–TiO ₂ –NT/Nafion [®] , PVA/TiO ₂ /Nafion [®] , PVA/nt-TiO ₂ /PSSA and P ₂ O ₅ –SiO ₂ –TiO ₂ /PVA
Poly(ether ether ketone)-based nanocomposite PEMs	(RSiO _{1.5}) _n /SPEEK, TiO ₂ /SPEEK, TiO ₂ /PANI/SPEEK, TiO ₂ /SO ₃ H/SPEEK, functionalized TiO ₂ submicrospheres/SPEEK and TiO ₂ (Rutile)/SPEEK
TiO ₂ -modified polytetrafluoroethylene, PANI, polyethersulfone (PES) and polysulfone (PS) nanocomposite PEMs	TiO ₂ /PAA/PTFE, PANI/mesoporous TiO ₂ , TiO ₂ /SPES, (S–TiO ₂)/SPSEBS SPSU and sulfated TiO ₂ /NMPA
TiO ₂ solar cells	TiO ₂ /Nafion [®] /Pt and DSSC by photocured polymer electrolyte membrane
Carbon materials and metal–carbon nanotube (CNTs)–TiO ₂ composites	Ru ₈₅ Se ₁₅ /TiO ₂ /C, Pt/TiO ₂ /C, Pd/TiO ₂ /C, Pt/(Ti _x Sn _{1–x} O ₂)/C, TNTs/Pt/C, TiO ₂ (Rutile)/C (semi-graphitic), TiO ₂ /GN and TiO ₂ nanowire/GN

PVDF-HFP poly(vinylidene fluoride-co-hexafluoropropylene); *PVA* poly(vinyl alcohol); *PTFE* polytetrafluoro-ethylene; *PAA* polyacrylamide; *SPEEK* sulfonated poly(ether ether ketone); *PANI* polyaniline; *SPSEBS* polystyrene ethylene butylene polystyrene; *NMPA* nitrilotri(methyl triphosphonic acid); *SPSU* sulfonated polysulfone; *DSSC* flexible dye-sensitized solar cell; *TNTs* TiO₂ nanotubes; *GN* Graphene

Researchers focused on the use of novel polymers, and in parallel to this on the introduction of inorganic materials as fillers in the polymer matrix. As an example, modified perfluorinated polymer-based membranes containing hydrophilic metal oxides including titanium dioxide (TiO₂), zirconium dioxide (ZrO₂) or silicon dioxide (SiO₂) were produced. Other studies were reported on the use of heteropoly acids (phosphotungstic acid and silicatingtungstic acid). Mohammadi et al. [11] investigated Nafion[®] composite membranes containing ZrO₂ and TiO₂ nanoparticles. The TiO₂ additive (average size diameter around 25 nm) enhanced the water retention properties of these membranes. Furthermore, these nanocomposite membranes were found to exhibit better electrochemical performance of the cell even at a high temperature (110 °C) and humidity (30%). The metal–oxide-based inorganic fillers improved the mechanical properties, and also contributed to the blocking of the fuel such as methanol by increasing the transport pathway tortuosity and improving the proton conductivity, which resulted in better cell performance.

Deposition of TiO₂ nanoparticles (NPs) from a sol solution was carried out by Liu et al. [12] to prepare modified Nafion[®] 112 membrane films via spin coating, for which they observed a maximum cell voltage by introducing 0.009 mg cm^{–2} TiO₂ NPs. Similar results were obtained by Santiago et al. [13] with Nafion[®]-TiO₂

Table 2 Perfluorinated organic–inorganic nanocomposite PEMs

Author/s	Membrane type	Achievement
Li et al. [14]	TiO ₂ /PVDF-HFP	Ionic conductivity and ions transport activation energy enhanced ($0.94 \times 10^{-3} \text{ S cm}^{-1}$ and $18.71 \text{ kJ mol}^{-1}$) at 9.0 wt% mass fraction
Liccocia et al. [9]	TiO ₂ /Nafion [®] 115	Power density of up to 0.514 mW cm^{-2} for TiO ₂ /Nafion [®] versus 0.354 mW cm^{-2} obtained with Nafion [®] 115 at 0.56 V and 110 °C
Liu et al. [12]	TiO ₂ /Nafion [®] 112	Maximum cell voltage by introducing 0.009 mg cm^{-2} TiO ₂ NPs
Santiago et al. [13]	TiO ₂ /Nafion [®] hybrid membranes	Increase in the ohmic drop when TiO ₂ content was increased
Amjadi et al. [15]	TiO ₂ /Nafion [®]	Water uptake of Nafion [®] /TiO ₂ membrane with 3 wt% doping found more than double with respect to pure Nafion [®] membrane
Zhengbang et al. [16]	TiO ₂ /Nafion [®]	Conductivity of fabricated composite membranes was higher than that of original Nafion [®] ; TiO ₂ nanowire (5 wt%) also improved the mechanical properties of the composite membrane at different temperatures and humidity conditions
Cozzi et al. [17]	TiO ₂ -RSO ₃ H/Nafion [®]	Proton conductivity was 0.08 S cm^{-1} at 140 °C for the composite membrane containing 10 wt% TiO ₂ -RSO ₃ H; also higher ion-exchange capacity (IEC) was registered
Beauger et al. [18]	TiO ₂ aerogels/Nafion [®] doped with Nb, Ta and V	Improved electronic conductivity from $10^{-6} \text{ S cm}^{-1}$ for pure TiO ₂ aerogels to $8.3 \times 10^{-2} \text{ S cm}^{-1}$ after doping TiO ₂ aerogels at 10 at.% for Nb

PVDF-HFP poly(vinylidene fluoride-co-hexafluoropropylene)

hybrid membranes, which showed an increasing ohmic drop when the TiO₂ content was increased. Li et al. [14] developed a composite TiO₂/PVDF-HFP membrane, and observed that the ionic conductivity of the membrane at room temperature and the ions transport activation energy were enhanced ($0.94 \times 10^{-3} \text{ S cm}^{-1}$ and $18.71 \text{ kJ mol}^{-1}$, respectively) upon 9.0 wt% mass fraction.

Nafion[®]/TiO₂ nanocomposite membranes were prepared by in situ sol–gel and casting methods, in order to compare both synthesis methods. The former was performed by soaking the Nafion[®] membranes in tetrabutylortotitanate (TBT) and methanol solution, whereas a Nafion[®]/TiO₂ composite membrane was fabricated with 3 wt% of TiO₂ particles by the solution casting method. The sol–gel method was found to lead to more uniform distribution of Ti particles in the Nafion[®]/TiO₂ composite membrane than the ones produced by casting. Water uptake of Nafion[®]/TiO₂ membrane with 3 wt% doping level was found to be more than double with respect to that of the pure Nafion[®] membrane. The membrane electrode assembly (MEA) prepared from Nafion[®]/Titania nanocomposite membrane showed the highest PEMFC performance in terms of voltage *versus* current density at high temperature (110 °C).

Furthermore, Amjadi et al. [15] investigated the synthesis of Nafion®/TiO₂ membranes for proton-exchange membrane fuel cell (PEMFC) operating at high temperatures.

Zhengbang et al. [16] developed and studied the performance of TiO₂ nanowire-reinforced Nafion® composite membranes, by self-assembly of positively charged TiO₂ nanowires and negatively charged Nafion® molecules at low pH conditions. They found that the conductivity of the fabricated composite membranes was higher than that of the original Nafion® at low temperatures. The TiO₂ nanowires associated with the –SO₃ hydrophilic sites through self-assembly influenced the proton transport, which induced a stable cell performance. TiO₂ nanowire (5 wt%) also improved the mechanical properties of the composite membrane at different temperatures and humidity conditions.

Cozzi et al. [17] performed extensive research on organically functionalized titanium oxide/Nafion® composite proton-exchange membranes. They synthesized an organically modified ceramic material (TiO₂–RSO₃H) by covalently grafting propylsulfonic acid groups on the surface of TiO₂ nanoparticles, and subsequently used it as filler in Nafion-based composite membranes. The synthetic pathway for the surface functionalization of TiO₂ nanoparticles is shown in Fig. 3.

The authors reported superior performance of Nafion®/TiO₂–RSO₃H composite membranes compared to Nafion® (improvement up to 40%). In this regard, proton conductivity of the hybrid material was confirmed to be up to 0.08 S cm^{–1} at 140 °C for the composite membrane containing 10 wt% TiO₂–RSO₃H, and also higher ion-exchange capacity (IEC) was registered. Furthermore, the filler led to cell response enhancement, both in terms of higher delivered power density and lower methanol crossover.

Beauger et al. [18] synthesized doped TiO₂ aerogels as alternative catalyst supports for PEMs. Nb-, Ta- and V-doped TiO₂ aerogels were tested to increase the electronic conductivity of TiO₂. All dopants improved the electronic conductivity and whatever the dopant, the electronic conductivity was increased with the dopant level. The pure TiO₂ aerogel had about 10^{–6} S cm^{–1} electronic conductivity whereas the maximum value was obtained after doping at 10 at.% for Nb

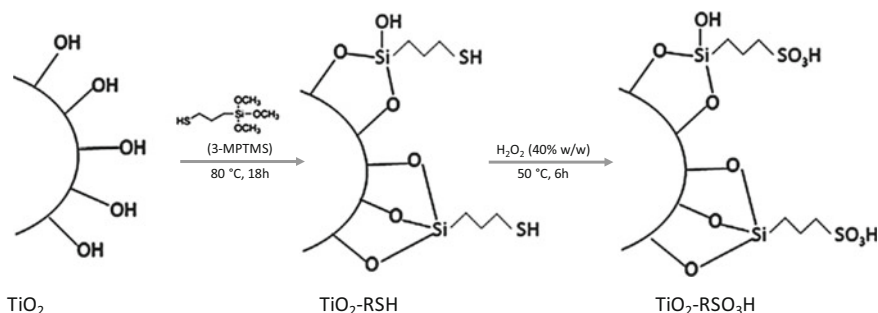


Fig. 3 Synthetic pathway for surface functionalization of TiO₂ nanoparticles [14]

($8.3 \times 10^{-2} \text{ S cm}^{-1}$). The results showed, at all levels of performance, that the best dopants were Nb, Ta and finally V. Within this context Gojković et al. [19] used Pt/Nb–TiO₂ and Pt–Ru/Nb–TiO₂ as anode catalysts supporters for PEMFCs. Results indicated good conductivity of the supporting material compared with Pt/TiO₂ membranes.

2.2 Acid–Base Polymer Complex-Based Organic–Inorganic Nanocomposite PEMs

Acid–base polymer complex-based organic–inorganic nanocomposites have been recently introduced for PEMs Table 3. The main acid–base polymer based organic–inorganic composites lists.

Houn-Rhee et al. [20] grafted thiol and sulfone groups onto the surface of titanate nanosheets to perform organic acid functionality (HSO_3^-) to their surfaces. Results showed higher ionic conductivity values for nanocomposite membranes containing 3–7 wt% HSO_3^- titanate than composite membranes containing 3 wt% TiO₂/P25 but lower than Nafion[®] 115. However, these authors found out that methanol and water permeability rates decreased with increasing the amount of HSO_3^- titanate added into the Nafion[®] matrix, as can be seen in Table 4.

Jun et al. [21] studied the functionalization of titania nanotube composite membranes (TiO₂–NT) using 3-mercaptopropyl-tri-methoxysilane (MPTMS) as a sulfonic acid functionalization agent. Results showed a considerable increase in the

Table 3 Acid–base polymer complex-based organic–inorganic PEMs

Author/s	Membrane type	Achievement
Houng-Rhee et al. [20]	TiO ₂ /SO ₃ H/Nafion [®]	Higher ionic conductivity values for nanocomposite membranes containing 3–7 wt% HSO_3^- titanate compared with composite membranes containing 3 wt% TiO ₂ /P25
Jun et al. [21]	F–TiO ₂ –NT/Nafion [®]	Improvement in water permeability: water uptake of F–TiO ₂ –NT/Nafion [®] composite was about 7 and 4% higher than Nafion [®] 112 and recast Nafion [®] respectively
Yang et al. [22]	PVA/TiO ₂ /Nafion [®]	Ionic conductivity of PVA/TiO ₂ composite polymer membrane proportional to amount of TiO ₂ , achieving 0.0901 S cm^2 at 70 °C with 15 wt% of TiO ₂
Yang et al. [23]	PVA/nt–TiO ₂ /PSSA	Good electrochemical performance, of air-breathing direct methanol fuel cell
Mroczkowska-Szerszen et al. [24]	P ₂ O ₅ –SiO ₂ –TiO ₂ /PVA	Stable values of activation energy over examined temperature range

PVA poly(vinyl alcohol); PSSA polystyrene sulfonic acid; NT nanotubes

Table 4 Methanol and water permeability rate of nanocomposite membranes containing 3–7% HSO₃-titanate and Nafion® 115

Membrane	H ₂ O permeability (μmol/min)	MeOH permeability (μmol/min)
Nafion® 115	49	11
3% HSO ₃ -titanate	43	9.1
5% HSO ₃ -titanate	38	8.6
7% HSO ₃ -titanate	35	8.4
10% HSO ₃ -titanate	33	8.3

proton conductivity of F–TiO₂–NT in respect of TiO₂–NT. At the temperature of 80 °C, the conductivity of F–TiO₂–NT was as high as 0.08 S cm^{−1} versus 0.03 S cm^{−1} for the TiO₂–NT membranes. Moreover, these authors presented F–TiO₂–NT/Nafion® composite membranes as potential replacements for commercial Nafion® membranes in high temperature PEMFCs because their improvement in water permeability. The water uptake of F–TiO₂–NT/Nafion® composite is about 7 and 4% higher than Nafion® 112 and recast Nafion® respectively.

Yang et al. [22] studied poly(vinyl alcohol)/TiO₂ composite polymer membranes on alkaline direct alcohol fuel cell (DAFC). The DAFC was formed of a cathode based on MnO₂/C catalysts, while the anode was made of Pt/Ru and PVA/TiO₂ composite polymer membrane. Results showed that the ionic conductivity of PVA/TiO₂ composite polymer membrane was proportional to the amount of TiO₂, achieving 0.0901 S cm² at 70 °C with 15 wt% of TiO₂. Finally, the authors reported, in terms of the maximum power density, that the electrochemical performance of alkaline DAFC with methanol was better than that of DAFC with ethanol.

Yang et al. [23] developed a PVA/nt-TiO₂/PSSA composite polymer membrane with good electrochemical performance, for air-breathing direct methanol fuel cell based.

Mroczkowska-Szerszen et al. [24] studied the physicochemical properties of alkoxy compound and nanopowder P₂O₅–SiO₂–TiO₂/PVA composite membrane. They fabricated a composite glassy membrane by means of an optimized sol–gel process followed by post-thermal treatment of the resultant hydrogel. The elect tests of the samples in the fuel cells performed using hydrogen showed stable values of the activation energy over the entire temperature range under study.

2.3 TiO₂-Modified Polytetrafluoroethylene Membranes

Polytetrafluoroethylene (PTFE) exhibits superior properties to many other polymers in terms of chemical stability, thermal resistance, low water absorption, potential biocompatibility, good mechanical strength and erosion resistance, making it an attractive material for anti-corrosion coatings and fuel cell composite membranes. PTFE can be processed to porous fibres or thin films through solvent-free melt

spinning or extrusion and post-stretching strategies. Qian et al. [25] fixed TiO₂ functional thin layer on super hydrophobic PTFE UF membrane via plasma-enhanced graft of poly acryl acid (PAA) prior to coating TiO₂. TiO₂ attached on the PTFE-based UF membranes through the chelating bidentate coordination between surface-grafted carboxyl group and Ti⁴⁺. The novel TiO₂/PAA/PTFE membranes also exhibited excellent antifouling and self-cleaning performance due to the intrinsic hydrophilicity and photocatalytic properties of TiO₂.

2.4 Poly(ether ether ketone)-Based Nanocomposite PEMs

The good mechanical and thermal stabilities as well as low cost of sulfonated PEEK (SPEEK) qualify it as a very promising PEM. Moreover, it also allows direct electrophilic sulfonation and solution casting in organic solvents and shows high proton conductivity, governed by the degree of hydration and functionalization. A brief summary of SPEEK-based nanocomposite PEMs is provided in Table 5.

Various authors have reported studies in respect SPEEK preparation [26, 27]. Too highly sulfonated SPEEK membranes (above 60% degree sulfonation, where 100% sulfonation corresponds to one sulfonic acid group per repeat unit) appears to suffer from excessive swelling under the humidified fuel cell conditions and lose their dimensional stability with high methanol crossover. Membrane dehydration is also a serious problem for shrinkage and fuel crossover.

TiO₂ has also been used as a filler to modify the properties of SPEEK membranes, specifically to enhance the transport phenomena. Karthikeyan et al. [28] used 3-aminopropyltriethoxysilane (APTMS) and imidazole glycidoxypopyl

Table 5 Poly(ether ether ketone)-based nanocomposite PEMs

Author/s	Membrane type	Achievement
Karthikeyan et al. [28]	(RSiO _{1.5}) _n /SPEEK	Methanol and water permeabilities lower than pristine SPEEK
Dou et al. [30]	TiO ₂ /SPEEK	Improvement in water uptake and reduction in methanol permeability
Tripathi et al. [31]	TiO ₂ /PANI/SPEEK	Low methanol permeability and slow water dehydration
Ayyaru et al. [32]	TiO ₂ /SO ₃ H/SPEEK	Higher peak power density compared to that of cells with SPEEK-TiO ₂ and SPEEK membranes
Wu et al. [33]	Functionalized TiO ₂ submicrospheres/SPEEK	Higher selectivity and proton conductivity ($5.98 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C, 100% RH) than TiO ₂ /SPEEK membranes
Narayanaswamy et al. [34]	TiO ₂ (Rutile)/SPEEK	Power density 98.1 mW m ⁻² and current density 300 mA m ⁻² yielded by SPEEK +7.5% TiO ₂ composite membrane

SPEEK sulfonated poly(ether ether ketone); PANI polyaniline

trimethoxysilane as precursors to generate $(\text{RSiO}_{1.5})_n$ in a SPEEK matrix through a sol–gel process. Methanol and water permeabilities of these membranes were noted to be lower than pristine SPEEK. The APTMS precursor derived membrane showed lower permeability, but the direct methanol fuel cell (DMFC) performance for the membrane with imidazole glycidoxypopyl trimethoxysilane precursor was found to be better, as a result of good proton conductivity.

Vona et al. [29] used either a basic catalyst (pyridine) or a chelating agent (2, 4-pentandione) to control the inorganic network features in the SPEEK matrix. Sol–gel procedure with varied nanosized TiO_2 content was also used to obtain SPEEK- TiO_2 hybrid membranes, which showed both enhanced water uptake as well as retention along with reduction in methanol permeability [30].

On the other hand, Tripathi et al. [31] carried out the modification of polyaniline (PANI) surface SPEEK composite membranes with nanosized Si, Zr and Ti oxides by means of sol–gel procedure. The developed nanocomposite membrane exhibited low methanol permeability and slow water dehydration, whereas no membrane stability loss, explained due to a synergetic effect.

Titanium dioxide (TiO_2) is a semiconductor with photocatalytic properties, which improves membrane fouling performance and hydrophilic characteristics. Ayyaru et al. [32] fabricated a nanocomposite SPEEK membrane with incorporated sulfonated TiO_2 particles ($\text{TiO}_2\text{--SO}_3\text{H}$) in a MFC. It was found that the oxygen mass transfer coefficient and the internal resistance of the SPEEK membrane decreased with increasing the $\text{TiO}_2\text{--SO}_3\text{H}$ percentage. Moreover, the MFC with the prepared SPEEK- $\text{TiO}_2\text{--SO}_3\text{H}$ membrane showed sensibly higher peak power density if compared to that of cells with SPEEK- TiO_2 and SPEEK membranes.

Wu et al. [33] prepared SPEEK organic–inorganic hybrid proton-exchange membranes with aminoacid functionalized titania submicrospheres. For the synthesis and functionalization of pristine TiO_2 (uniform particle size around 200 nm), the authors used four kinds of aminoacids including oxidized L-cysteine ($\text{TiO}_2\text{--Scys}$), o-phospho-L-serine ($\text{TiO}_2\text{--Pser}$), aspartic acid ($\text{TiO}_2\text{--Asp}$) and histidine ($\text{TiO}_2\text{--His}$). The methanol crossover of the hybrid membranes was reported to be reduced by two folds, along with the enhancement of the anti-swelling property and thermal stability of the hybrid membranes. In particular, the $\text{TiO}_2\text{--Pser}$ membrane exhibited the highest selectivity. Whereas, the $\text{TiO}_2\text{--Scys}$ embedded membrane exhibited the highest proton conductivity (about $5.98 \times 10^{-3} \text{ S cm}^{-1}$ (20 °C, 100% RH) at 15 wt% of the filler. In contrast, the lowest conductivity found for the $\text{TiO}_2\text{--His}$ embedded membrane, may be due to the strong acid–base interaction between the basic imidazole groups of histidine and the sulfuric acid groups of SPEEK.

Narayanaswamy et al. [34] prepared a polymer composite electrolyte membrane of TiO_2 (Rutile) + SPEEK by a sol–gel method. The composite membranes prepared by solvent casting method have antifouling properties as well as enhanced oxygen mass transfer coefficients and are transport capable to cations other than protons. These membranes also showed improved proton conductivity and electrochemical properties, along with ion exchange and water absorption capacity. In addition, the prepared composite membranes showed higher maximum power

density and current density (highest power density 98.1 mW/m² and current density 300 mA/m² yielded by SPEEK +7.5% TiO₂ composite membrane) than commercial Nafion® 117s.

2.5 PANI Based Membranes

PANI-doped mesoporous metal oxides have been tested as MFC anode materials [35, 36]. A unique nanostructured PANI/mesoporous TiO₂ composite was investigated as an anode in *E. coli* MFC [35]. According to these authors the best performance was observed for the composite with 30 wt% PANI, providing two-fold higher power density (1495 mW/m²).

Table 6 presents the summary of the leading TiO₂-modified polytetrafluoroethylene, PANI, polyethersulfone (PES) and polysulfone (PS) nanocomposite PEMs.

2.6 PES Based Membranes

PES or sulfonated PES (SPES)-based membranes are widely used for electrochemical processes, and in particular for PEMFCs, mainly because of their excellent workability and mechanical strength. Devrim et al. [37] synthesized SPES-TiO₂

Table 6 TiO₂-modified polytetrafluoroethylene, PANI, polyethersulfone (PES) and polysulfone (PS) nanocomposite PEMs

Author/s	Membrane type	Achievement
Qian et al. [25]	TiO ₂ /PAA/PTFE	Excellent antifouling and self-cleaning performance
Qiao et al., Wang et al. [35, 36]	PANI/mesoporousTiO ₂	Power density of 1495 mW/m ² for the composite with 30 wt% PANI
Devrim et al. [37]	TiO ₂ /SPES	Conductivity in the range 10 ⁻³ –10 ⁻² S cm ⁻¹ and 300 mA cm ⁻² current density at 0.6 V for H ₂ -O ₂ /PEMFC at 1 atm and 85 °C
Ayyaru et al. [39]	(S-TiO ₂)/SPSEBS	Improved proton conductivity respect of SPSEBS membrane and exhibited the highest peak power density (1345 ± 17 m Wm ⁻²)
Aslan et al. [40]	SPSU and sulfated, TiO ₂ /NMPA	Maximum proton conductivity of 0.002 S cm ⁻¹ at 150 °C, and methanol permeability of the composite membranes lower than commercial Nafion® 112

PTFE polytetrafluoroethylene; PAA poly acryl acid; SPEEK sulfonated poly(ether ether ketone); PANI polyaniline; SPSEBS polystyrene ethylene butylene polystyrene; NMPA nitrilotri(methyl triphosphonic acid); PSU sulfonated polysulfone

composite membranes by blending of TiO_2 with SPES. The prepared composite membranes showed a conductivity in the range 10^{-3} – $10^{-2} \text{ S cm}^{-1}$ and 300 mA cm^{-2} current density at 0.6 V for H_2 – O_2 /PEMFC at 1 atm and 85°C . Also, brittle nature of these membranes was explained to be due to low miscibility of both components.

Park et al. [38] fabricated proton-conducting membranes for high temperature fuel cells by introducing TiO_2 NPs in a poly (styrene sulfonic acid) polymer matrix. Ayyaru et al. [39] developed sulfonated TiO_2 (S– TiO_2)/polystyrene ethylene butylene polystyrene (SPSEBS) nanocomposite membranes by solution casting. The obtained results demonstrated that the incorporation of sulfonated TiO_2 improved the proton conductivity of the SPSEBS membrane and exhibited the highest peak power density ($1345 \pm 17 \text{ m W m}^{-2}$). Moreover, the composite membrane was found to provide more than fourfold higher power density than Nafion[®] in MFCs. The SPSEBS-S- TiO_2 membrane (7.5%) exhibited the highest ion-exchange capacity (IEC), water uptake and proton conductivity capacity.

2.7 Polysulfone-Based Membranes

Aslan et al. [40] conducted investigation on nanocomposite membranes based on sulfonated polysulfone and sulfated nano-titania/nitritotri(methyl triphosphonic acid) (NMPA) for proton-exchange membrane fuel cells. They prepared proton-conducting nanocomposite membranes via ternary mixtures comprising sulfated nanotitania (TS), sulfonated polysulfone (SPSU) and nitritotri(methyl triphosphonic acid) (NMPA). The produced membranes were thermally stable up to 270°C .

The maximum proton conductivity of SPSU-TS-NMPA was 0.002 S cm^{-1} at 150°C , and methanol permeability of the composite membranes was lower than that of commercial Nafion[®] 112. These results were explained on the basis of complexation between SPSU/TS and NMPA, which inhibited the exclusion of NMPA on swelling in excess water, as supported by spectroscopic measurements and water uptake studies. The proton conductivity results of Aslan et al. [40] have been compared with those obtained by other authors (Fig. 4).

2.8 TiO_2 Solar Cells

Seger et al. [41] constructed a proton-exchange membrane under UV excitation. The PEM was assembled using TiO_2 photocatalyst at the anode, Pt electrocatalyst at the cathode and both pressed on a Nafion[®] membrane. Hydrogen was continuously generated by the irradiation of UV light when MEA was inserted under a methanol fuel cell.

The results showed an increase in the photocurrent on increasing the amount of TiO₂. However, there was an optimal point around 3.0 mg/cm² of TiO₂ upon which 37 μ A/cm² photocurrent could be achieved. The photocurrent approached to maximum value at 0.2 M methanol concentration. Nevertheless, concentrations above 0.1 M of methanol may cause some problems.

The previous work reported TiO₂ solar cells are summarized in Table 7.

Bella et al. [42] demonstrated that electrodes and electrolytes in the form of membranes can be successfully coupled, ensuring better handling and processability in contrast with traditional gel electrolytes systems and ex situ fabricated photoanodes. They fabricated a flexible dye-sensitized solar cell (DSSC) by means of an innovative combination of vertically aligned TiO₂ nanotubes, grown on to bendable titanium mesh, and a photocured polymer electrolyte membrane

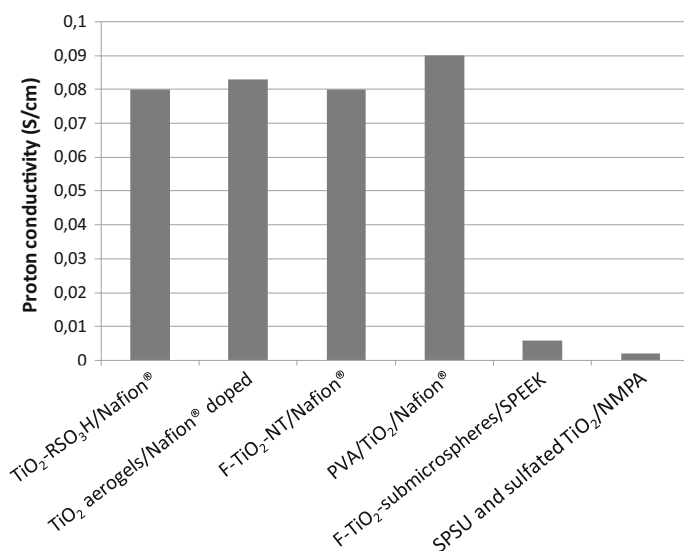


Fig. 4 Reported proton conductivity provided by different organic-TiO₂ nanocomposite membranes for PEMFC: TiO₂-RSO₃H/Nafion® [14], TiO₂ aerogels/Nafion® doped [16], F-TiO₂-NT/Nafion® [11], PVA/TiO₂/Nafion® [22], F-TiO₂ submicrospheres/SPEEK [33], SPSU and sulfated TiO₂/NMPA [40]

Table 7 TiO₂ solar cells

Author/s	Membrane type	Achievement
Seger et al. [41]	TiO ₂ /Nafion®/Pt	Hydrogen continuously generated by UV light irradiation; 37 μ A cm ⁻² photocurrent with 3.0 mg cm ⁻² of TiO ₂
Bella et al. [42]	DSSC by photocured polymer electrolyte membrane	Conversion efficiency equal to 3.4% under sun irradiation

DSSC flexible dye-sensitized solar cell

(synthesized of difunctional BEMA and monofunctional PEGMA). The authors reported sunlight to electricity conversion efficiency equal to 3.4% under sun irradiation.

2.9 Carbon Materials and Metal–Carbon Nanotube (CNTs)–TiO₂ Composites

The role of metals in the metal–carbon nanotube (CNT) composite depends on the nature of metal. The main role of the metal oxides such as MnO₂, SnO₂ and TiO₂ is to facilitate the electron transfer between the microbes and the anode. The MFCs with metal–CNT composite modified anodes show significantly improved performance than those with pure CNTs and the bare anode support. A terse summary of the investigations related with carbon materials and metal–carbon nanotube composites is presented in Table 8.

Table 8 Carbon materials and metal–carbon nanotube (CNTs)–TiO₂ composites

Author/s	Membrane type	Achievement
Xu et al. [43]	Ru ₈₅ Se ₁₅ /TiO ₂ /C	Positive influence on the electrochemical stability of the membrane, reaching power densities of 171 and 124 mW cm ^{−2} at 500 mA cm ^{−2} for Ru ₈₅ Se ₁₅ /TiO ₂ /C and Ru ₈₅ Se ₁₅ /C MEA respectively
Chao et al. [44]	Pt/TiO ₂ /C	MEA with 5% Pt/TiO ₂ found to provide the highest current density
Matos et al. [45]	Pd/ TiO ₂ /C	Higher conductivity than membranes based on TiO ₂ /C
Li et al. [46]	Pt/(Ti _x Sn _{1−x} O ₂)/C	The Pt/Ti _{0.9} Sn _{0.1} O ₂ –C catalyst exhibited the highest activity in contrast with commercial Pt/C catalysts and Pt/TiO ₂ –C
Zhang et al. [47]	TNTs/Pt/C	Maximum power density of 206–305 mW cm ^{−2} upon ultralow Pt loading
Garcia-Gomez et al. [48]	TiO ₂ (Rutile)/C (semi-graphitic)	Maximum current density obtained in a half microbial fuel cell equal to 0.8 mA/cm ²
Zhao et al. [50]	TiO ₂ /GN	Improvement of the performance of GN as MFC anode material
Zhou et al. [51]	TiO ₂ nanowire/GN	Internal resistance reduction in the sulphur cathode and physically immobilize the dissolved lithium polysulfides for Li/dissolved polysulfide batteries; 1327 mA hg ^{−1} specific capacity at 0.2 °C rate, high coulombic efficiency (~100%) and long life cycle (over 200 cycles)

TNTs TiO₂ nanotubes; GN graphene

2.9.1 Carbon-TiO₂ Composites

Xu et al. [43] synthesized Ru₈₅Se₁₅/TiO₂/C (5 wt% TiO₂ and 20 wt% Ru₈₅Se₁₅) to use as electrocatalysts in membrane fuel cells. The cathode of the membrane electrode assembly (MEA) was formed by a mix of Nafion[®], Ru₈₅Se₁₅/TiO₂/C and ethanol to form homogeneous slurry, whereas the anode was made of commercial 28.4 wt% Pt/C catalyst. Finally, the MEA (5 cm² active area) was made by hot-pressing the anode and the cathode to the Nafion[®] 212 membrane. This fuel cell was evaluated with hydrogen on the anode side and nitrogen on the cathode, under a potential cycling accelerated aging test (AAT) between 0.6 and 1.0 V for 1000 cycles. Results revealed that TiO₂ provided a positive effect on the electrochemical stability to the membrane, reaching power densities of 171 and 124 mW cm⁻² at 500 mA/cm⁻² for Ru₈₅Se₁₅/TiO₂/C and Ru₈₅Se₁₅/C MEA respectively.

On the other hand, Chao et al. [44] investigated the addition of platinum (Pt)/TiO₂ particles by the impregnation method on C/TiO₂ for the anode of MEA. The anode was made of 20 wt% Pt/C catalyst, 5 wt% Nafion[®], 20 wt% Pt/TiO₂ and alcohol whereas the cathode was prepared with the same reagents without Pt/TiO₂. Finally, the Nafion[®] 112 membrane was pressed between the anode and the cathode. Results revealed that the electrochemically active surface areas decreased as the Pt/TiO₂ addition increased. Nevertheless, the water contact angle become smaller as the amount of Pt/TiO₂ particles was increased. MEA with 5% Pt/TiO₂ was found to provide the highest current density at different anode humidifier temperatures ranging from 25 to 75 °C.

Matos et al. [45] reported promising results on hybrid inorganic/organic materials for the direct formic acid fuel cells with palladium (Pd)-based catalysts. They developed Pd-based catalysts supported on hybrid TiO₂-C materials from different carbon origins by solvothermal and slurry synthesis. The authors tested them by electrooxidation of formic acid. The authors noted up to three times higher activity per Pd mass for the carbonized hybrid TiO₂-C supports with mesopore texture and high anatase/rutile ratio in the TiO₂ framework than the catalyst prepared on a commercial Vulcan XC-72 carbon black. Also, during Pd deposition, hybrid TiO₂-C supports acquire high conductivity. These behaviours were explained by their higher hydrophilicity, which ensures good access of formic acid to the Pd crystallites in the catalyst layer, and high enough conductivity to enhance electron flow from the active sites of Pd to the current collector. This fact would permit reducing the amount of expensive noble metal at the anode.

A new type of SnO₂-TiO₂ solid solution (Ti_xSn_{1-x}O₂) support was prepared by Li et al. [46] via a solvothermal method with substitution of Ti⁴⁺ by Sn⁴⁺ in the TiO₂ lattice, for methanol oxidation. In addition, Ti_xSn_{1-x}O₂ was combined with conventional carbon black (Vulcan XC-72) to synthesize a hybrid support (Ti_xSn_{1-x}O₂-C) for depositing Pt nanoparticles. The well-dispersed Pt nanoparticles (2–3 nm) were observed to get mostly deposited on the boundaries of Ti_{0.9}Sn_{0.1}O₂ and carbon blacks. The Pt/Ti_{0.9}Sn_{0.1}O₂-C catalyst exhibited the highest activity in contrast to commercial Pt/C and Pt/TiO₂-C catalysts, in terms of methanol oxidation and CO stripping. This was due to its triple junction structure, which can help improve Pt

utilization with increased electrochemical active surface areas. Moreover, the high OH content on $\text{Ti}_{0.9}\text{Sn}_{0.1}\text{O}_2$ and the strengthened metal support interactions, both promoting the oxidation of poisoning CO absorbed on Pt active sites.

Zhang et al. [47] fabricated an oriented ultrathin catalyst layer (UTCL) for developing low cost fuel cells. The UTCL comprising high electrical conductivity TiO_2 nanotubes (TNTs) via a plasma-enhanced chemical vapour deposition, which helped in improving the electrical conductivity of the TNTs. Subsequently, Pt catalysts were deposited on the TNTs by the radio frequency (RF) sputtering, leading to oriented C-TNTs-Pt electrode. The maximum power density of $206\text{--}305\text{ mW cm}^{-2}$ upon ultralow Pt loading was observed. Figure 5 demonstrates the comparative magnitudes of power density realized from different organic TiO_2 nanocomposite membranes.

Garcia-Gomez et al. [48] synthesized a new dual nanofiber material based on TiO_2 (Rutile)-C(semi-graphitic)/C(semi-graphitic) mats with a side by side configuration for its use in microbial fuel cells. The prepared nanostructured material exhibited high surface area and biocompatibility, and it was found to provide excellent electrical performance with a maximum current density obtained in a half microbial fuel cell equal to 0.8 mA/cm^2 .

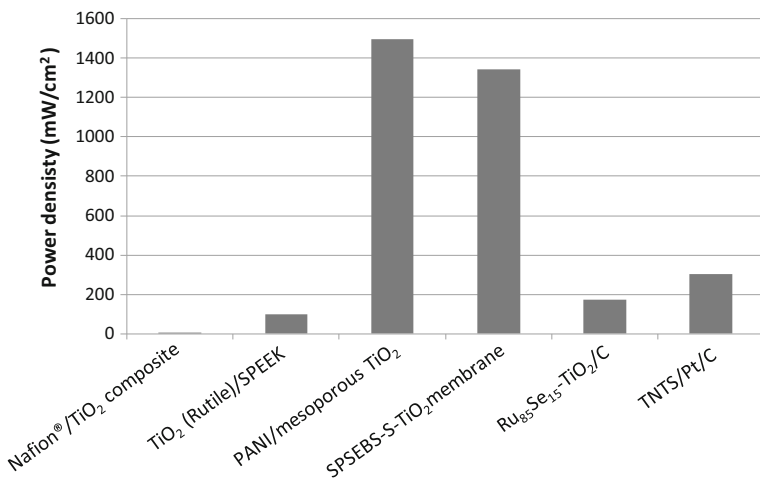


Fig. 5 Power density provided by different organic- TiO_2 nanocomposite membranes for PEMFC: Nafion®/ TiO_2 [9], TiO_2 (Rutile)/SPEEK [34], PANI/mesoporous TiO_2 [35], SPSEBS-S- TiO_2 membrane [38], $\text{Ru}_{85}\text{Se}_{15}/\text{TiO}_2/\text{C}$ [43], TNTs/Pt/C [47]

2.9.2 Graphene (GN)-TiO₂ Composites

It has been reported in the literature that GN as MFC anode is effective in achieving improved electron transfer between the microorganisms and the anode. Zhang et al. [49] reported graphene modification on the anode significantly increased electricity generation in MFCs. On the other hand, to improve the performance of GN as MFC anode material Zhao et al. [50] synthesized hybrid metal–GN ($M = \text{TiO}_2$) by a microwave-assisted hydro (solvo) thermal process, in which TiO₂ nanoparticles were assembled on graphene.

Zhou et al. [51] developed free-standing TiO₂ nanowire/graphene hybrid membrane for Li/dissolved polysulfide batteries. In these kinds of batteries, graphene membrane with high electrical conductivity serves as a current collector in order to effectively reduce the internal resistance in the sulphur cathode and physically immobilize the dissolved lithium polysulfides. In this case, the TiO₂ nanowires inserted into the graphene membrane conferred it a hierarchical composite structure, in which the TiO₂ nanowires offer strong chemical binding with the lithium polysulfides along with a strong catalytic effect for polysulfide reduction and oxidation. This latter fact promotes fast redox reaction kinetics with high capacity and low voltage polarization. The developed membrane hybrid electrode is known for its high specific capacity (1327 mA hg⁻¹ at 0.2 °C rate), high Coulombic efficiency (approaching 100%) and long life cycle (over 200 cycles).

3 Conclusions

In the future, fuel cells appear to become a key technology within the energy management framework of many devices, machines and energy networks, if technical and economic feasibility are improved sensibly.

Many studies in order to overcome the limits of the technology are nowadays in progress. A promising and interesting development path appears to be the improvement of the membrane properties used in fuel cells by nanotechnologies.

All membranes already used in the past appear to sensibly benefit from the application of nanotechnologies, with an increase of the fuel cell efficiency and durability. The advantage of this approach is to improve existing and well-known products, already used in the past in similar devices. On the other hand, novel membranes produced with the help of nanotechnologies for fuel cell applications appear to be more promising, and are now performing their test in time.

A definitive solution to provide a perfect membrane to a fuel cell does not exist, but the intensive efforts of many research groups worldwide and the achieved research progresses may surely provide in the very next years an answer to this problem.

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