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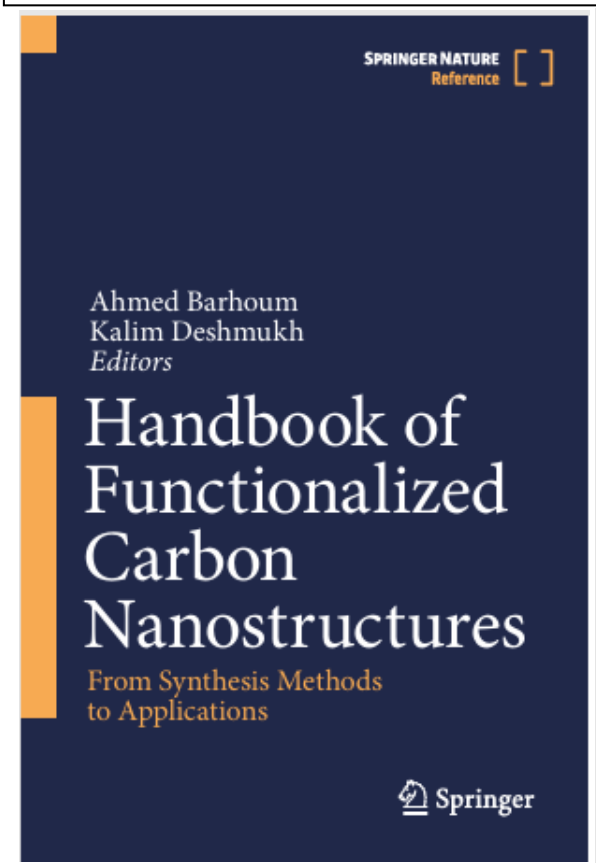

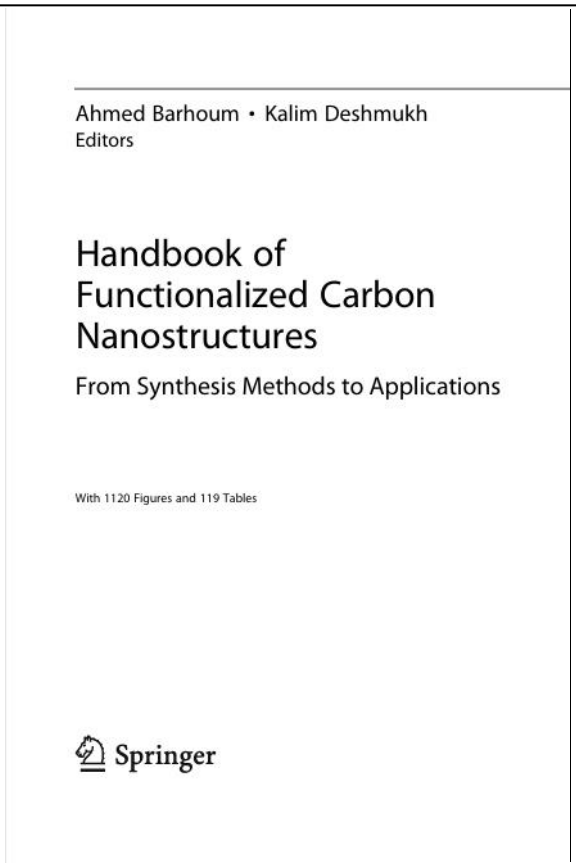

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Functionalized Carbon Nanostructures for PEMFCs

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Functionalized carbon nanostructures for PEMFCs: Catalyst and Membrane

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Abstract

As the most effective and environmentally friendly tools for transforming chemical energy to electrical energy, numerous studies are being conducted on fuel cells. Because of their efficiency, compact design, and quick start-up, proton exchange membrane fuel cells (PEMFCs) are regarded as one of the most prevalent fuel cell types under development nowadays. Electrocatalysts and proton exchange membranes (PEMs) are the primary elements of PEMFCs. Owing to superior electrical conductivity and large surface area, carbonaceous materials have received increased attention as promising candidates for fillers for the membrane and support material for the electrocatalyst. In case of the membrane, using carbonaceous materials can provide an alternative solution for improving its conductivity and assisting the humidification of PEM.

Regarding the catalysts, the ability of functionalized carbon materials to stabilize active metal and metal oxide nanoparticles makes them favourable catalyst supports and composite type supports with a stable oxide coating over the carbonaceous backbone. This chapter focuses on the development of functionalized carbon and innovative functionalized carbon nanomaterials used for catalyst supports, including carbon nanotubes, graphene derivatives, etc. Furthermore, the use of nanofillers for the PEM, such as functionalized single and multi-walled carbon nanotubes, graphene oxide, fullerene, and graphene, will be detailed.

Keywords

Covalent functionalization, non-covalent functionalization, hydrophilicity, oxidative treatment, sulfonation, composite, nanofillers

1 Introduction

Fuel cells are electrochemical appliances that transform chemical energy of a fuel instantaneously into electrical energy [1]. Proton exchange membrane fuel cell (PEMFC) is an effective replacement for conventional fossil fuel-based systems [2]. The PEMFC offers benefits such as substantial power density, low operating temperature, rapid start-up, and great efficiency when powered by hydrogen or alcohol as a fuel.

Electrocatalysts and proton exchange membrane (PEM) are the primary elements of PEMFCs. The PEMFCs employ platinum catalysts with carbon support that are commercially available on the market. Reducing the amount of platinum utilized is still one direction for

research and development. The upgrading of the stability and durability of catalysts and the electrodes built from them is also at the core of the advancements. Regarding the catalysts, the ability of functionalized carbon materials to stabilize active metal and metal oxide nanoparticles makes them advantageous catalyst supports and composite type supports with stable oxide coating over the carbonaceous backbone [3].

To improve the dispersion of catalytically active metal centres, it is recommended to use supports with a large surface area having anchoring sites with high number. An increase in the number of the functional groups on the surface and/or surface defects of the support responsible for the anchoring of active metal centres will lead to an increase of the metallic phase dispersion, providing a high surface-to-volume ratio and, consequently, high utilization of the catalyst. Eventually, a high number of anchoring sites can potentially lead to the formation of smaller particles, which in turn leads to higher specific surface area (SSA) of metallic species.

Besides ensuring the appropriate deposition conditions at molecular level, some macroscopic characteristics of the support should also be provided. Wettability of the support by the solution of the metallic precursor has crucial importance. Additionally, dissociation of metallic precursors to ionic species may generally happen in polar solvents, which makes hydrophilicity of the surface also inevitable. Moreover, compatibility of ions with the metal species containing surface must be ensured, too, via fine-tuning of surface charge (ζ potential).

An appropriate deposition is a prerequisite of high dispersion. However, the high dispersion is due not only to the choice of suitable deposition conditions. The interaction between the deposited particles and the support must be considered. In some cases, there is a strong interaction between the support and metallic particle, which can eventually perform a vital role in the behaviour and stability of catalyst. Due to the strong chemical interaction established via anchoring between metal ions and the support, it is possible to avoid migration, sintering, and agglomeration during subsequent thermal treatments. Generally, this is not the case when carbon is the support since the deposited metallic particles may be easily removed from its surface, resulting in loss of activity.

Therefore, the inert carbon surface requires appropriate chemical modification to increase hydrophilicity and to enhance the contact between the active phase and the support surface. Therefore, the functionalization of the carbonaceous support materials is a necessary step for

better deposition of metal particles, during which the functional groups of the surface act as anchoring sites of the metal, contributing to high dispersion and stability of the metallic phase [4]. Anchoring of the metal precursors on these centres can be done by different techniques, including adsorption, ion-exchange, or coordination reactions [5–7]. Commonly used procedures for surface functionalization of the carbonaceous catalyst supports include treatment with H_2O_2, O_3, NaOH, $(NH_4)_2S_2O_8$ or acids such as citric acid (CA), nitric acid, or a mixture of nitric acid and sulphuric acid [8–14].

Thus, the role of functionalization is 3-fold: (i) ensuring deposition conditions on molecular level (anchoring sites), (ii) ensuring deposition conditions on macroscopic level (wettability, hydrophilicity, surface charge), and (iii) ensuring good contact between the support and deposited particles. In addition, the functionalized support not only provides an anchoring platform for the metal nanoparticles but contributes to oxygen reduction reaction (ORR) activity by providing active sites through heteroatom doping [15].

Regarding the membranes, PEMs prohibit the mixing of reactants on both anode and cathode side and let the protons permeate through while deflecting the electrons in the direction of an external circuit. High ionic conductivity, minimal H_2 crossover, and strong thermal, electrochemical, and mechanical properties are required of the membrane in both dry and wet states.

Perfluorosulfonic acid (PFSA) polymers (Nafion), which have sufficient mechanical and chemical durability at low and moderate temperatures, are amongst the most extensively utilized polymers for PEMFCs in a fully hydrated environment [16]. While for higher temperature or lower humidity conditions, alternative polymers including sulfonated poly (aryl ether sulfone) (SPAES), sulfonated poly (ether ether ketone) (SPEEK), sulfonated poly (ether ether sulfone) (SPEES), sulfonated poly (ether sulfone) (SPES), polybenzimidazole (PBI), modified cellulose, polyvinylidene difluoride, chitosan (CS), and poly (vinyl alcohol) (PVA) exhibits excellent thermal and mechanical stability with low cost, good film forming and hydrophilicity. Nevertheless, the mentioned polymers including Nafion should be modified for better performance either for enhancing chemical stability or reducing swelling in water, which lessens mechanical stability. One of the most promising ways is to modify the microstructure of polymer by introducing other organic or inorganic fillers/components and producing the so-called composite or hybrid membrane. A wide range of inorganic fillers, particularly those with hygroscopic properties, have been used, including metal oxides, nanostructured clays, and carbon-based materials.

Among those, graphene, graphene oxide, carbon nanotubes (CNTs), fullerenes, their derivatives, and functionalization have been actively researched [17, 18]. Functionalized carbon nanostructure drew attention not only due to low production cost and non-toxicity but also because their special structure advances the membrane properties in terms of enhancing the membrane's chemical, thermomechanical properties and, more importantly, they improve the proton conductivity based on their structure. Additionally, using functionalized or non-functionalized carbon nanomaterials as filler allows more homogeneous dispersion of the filler in the membrane due to the very low loading required [19].

Among the most important challenges of functionalization is that the chemicals and processes used causing as little environmental damage as possible, and that the least amount of polluting waste material is generated. The functionalized carbon should, if possible, preserve or improve the favourable properties of the parent carbon material. In addition, the functionalization of the carbon nanomaterial should provide such beneficial properties (e.g., improved performance, increased lifetime, and increased heat tolerance, etc.) that make its use in PEMFCs economical. In terms of future use, functionalized nanocarbon should be available to produce in large quantities.

This work analyses in detail the effect of functionalization treatment of various types of carbon black (Section 2) and innovative carbon nanomaterials, including carbon nanotubes, graphene derivatives, etc. (Section 3), on the activity and stability of electrocatalysts obtained using them. Furthermore, the use of nanofillers for the PEMs, such as functionalized carbon nanotubes, graphene oxide, fullerene, and graphene, will be detailed (Section 4).

2 Functionalization of conventional carbon support materials for PEM fuel cell application

2.1 Short overview

In addition to the already listed requirements, such as high SSA and strong interaction of metal nanoparticles with the support, special requirements for promising electrocatalysts also include [20]: (i) notable degree of stability in the expected pH/potential range, (ii) outstanding electrochemical corrosion resistivity, (iii) significant proton as well as electronic conductivity, and (iv) appropriate porosity for proper mass-transport of reactants and products to minimize water flooding of the electrodes.

Taking the last point into account, the application of hydrophilic-hydrophobic dual catalyst layers (dual-CL) for PEMFCs can be very important, especially in low humidity conditions.

As described in ref. [21], the hydrophilic catalyst preparation was done by depositing Pt nanoparticles on an oxygen-functionalized carbon support, whereas for the hydrophobic catalyst layer, commercial Pt/C was chosen. As shown in Fig. 1, membrane electrode assembly (MEA) was prepared based on dual-CL electrodes consisting of hydrophilic inner layer and hydrophobic outer layer.

The dual-CL MEA exhibits improved cell performance and stability compared to MEAs containing only a single hydrophilic or hydrophobic catalyst layer. It should be emphasized that hydrophilicity on the anode side is the most important for performance improvement.

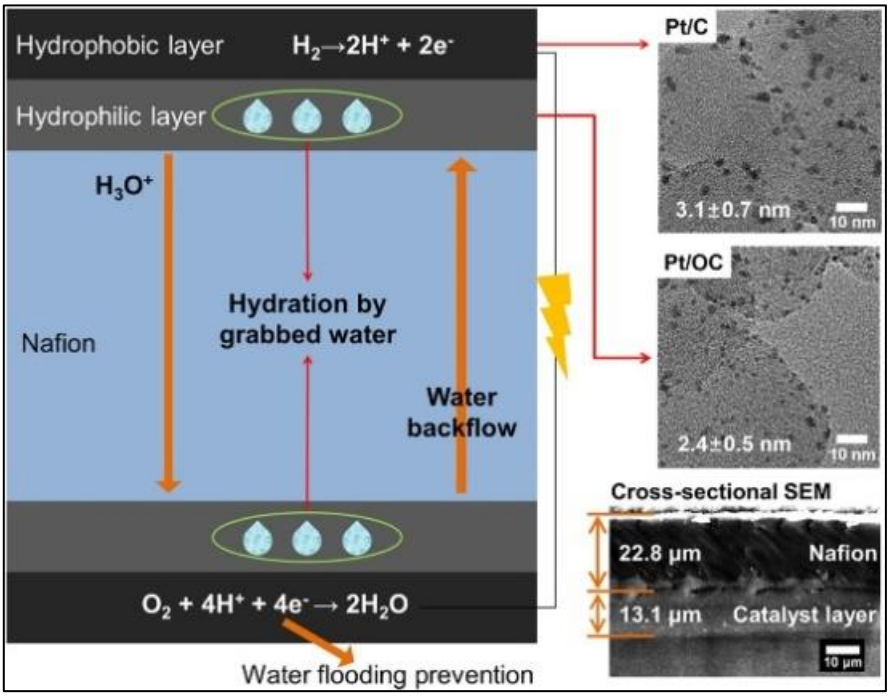

Fig. 1. A scheme for dual-CL MEA (Pt/OC: Pt supported on oxygen-functionalized carbon) (Reprinted with permission from [21] 2022, Elsevier 5440670762512).

In this respect, structure-to-property correlation analysis, done in ref. [22], indicates that the optimum between high electrocatalytic activity and high corrosion resistance can only be achieved by balancing the optimum chemical and morphological composition of the surface, since samples with excellent ability to resist electrochemical corrosion, but moderate activity, have significant quantity of graphitic carbons and a huge number of large, slightly close-packed elongated pores. In contrast, samples exhibiting the greatest potential activity having a high SSA, high roughness, and large amounts of oxygen-containing functional groups are much less resistant to corrosion. The relationship established in ref. [22] between the

electrochemical characteristics of carbon blacks and their chemical structure and morphology was summarized in Fig. 2.

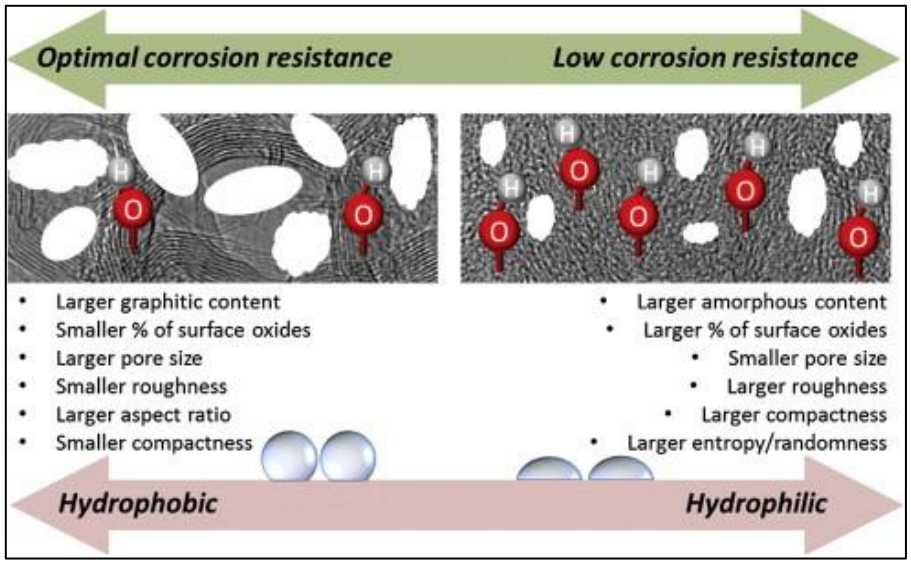

Fig. 2. Structure-to-property relationship for carbon black samples with optimal and low corrosion resistance (Reprinted with permission from [22], 2022, Elsevier 5440660266706).

As suggested by the structure-to-property correlation analysis (see Fig. 2), highly hydrophobic supports should have optimal corrosion resistance. The wettability of the support material plays a crucial role in the effective removal of gases and liquid products from the catalytic layer. This property, whether the support is hydrophilic or hydrophobic, significantly impacts the mass-transport characteristics and, consequently, the long-term stability of the electrode.

Several examples of the effect of various functionalization treatments on the electrocatalytic characteristics of carbon-supported catalysts are presented in Table 1.

Table 1. Effect of various types of functionalization treatment on the electrocatalytic properties of carbon-supported catalysts. Some examples.

Carbon material	**Type of functionalization treatment**	**Catalyst**	**Effect of the functionalization treatment / supported catalyst properties**	**Ref.**
Vulcan XC-72R MWCNT (NT)	CA/H_2O: sonication (15 min), calcination (N_2, 300 °C, 30 min); 5 M HNO_3: boiling at 95 °C for 8 h	Pt: 17 wt.%, Pt:M= 3:1 (M= Ge, In) PtM/C, PtM/C-CA, PtM/C-HNO_3 PtM/NT, PtM/NT-CA, PtM/NT-HNO_3	PtM/NT-HNO_3: the highest activity in DMFC (80 mW/cm^2) PtIn catalysts: low activity in DMFC	[13]
Vulcan XC-72R (CB)	HNO_3/HCl/H_2O: stirring at 80 °C for 12 h	Pt: 15 wt.%, Pt/CB vs. Pt/CB_O	Pt/CB_O: high ECSA and ORR activity Pt/CB: high stability	[23]
Ketjen black ECP300 (855 m^2/g)	H_2O_2/H_2O: heating at 95 °C for 24 h	PtRu: 60 wt.%, PtRu/C vs. PtRu/C-H_2O_2	Increased O-FGs concentration led to (i) a reduction in conductivity and the metal particle size, but (ii) an increase of activity in DMFC	[24]
Vulcan XC-72R	10 wt.% H_2O_2: reflux (105 °C, 3 h) 65 wt.% HNO_3:reflux (120 °C, 3 h)	Pt: 40 wt.%, Pt/C vs. Pt/C-H_2O_2, Pt/C-HNO_3	Stability increased during the DMFC tests: Pt/C < Pt/C-HNO_3 < Pt/C-H_2O_2	[25]
Vulcan XC-72R	HNO_3/H_2O (60% v/v) 60% H_2O_2/H_2O, stirring for 48 h	Pt: 40 wt.%, Pt/C vs. Pt/C-H_2O_2, Pt/C-HNO_3	H_2/CO: more severe CO poisoning for Pt/C than over Pt/C-HNO_3; Pt/C-H_2O_2: relatively stable in the early stages of the reaction	[26]
Acetylene Black (AB) Ketjen Black (KB) Vulcan XC (VC)	H_2SO_4/HNO_3= 3/1; ultra-sonication for 4 h	Pt: 20 ± 3 wt.%, Pt/AB, Pt/f-AB, Pt/KB, Pt/f-KB, Pt/VC, Pt/f-VC	ECSA: 52 m^2/g (Pt/AB) and 78 m^2/g (Pt/f-AB) ECSA loss: 6% (Pt/AB) and 16% (Pt/f-AB) vs. 55% for commercial Pt/C	[27]
OMC	H_2SO_4/HNO_3= 1/1; reflux (25 °C, 4 h) H_2O_2: reflux (80 °C, 4 h) AEPTMS/$C_6H_5CH_3$: reflux (110 °C, 24 h, N_2 flow)	Pt: ~17.5 ± 1.0 wt.%, Pt/OMC vs. Pt/OMC-H_2SO_4, Pt/C-H_2O_2, Pt/AEPTMS, Pt/Vulcan	Pt/OMC-H_2O_2: desirable conductivity (6.7 S/cm), high Pt dispersion (2.9 nm), the best activity in the ORR (onset potential= 0.95 V)	[28]
Vulcan XC-72R	cc. H_2SO_4 (SA) or cc. HSO_3Cl (CSA)	PtRu: ~20 wt.%, PtSn: ~20 wt.% PtRu/C vs. PtRu/C-SA, PtRu/C-	Increased particle dispersion, better water uptake and proton transport, reduced Pt	[29]

	heating in autoclave at 180 °C for 24 h	CSA, PtSn/C vs. PtSn/C-SA, PtSn/C-CSA	agglomeration, and higher resistance to poisoning achieved after functionalization of carbon supported catalysts provide high activity in DMFC and DEFC	
Vulcan XC-72R KB EC-600JD X: special carbon	pPDA or sulfanilic acid/HNO_3/H_2O: sonicating (2 h), + $NaNO_2$/H_2O, heating (70 °C, 12-24 h); 30/50% HNO_3 (reflux 4-6 h) + NH_3 heating at 200 °C for 4-6 h;	Pt: ~20 wt.%, Functionalizing agent: scheme 1: pPDA; scheme 2: NH_3; scheme 3: sulfanilic acid	An increase in activity after functionalization according to schemes 1 and 2, but activity declines after functionalization with sulfonate groups (scheme 3); KB-based catalysts possess the highest activity. The NH_3-functionalized X is the most stable	[30]

AEPTMS: 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane; **CA**: citric acid; **CB**: carbon black; **KB**: Ketjen Black; **NT**: multiwall carbon nanotube; **OMC**: ordered mesoporous carbon; **O-FGs**: oxygen-containing functional groups; **pPDA**: para-phenylenediamine; **Sulfanilic acid**: (4-aminobenzenesulfonic acid, p-$H_2NC_6H_4SO_3H$); **VC**: Vulcan XC-72R.

The study conducted in ref. [23] effectively demonstrated the acceleration of degradation following stability testing of Pt-based catalysts deposited on carbon black that had been functionalized with a mild acid (CB_O). In order to extract the influence of only O-containing functional groups, a mild acid treatment employing a solution of HNO_3/HCl was carried out to retain the other structural characteristics of the carbon black support (referred to as CB in Table 1). Although the Pt/CB_O catalyst had more Pt facets of greater exposure and it possessed higher ORR activity and electrochemical surface area (ECSA) in comparison to non-functionalized Pt/CB, it was more susceptible to agglomeration in the degradation test. Finally, Pt/CB_O catalyst showed lower ORR activity than the Pt/CB catalyst. A schematic illustration of the differences in Pt particle size occurring during accelerated degradation tests (ADTs), which cause easy Ostwald ripening and dissolution of the Pt nanoparticles, was presented in Fig. 3.

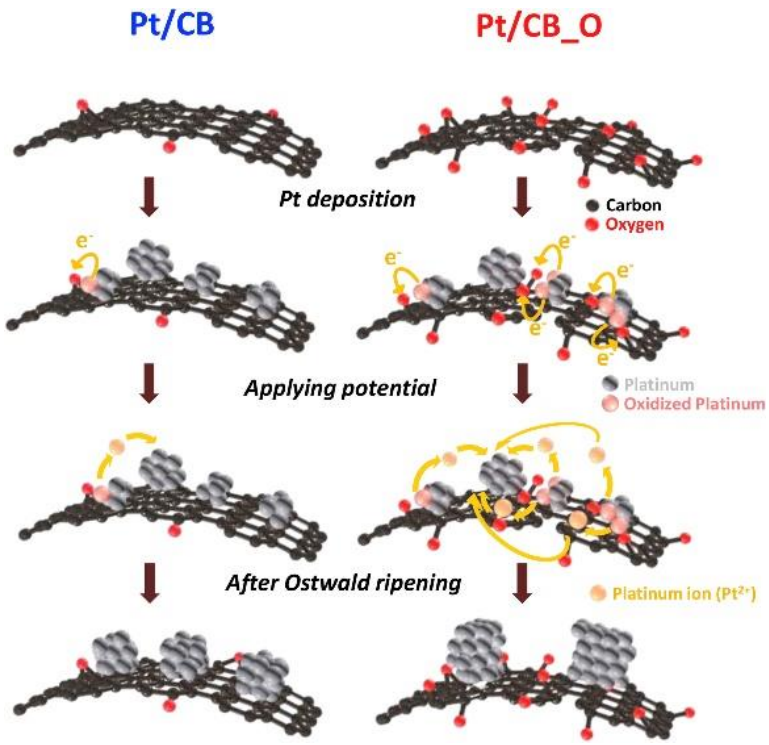

Fig. 3. Schematic illustrations of changes in Pt nanoparticle size before and after the ADTs in pristine Pt/CB and oxygen-functionalized Pt/CB_O catalysts (Reprinted with permission from [23], 2022, Elsevier 5440670471929).

In this connection, it should be emphasized that functionalization treatments along with changing the surface chemistry, can alter some of the initial bulk properties of the carbon

supports such as their morphology, texture, structure, surface potential or even electronic conductivity [31, 32].

The carbon black electrical conductivity is affected by (i) its bulk structure, and (ii) the presence of surface O-containing functional groups. Higher degree of surface functionalization leads to lower conductivity. As shown in Table 1, the preliminary chemical modification of carbon black with H_2O_2 in the preparation of bimetallic PtRu electrocatalysts provides a significant amount of acid sites required for the anchoring of metal precursors, leading to better metal particle dispersion, as well as high activity of methanol oxidation [24]. However, as noted above, the presence of a significant number of functional groups causes a reduction in electrical conductivity.

Thus, identifying the characteristics of the sample that correspond to the optimal morphological and chemical composition of the surface may be used to determine the type of modifications to be carried out [22].

2.2 Functionalization of conventional carbon materials with O-containing functional groups

A characteristic example of the chemical activation of carbons via an oxidation reaction is the insertion of oxygen-containing functional groups (*e.g.*, carboxylic (-COOH), anhydride (-COOCO-), hydroxyl (-OH) and carbonyl (-C=O) groups), which are responsible for both the acid/base and the redox properties of carbon [8, 20, 33]. Despite this, there are conflicting findings in the literature addressing the influence of oxidative carbon pre-treatment on platinum dispersion [8, 34]. The most common opinion is that with an increase in the number of oxygen surface groups on the support, the dispersion also increases.

It has been found that the degree of functionalization of the surface depends to a large extent on the severity of the functionalizing treatment. In this regard, the influence of various oxidizing agents affects the nature and the number of the oxygen-containing functional groups formed on the carbon surface, which can be classified as strong and weak acid sites [35]. Thus, treatment of carbon with, for example, H_2O_2 or O_3 leads to a significant density of weak acid sites, but the density of strong acid sites remains low, whereas treatment of carbon with HNO_3 results in substantial amount of both weak and strong acidic surface sites. It has been suggested [35] that the different H_2PtCl_6 adsorption behaviour of carbon subjected to different functionalization procedures indicates a stronger interaction of the metallic precursor with the weakly acidic carbon (e.g. those exposed to H_2O_2 treatment) compared to strongly acidic

HNO_3-treated carbon. So, carbons that have been functionalized with weak oxidizing agents exhibit the formation of moderately acidic sites and are characterized by a strong interaction with H_2PtCl_6 during the impregnation process, thereby provide a substantial Pt dispersion on the support surface.

It should be noted that the results of these fundamental studies of the influence of functionalization treatment of carbon supports developed in the field of catalysis [8, 35] are absolutely applicable to predict the activity and stability of electrocatalysts that contain a much higher Pt content. In this regard, treatment of the carbon support with less acidic oxidizing agents, such as H_2O_2, is considered to be an effective way for enhancing the stability of carbon-supported electrocatalysts. Thus, it has been demonstrated that during the tests in the DMFC single cell the 40 wt.% Pt/C cathode catalyst prepared from the H_2O_2-treated carbon support possesses superior stability than that synthesized from the HNO_3-treated carbon support (see Table 1) during 2000 cycles within the 0.6-1.05 V potential range [25], which is a characteristic potential interval of the cathode in low-temperature fuel cells.

Upon preparation of the Pt/C electrocatalysts (see Table 1), the influence of the carbon treatment with HNO_3 or H_2O_2 and the type of reducing agent on the activity in the electrooxidation of CO and hydrogen has been demonstrated [26]. According to this study, two aspects influence the activity in the CO electrooxidation: the nature of the Pt nanoparticles (e.g., shape, size, etc.) and the nature of the support; however, the influence of the nature of the support is most pronounced. In addition, the presence of a single CO stripping peak on the samples prepared using HNO_3- or H_2O_2-treated carbons indicates the homogeneity of the surface of the catalysts after functionalization.

Three different types of carbon blacks stability used with and without functionalization as supports for Pt electrocatalysts (see Table 1) was recently investigated by Prithi *et al*. [27]. Greater extent of graphitization and more efficient functionalization has been demonstrated on acetylene black (AB) carbon with low surface area compared to Vulcan carbon and Ketjen black. For imitating the PEM fuel cell environment and evaluation their corrosion behavior, accelerated test protocols were used. A great electrochemical activity with ECSA of 52 $m^2 g^{-1}$ and 78 $m^2 g^{-1}$ and impressive corrosion resistance with ECSA drop of 6 % and 16 % was demonstrated for Pt electrocatalysts supported on AB and its functionalized form (f-AB), respectively. These results are well within the international standards set by the Department of

Energy (DoE) (<40 % ECSA loss). Thus, it has been proposed that the f-AB may serve as a potential corrosion resistant support for Pt electrocatalysts in PEMFCs with improved performance and increased lifetime.

Nevertheless, it should be noted that there is also an opposite opinion that the presence of oxygen surface functional groups on carbon reduces the metal dispersion. According to Fraga *et al*. [36], surface basic sites of carbon serve as anchoring sites for the active metal precursor (e.g., hexachloroplatinic anion $PtCl_6^{2-}$) and are mostly accountable for the strong metal adsorption on support. It was reported that as the density of total oxygen groups on the carbon surface increased, metal–carbon interactions reduced due to the decline in the number of important surface basic sites, which, according to the authors, is an essential factor in metal adsorption. In ref. [37], it has been reported that the specific interaction of metal particles with the edges and corners or surface defects of graphitic layers is the controlling factor responsible for the metallic dispersion. Based on the results of microcalorimetric measurements of CO adsorption performed using Pt and Ru catalysts deposited on three different types of graphite with high surface area having different functional group quantity, but similar in texture characteristics, it was shown that the presence of O-containing functional groups at the graphite surface can lead to a decrease in the metal-support interaction. According to the authors, due to the fact that the thermal stability of some O-containing functional groups is restricted to temperatures close to 400 °C, the metal dispersion mainly depends on the temperature required for the reduction and/or decomposition of the metallic precursors. Moreover, the decomposition of surface oxygen functional groups will lead to re-dispersion of the metal nanoparticles. In this regard, the presence of less stable functional groups can adversely affect both the final dispersion of the deposited metal and resistance of metal nanoparticles to detachment, agglomeration and sintering. Therefore, as mentioned above, the predominant formation of weak acid sites, which decompose at temperatures above 400 °C (e.g., phenol, lactone, carbonyl groups), will contribute to a high dispersion of Pt on the surface of carbon [35].

2.3 Functionalization of conventional carbon materials with N- or S-containing functional groups

The influence of surface modification of ordered mesoporous carbons (OMCs) using the typical acid-oxidation (H_2SO_4/HNO_3), H_2O_2 oxidation, and 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (AEPTMS) grafted approaches (see Fig. 4 and Table 1 for

details) on the electrocatalytic performance of Pt catalysts towards the ORR was compared in ref. [28].

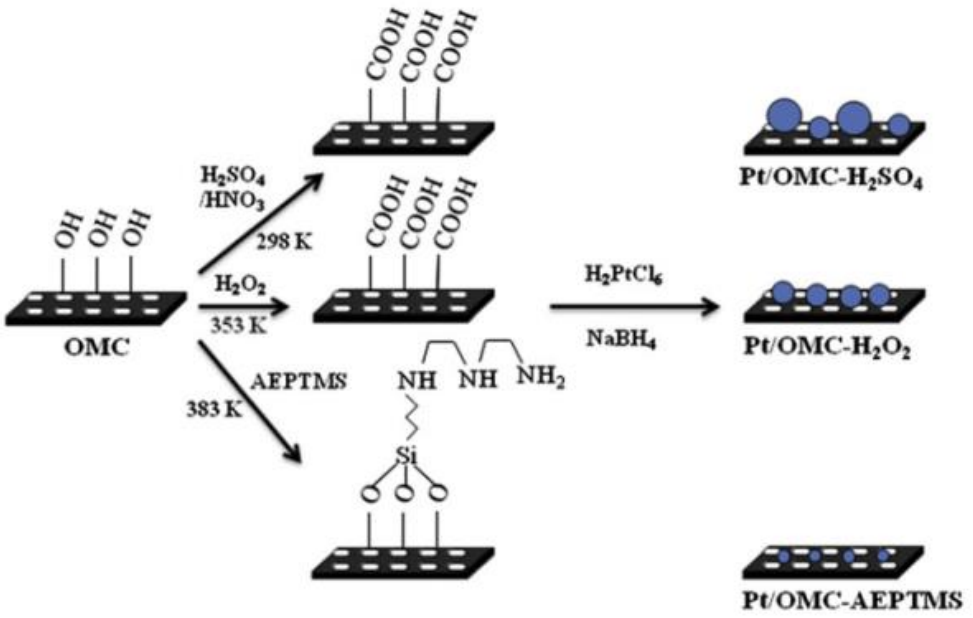

Fig. 4. Scheme of preparation of Pt on modified OMCs (Reprinted with permission from [28], 2022, Elsevier 5440671210483).

Functionalization with H_2O_2 was one of the three surface modification techniques that proved to be the most simply regulated OMC surface modification method, resulting in Pt nanoparticles with a size of about 3 nm and good electrical conductivity (6.7 S cm^{-1}). As a result, the Pt/OMC-H_2O_2 sample outperformed Pt/OMC, Pt/OMC-H_2SO_4, Pt/OMC-AEPTMS and reference Pt/C (C: Vulcan XC-72) electrocatalysts due to higher ORR activity.

Electrochemical analysis revealed that carbon pre-functionalized with sulphuric acid and chlorosulfuric acid (indicated in Table 1 as C-SA and C-CSA, respectively) and used as a support for PtRu and PtSn catalysts outperformed the activity of bimetallic catalysts synthesized using untreated Vulcan carbon in methanol/ethanol oxidation [29].

It is conceivable that Nafion® ionomer and the functionalized carbon support can interact much more effectively as a consequence of the sulfonic groups that have been attached onto the carbon surface. The enhanced electrocatalytic activity of the aforementioned PtRu and PtSn catalysts can be assigned to a superior particle distribution (greater platinum utilization), improved water uptake (wettability), more efficient proton transfer, lower platinum agglomeration (particles stabilization due to functional groups), and better resistance to

poisoning suggesting that it is an effective strategy to functionalize, boost efficiency, and decrease the cost of fuel cell catalysts.

The influence of the functionalizing carbon supports with N- and S-containing functional groups on the ionomer surface coverage in the cathode catalyst layer as along with its durability and performance has recently been demonstrated by Fang *et al*. [30]. In ref. [38] it was shown that the surface functionalization of the carbon support with N-containing surface groups, which are positive functional groups, influences the homogeneousness of ionomer (negative-charged sulfonate groups) distribution on carbon, that may additionally impact on the mass-transfer resistance.

From this point of view, it was important to compare the behaviour of three carbon support materials previously functionalized with positively (para-phenylenediamine (pPDA) and ammonia) and negatively (sulfanilic acid) charged species (see Table 1). According to full-cell tests, performance of supports treated with pPDA or ammonia enhanced at high current densities, however the samples functionalised with sulfonate groups possessed reduced performance [30]. However, regardless of the nature of the functionalizing agent, it has been found that a higher rate of carbon loss occurs owing to the selective oxidation of the functional groups attached via weaker covalent bonds. Despite the higher rates of decay throughout the accelerated stress tests the most durable NH_3-functionalized carbon support possessed end-of-life performance analogous to the initial performance after 5,000 cycles in the potential range of 1.0-1.5 V at 0.5 V s^{-1}.

2.4 The role of carbon functionalization in the development of composite materials

Combination of Pt nanoparticles, metal oxides (*e.g.*, TiO_2), and carbonaceous materials have been found to be promising electrocatalysts as they combine the remarkable electrical conductivity of carbon and corrosion-resistant properties of the oxide via the synergistic effect amongst carbon, metal oxides and Pt [20, 39]. Moreover, in the case of an oxide such as TiO_2, a significant improvement in electrochemical performance can be associated with the strong metal-support interaction (SMSI) between Pt nanoparticles and titanium oxide. In addition, the TiO_2 coating can favourably impact the catalytic behaviour by changing the pore structure leading to a significant reduction in micropore volume of TiO_2-coated activated carbon compared with an un-coated one [20, 39]. Accordingly, the study of coating carbonaceous materials with TiO_2 nanoparticles has currently been an attractive and challenging topic of

research. In this regard, the functionalization of the carbonaceous support can contribute not only to better deposition of the active metal but also of the metal oxide.

Adsorbed glucose has been found to be an efficient tool for controlling the size of deposited TiO_2 particles with uniform coverage and increasing the conductivity of TiO_2/C composites [40]. The formation of a homogeneous coating of very fine TiO_2 nanoparticles on the carbon backbone was demonstrated on the carbon functionalized with glucose, HNO_3, or a mixture of HNO_3-H_2SO_4 acids [41, 42]. Smaller average Pt nanoparticles size and higher activity in methanol oxidation for Pt supported on CA-modified carbon than on HNO_3-H_2SO_4-treated carbon materials have been presented in ref. [43]. Odetola *et al*. [44] found that Pt/TiO_2/C catalysts, synthesized with glucose functionalized Vulcan XC-72 carbon, had higher activity in the ORR and superior stability through the accelerated stress tests. Thus, the strong interaction between TiO_2/C and Pt, leading to carbon coating with TiO_2, prevents agglomeration and corrosion of Pt nanoparticles.

The aim of our recent studies [39, 45] was to establish a technique for the synthesis of composite materials containing $Ti_{(1-x)}Mo_xO_2$ mixed oxide coated Black Pearls 2000 carbon, which was previously functionalized using a two-step consecutive treatments with HNO_3 and glucose. The objective of the research was to (i) assess the potential benefits of carbon functionalization with respect to the electrocatalytic behaviour and stability of Pt electrocatalysts supported on $Ti_{0.8}M_{0.2}O_2$-C composite, and (ii) identify the most appropriate $Ti_{0.8}Mo_{0.2}O_2$/C ratio in composite materials to preserve the stability of the mixed oxide coating on carbon over 10,000 cycles of long-term stability testing. We found that on these catalysts, the higher the mixed oxide content in the composite, the higher the resistance to CO. However, it has been shown that increasing of carbon content in the composite materials up to 75 wt.% leads to a more homogeneous microstructure, which is a decisive factor for improving long-term stability. Given that the resistance in the fuel cell increases with increasing oxide content in the catalyst, based on our results, Pt electrocatalysts with the $Ti_{0.8}Mo_{0.2}O_2$/C= 25/75 ratio have the greatest potential.

3 Functionalization of novel carbonaceous materials for PEMFC catalysts

Due to their conductivity, stability, and high SSA, novel carbonaceous materials such as CNTs, graphene, and graphene nanoplatelets (GNP) offer new solutions for the catalysts of

PEMFCs in both ORR and hydrogen oxidation reaction (HOR). However, these materials have a polar, strong hydrophobic character making their use in pristine form cumbersome; deposition of stable metal nanoparticles on them is among the biggest challenges [46–48]. Furthermore, graphene layers tend to stick together, thereby reducing the accessibility of the active metal supported by them [46]. However, these difficulties can be overcome via the functionalization of the novel carbonaceous materials [46–49]. In the literature, two main types of functionalization are distinguished: namely covalent and non-covalent ones both in the case of CNTs [48, 50] and graphene nanosheets (GNS) [46]. After functionalization, new types of carbonaceous materials show more favourable properties as catalyst supports, *i.e.*, the distribution of the supported metal is more uniform on them than on their non-functionalized counterparts and the metal nanoparticles show greater stability during electrochemical tests [46]. In addition, oxygen-containing functional groups can play an important role in the production of heteroatom-doped (most often N-doped) novel carbonaceous materials [51]. The latter can act as metal-free ORR catalysts.

Without claiming to be exhaustive, a few examples of the various functionalization of novel carbonaceous materials used for PEMFC electrocatalysts are listed in Table 2 (CNT-based electrocatalysts) and Table 3 (GNS-based electrocatalysts).

Table 2. Some examples of the various functionalization carbon nanotubes (CNT) used for PEMFCs

Carbon material	**Type of functionali-zation**	**Type of functional group/ type of interaction**	**Type of functionalization treatment**	**Catalyst**	**Effect of the functionalization treatment / supported catalyst properties**	**Ref.**
SWCNT	covalent	O-FGs	sonication with H_2SO_4/HNO_3 (1:3 molar ratio, 2 h), washing, centrifugation, drying	Pt: ~24 wt.%	power density (at 0.6 V) ($mWcm^{-2}$): Pt/FCNT=340 Pt/RCNT ~280	[52]
SWCNT	covalent	**O-FGs (-COOH)**	as-prepared electric arc synthesized SWNT→ a) high temperature oxidation, dissolution in HCl (non-functionalized SWNT (SWNT-NF); b) 90 min, 16 M HNO_3, reflux, →low speed centrifugation (SWNT-MF); c) 90 min, 16 M HNO_3, reflux, →low speed centrifugation, →0.0125 M NaOH treatment (SWNT-LF); d) 3 h, 16 M HNO_3, treatment→ low speed centrifugation → high speed centrifugation (SWNT-HF)	Pt: 30 wt.% (ethylene glycol based in situ reduction) applied on both anode and cathode side	ECSA: Pt/SWNT-LF> Pt/SWNT-MF> Pt/SWNT-NF> Pt/SWNT-HF P_{max} : Pt/SWNT-LF> Pt/SWNT-MF> Pt/SWNT-HF> Pt/SWNT-NF (aggregation)	[53]
MWCNT	covalent	O-FGs	after ultrasonication	Pt from $PtCl_2$ via	H_2SO_4/HNO_3: low yield of	[47]

			a) reflux with 98% H_2SO_4/70% HNO_3 (140 °C, 5h); b) reflux with 70% HNO_3 (140 °C, 6 h); c) reflux with 0.38 M $K_2Cr_2O_7$/4.5 M H_2SO_4 (60 °C, 6 h); washing, centrifugation, drying	a) two-step sensitization-activation coating process with $SnCl_2$/HCl, $PdCl_2$/NH_4Cl/NH_4OH; b) direct coating	functionalized CNT; $K_2Cr_2O_7$/H_2SO_4: well functionalized external surface, more Pt nanoparticle aggregated; HNO_3: well functionalized external surface	
MWCNT	covalent	O-FGs	H_2SO_4/HNO_3 (4 h, 120°C) reflux, magnetic stirring with varied ratio of H_2SO_4/HNO_3 (3:0, 3:1, 1:1, 1:3), washing, ultrafiltration, drying	Pt-Fe-Ni/CNT, Pt-Ni/CNT Pt-Fe/CNT Pt/CNT Pt/C	increasing H_2SO_4 ratio →higher content of functional groups; P_{max} ($mWcm^{-2}$): Pt-Fe-Ni/CNT=20.9 Pt-Ni/CNT=19.1 Pt-Fe/CNT=18.2 Pt/CNT=14.7 Pt/C=4.4	[54]
MWCNT	covalent	O-FGs	slow oxidation with aqueous solutions of H_2O_2 (8M (A); 4M (B)) at RT	PtRu (Pt: 20 wt.%, Ru: 10 wt.%) A101, B101, J-M (ref.: Johnson-Matthey Co.)	P_{max} (Wmg^{-1}): A101=1.4 B101=1.6 J-M=0.98	[55]
MWCNT	covalent	N-containing	acyl chlorination reaction (DMF, thionyl chloride coupling agent, 24 h, 70°C, reflux under N_2) → amination reaction (DMF, 130 °C, 3 days reflux, TETA, DETA, TEA, MN)	Pt: 28 wt.% Pt/MWCNTs Pt/MWCNTs-TETA Pt/MWCNTs-DETA Pt/MWCNTs-MN	ECSA ($m^2g_{Pt}^{-1}$); P_{max} ($mWcm^{-2}$): Pt/MWCNTs=4.0; 23.9 Pt/MWCNTs-TETA=19.7; 64.5 Pt/MWCNTs-DETA=6.4; 36.4 Pt/MWCNTs-MN=10.4; 51.3 the least P_{max} decrease: Pt/MWCNTs-TETA	[56]
MWCNT	covalent	S-containing	diazo coupling reaction (4-	Pt: 45 wt.%	specific and mass activities:	[57]

			aminothiophenol, $NaNO_2$, HCl)	Pt/CNT-SH, Pt/CNT (raw CNT)	Pt/CNT-SH=4.7 μAcm^{-2}; 2.4 Ag^{-1} Pt/CNT=2.4 μAcm^{-2}; 1.1 Ag^{-1}	
MWCNT	non-covalent	σ-π interaction	THF solution of $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_4 \cdot 5H_2O$ with various Pt/Sn ratios → slurry with MWCNT→ sonication (30 min), heating (60 °C), drying, heating (300°C, H_2 flow 2h)	Pt: 20 wt.% Pt/MWCNT PtSn/MWCNT Pt/C(E-TEK)	THF: functionalization and anchoring agent; alloying of Pt with Sn → oxidation of ethanol at lower potentials with higher current and higher stability than on pure Pt	[58]
SWCNT	non-covalent	π-stacking	mild sonication of the mixture of SWCNT, aniline, H_2PtCl_6 ethanol, and water → pH adjustment with NaOH (8-10) and reflux (130 °C) → addition of HCl and $NH_4S_2O_8$ to get PANI by polymerization	Pt: 20 wt.% Pt-PANI/CNT Pt/CNT Pt/C	ECSA (m^2g^{-1}): Pt-PANI/CNT=64.5 Pt/CNT=58.4 Pt/C=50.2 durability: Pt-PANI/CNT>Pt/CNT>Pt/C	[50]
CNTs (10–15 nm in diameter)	non-covalent	wrapping with cationic surfactant	sonication of CNT, 5 wt.% PDDA and 1 wt.% NaCl; stirring (12h), drying in vacuum (80 °C, 24h)	Pt: ~40 wt.% Pt/PDDA-CNT Pt/CNT-U Pt/C	ECSA ($m^2g_{Pt}^{-1}$); ECSA loss (3500 cycles, %): Pt/PDDA-CNT=68.7; 24.7 Pt/CNT-U=65.3; 39.1 Pt/C=52.9; 44.2	[59]
NCNT	C-replace	doping	use of NH_3 xylene and Fe–Mo/Al_2O_3 in CVD method	Pt: 50 wt.% PtNW from H_2PtCl_6 by use of CATB and $NaBH_4$	$ECSA_{initial}$; $ECSA_{3500}$ ($m^2g_{Pt}^{-1}$): PtNW/NCNT: 81.23; 64.0 Pt/C=65.3; 25.7 P_{max} ($mWcm^{-2}$): PtNW/NCNT=966	[60]

CATB: cetyltrimethylammonium bromide**; DETA**: diethylenetriamine; **DMF**: N, N'-dimethylformamide; **ECSA**: electrochemical surface area, **FCB**: negatively charged SO_3H-carbon black; **FCNT**: functionalized carbon nanotube; **GO**: graphite oxide; **MN**: malononitrile; **MWCNT**: multi-walled carbon nanotube; **NCNT**: N-doped carbon nanotube; **NG**: natural graphite; **O-FGs**: oxygen-containing functional groups; **P_{max}**: maximum value of power density;

PANI: electron-conductive polyaniline; **PBI**: polybenzimidazole; **PDDA**: poly(diallyldimethylammonium chloride); **RCNT**: raw carbon nanotube; **SWCNT**: single-walled carbon nanotube; **SWNT-NF**: non-functionalized single wall carbon nanotubes; **SWNT-MF**: single wall carbon nanotubes of medium -COOH functionality; **SWNT-LF**: single wall carbon nanotubes of low -COOH functionality; **SWCNT-HF**: single wall carbon nanotubes of high -COOH functionality. **TEA**: triethyl amine; **TETA**: triethylenetetramine; **THF**: tetrahydrofuran.

Table 3. Some examples of the various functionalization of graphene nanosheets (GNS) used for PEMFCs

Carbon material	**Type of functiona-lization**	**Type of functional group/ type of interaction**	**Type of functionalization treatment**	**Catalyst**	**Effect of the functionalization treatment / supported catalyst properties**	**Ref.**
Thermally exfoliated GO (GO from NG by Hummers' method→ thermal shock at 1050 °C)	covalent	O-FGs	sonication in DMF, washing, drying→ sonication, stirring (1 h) with aqueous solution of CA→ filtration, washing, heat treatment (300 °C, 30 min)	Pt: 20 wt.% Pt/FG Pt/G Pt/C	ECSA loss (1000 cycles, %); P_{max} (Wcm^{-2}): Pt/FG=8.6; 0.455 Pt/G=14.1; 0.426 Pt/C=24.1; 314	[61]
GO	covalent	S-containing	diazo coupling: 4-aminothiophenol in 0.5 mol L^{-1} HCl and 0.05 mol L^{-1} $NaNO_2$ → GO, Fe powder	Pt: 40 wt.% Pt@rGO Pt@SC_6H_4–rGO	ECSA (m^2g^{-1}): Pt@rGO=9.4 Pt@SC_6H_4–rGO=12.8	[62]
Graphene oxide	covalent	S-containing	mixing $(NH_4)_2SO_4$ and graphene oxide (1:5) in deionized water sonication (30 min), freeze	M: ~30 wt.% Pt:Co:Fe E1=1:0:0 E2=29:3:7	ECSA ($m^2g_{Pt}^{-1}$): E1=29 E2=50 E3=67	[63]

			drying; then the heat treatment (235 °C, 30 min, Ar)	E3=29:4:4 E4=29:7:3 E5=29:8:1 E0=29:3:7 (no S)	E4=79 E5=68 P_{max}: E4 (530 $mWcm^{-2}$) > E0 (450 $mWcm^{-2}$)	
Mildly reduced GO (heating of $NaBH_4$ /GO dispersion, 80 °C, 1 h)	covalent	N-containing	diazo coupling: 4-aminobenzoic acid, HCl, $NaNO_2$→hydrazine reduction →heat treatment in the presence of isophthalic acid, 3,3'-diaminobenidine and polyphosphoric acid	Pt: 30 wt.% Pt/XC72 Pt/ PBI-XC72 Pt/graphene Pt/PBI-graphene Pt/PBI-graphene +FCB	ECSA ($m^2g_{Pt}^{-1}$); ECSA loss (1000 cycles, %) Pt/XC72=49.2; 38.0 Pt/ PBI-XC72=57.6; 31.2 Pt/graphene=34.7; 26.8 Pt/PBI-graphene=39.8, 17.8 Pt/PBI-graphene+FCB=43.3; 21.9	[64]

DMF: N, N'-dimethylformamide; **CA**: citric acid, **ECSA**: electrochemical surface area, **FCB**: negatively charged SO_3H-carbon black; **GO**: graphite oxide; **NG**: natural graphite; **O-FGs**: oxygen-containing functional groups; $\mathbf{P_{max}}$: maximum value of power density; **PBI**: polybenzimidazole.

3.1 Functionalization of carbon nanotubes for PEMFC catalysts

Functionalization of CNTs (both single-walled (SWCNTs) and multi-walled (MWCNTs) ones) practically goes back to the beginning of their use, when they were cleaned by acid treatment and activated by oxidative treatment (most often with a mixture of H_2SO_4 and HNO_3). However, a great number of other different oxidative agents such as O_3 [61], $(NH_4)_2S_2O_8$ [65], H_2O_2 [65], HF/H_2O_2 [66], aqua regia [67], HF/BF_3 [67], $K_2Cr_2O_7/H_2SO_4$ [47, 67], aqueous OsO_4 [67], $KMnO_4$ [65, 67], etc. have been used for functionalization, too. These oxidative treatments lead to the appearance of various types of O-containing functional groups on the surface of CNTs, such as alcoholic, carboxylic, aldehydic, ketonic, and esteric oxygenated ones [68].

Zhang *et al*. prepared functionalized SWCNTs via a conventional H_2SO_4/HNO_3 acidic treatment with sonication (indicated as FCNT in ref. [52]). The best fuel cell performance, with the highest current and power density output, was obtained using the Pt/FCNT (see Table 2). Jha *et al*. studied the effect of the amount of surface -COOH groups of functionalized SWCNT, which affected the ECSA and fuel cell performance due to the Pt aggregation (see Fig. 5 and Table 2) [53].

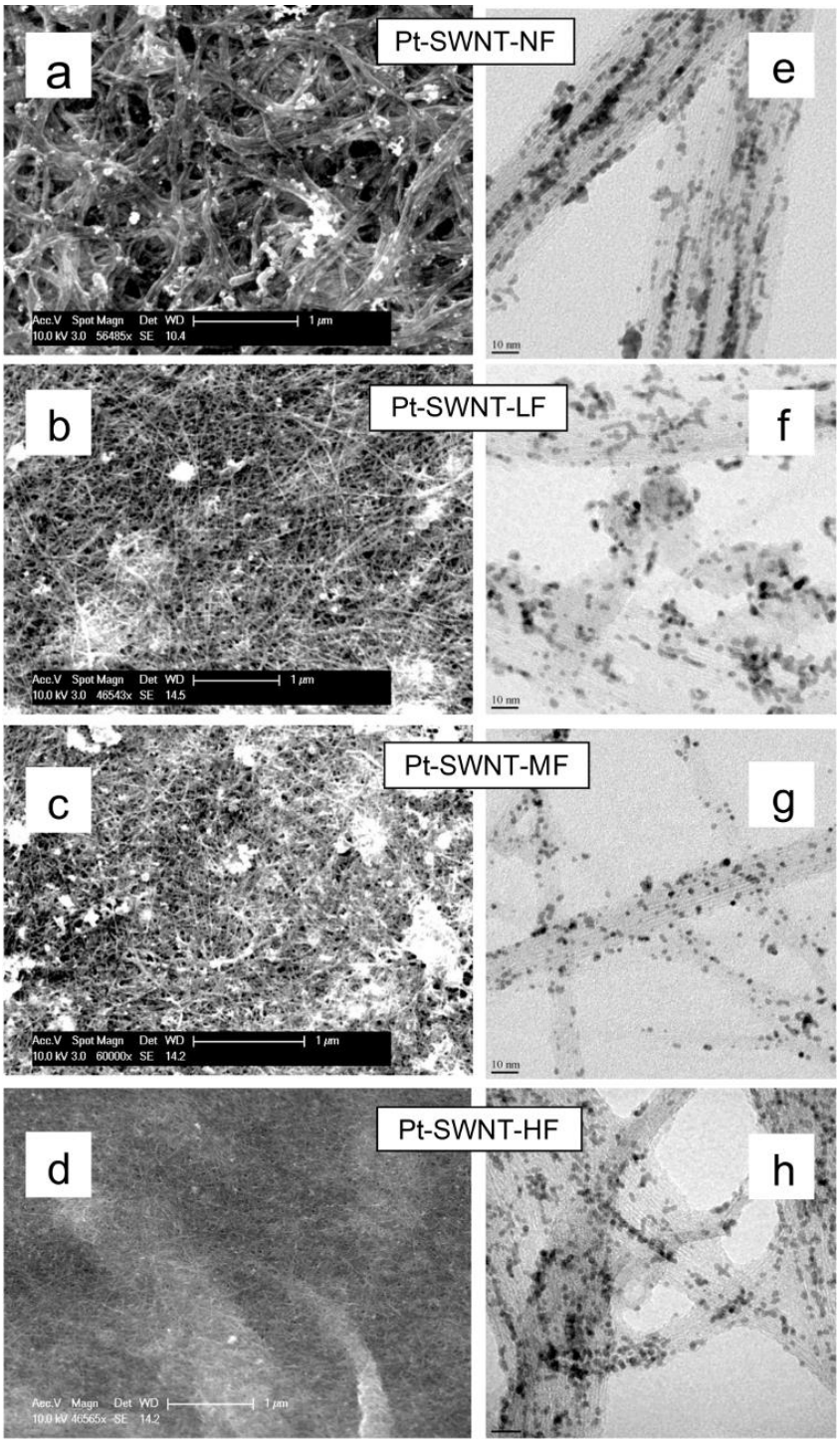

Fig. 5. SEM and TEM images of Pt supported SWNTs. (a–d) SEM images and (e–h) TEM images. SWNT-NF: non-functionalized single wall carbon nanotubes; SWNT-MF: single wall carbon nanotubes of medium -COOH functionality; SWNT-LF: single wall carbon nanotubes of low -COOH functionality; SWCNT-HF: single wall carbon nanotubes of high -COOH functionality. Details of the preparation are summarized in Table 2. (Reprinted with permission from [53], 2023, Springer Nature, 557251050169).

Platinum nanoparticles with diameter between 1 and 5 nm were effectively deposited on MWCNT that had been oxidative functionalized with HNO_3 or $K_2Cr_2O_7/H_2SO_4$, and $SnCl_2$/HCl solution was applied for sensitizing the CNTs toward Pt deposition. The CNTs' surface was thoroughly wetted, which led to effective Pt coverage. The Pt/CNT electrodes demonstrated high electrocatalytic activity in the ORR when evaluated in a single stack PEMFC [47]. The H_2SO_4/HNO_3 functionalized CNTs were used for the preparation of supported Pt-M (M = Fe, Ni, Fe-Ni) bi- and tri-metallic nanoparticles, which behaved as efficient electrocatalyst for PEMFC [54]. In order to prepare PtRu nanocomposites, MWCNTs were oxidized with aqueous H_2O_2. The surface chemical composition was found to influence the availability of the metal precursors and the metal dispersion on the surface MWCNTs [55]. Comparatively, MWCNTs oxidized with 4 M and 8 M H_2O_2 subsequently contained lower amount of phenolic hydroxyl and carboxylic groups, while possessing higher number of lactones and quinone/carbonyl groups, leading to fewer but more uniform distribution of smaller PtRu particles [55]. It should be noted that the treatment with HNO_3 can be followed by sonochemical one and an ionic liquid treatment can promote the formation of small, homogeneous Pt nanoparticles during the introduction of Pt [48].

In addition to oxygen-containing functional groups, the formation of other (N-, S-containing) ones was also proved to be useful. Roudbari *et al*. modified the MWCNTs by nitrogen groups in order to enhance the ORR activity [56]. N-containing functional groups were obtained from triethylenetetramine (TETA), diethylenetriamine (DETA), and malononitrile (MN) by use of a thionyl chloride coupling agent. The half-cell test results showed that Pt/TETA-modified MWCNTs electrode had the best performance in the ORR, but the stability of the Pt nanoparticles was also significantly improved by the modification, especially with TETA precursor (see data in Table 2). They came to the conclusion that nitrogen groups deposited on the surface of MWCNTs support led to a strong interaction between Pt and catalyst support, enhancing the electrocatalyst stability [56]. There is also an example of electrochemical modification with N-precursors: e.g., an ordered 4-aminobenzene monolayer was grafted onto the CNT paste electrode by electroreduction of 4-nitrobenzenediazonium tetrafluoroborate by scanning from 1.1 V to −0.3 V (vs. SCE) [48].

It has also been reported that the introduction of the –SH functional group makes it possible to obtain a more active and stable electrocatalyst compared to the non-functionalized materials [57]. Diazonium coupling reaction-assisted CNTs functionalization by thiolphenyl groups promoted both the electrochemical stability and dispersion of Pt nanoparticles attached on the CNT surfaces [57]. Silane-assisted treatment could provide -SO_3H groups on the CNT surface [48].

Surface modification by doping can be considered as a separate way of functionalization. N-doped carbon nanostructures and composites prepared from them have been described as promising new materials for PEMFC catalysts. N-doping techniques are classified into two major categories: (i) *in situ* doping i.e. direct synthesis of the N-containing material, (ii) „post-doping" i.e. post-treatment of carbonaceous materials with N-precursors (N_2, NH_3, etc.) [69]. Beside nitrogen, other elements such as S, B, etc. have also been used as dopant. Due to the enhanced anchoring of Pt onto the N-doped support, expressed in better dispersion and stability of the metal nanoparticles, Pt-based catalysts supported by N-doped carbon exhibit enhanced catalytic activity in the ORR. In addition, composites with non-noble metals (Fe, Co, etc.) showed increased activity in both proton exchange and alkaline fuel cells [70]. N-doped CNT provided excellent properties of Pt nanowire catalyst in comparison with traditional Pt/C [60] (see Table 2).

An important question is to what extent the functionalized carbonaceous material maintains the advantageous uniform polyaromatic system. From this point of view, non-covalent functionalization is seen as superior to covalent functionalization, since this process binds molecules to the carbonaceous material without changing its electrical or structural characteristics [71]. Non-covalent functionalization is often technically easier to solve and more environmentally friendly (no mineral acid waste is generated) compared to covalent functionalization. In a simple method, tetrahydrofuran was applied as a solvent for the metal precursors. Uniformly distributed Pt and PtSn nanoparticles on MWCNTs were synthesized in this way because tetrahydrofuran acted as both a functionalizing and anchoring agent. The formation of an intense σ-π interaction between MWCNTs and tetrahydrofuran was assumed [58]. Electron-conductive polyaniline (PANI) has been prepared to modify CNTs and to bridge Pt nanoparticles onto it (see Fig. 6) [50]. The sp^2-hybridized carbon atoms in a hexagonal network provided a large π-bond on the surface of CNT, which could interact with conjugated polymers via π-stacking with no alteration in the graphitized surface. This novel

Pt-PANI/CNT catalyst was electroactive and exhibited excellent electrochemical stability, promised various possible applications in PEMFCs [50].

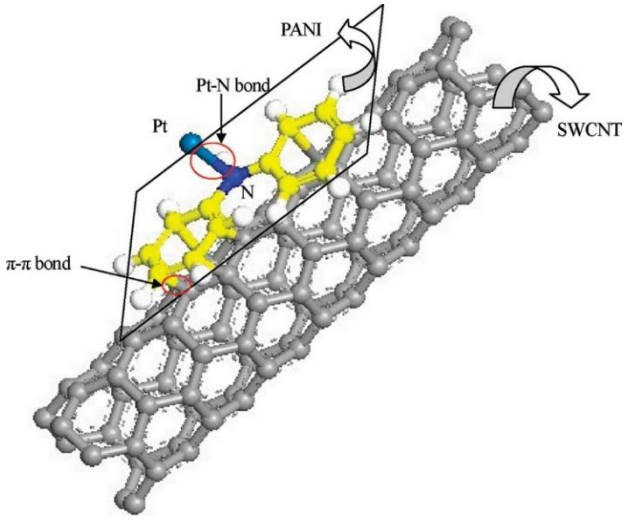

Fig. 6. Molecular interactions in the Pt-PANI/CNT catalyst (Reprinted with permission from [50]).

CNTs were successfully wrapped with poly (diallyldimethylammonium chloride) (PDDA), with a kind of the cationic surfactants, and used in PEMFC as support of Pt electrocatalyst. The strong electrostatic interaction amongst Pt nanoparticles and PDDA-CNT supports provided high dispersion and stability of the metal [59]. Similarly to CNTs, to enhance the effectiveness of carbon nanofibers, numerous functionalization have been set out [49].

3.2 Functionalization of graphene nanosheets for PEMFC catalysts

Regarding the GNSs (see Table 3), the first step of the most commonly applied methods for their production is the conversion of natural graphite into graphite oxide (GO) using strong oxidizing agents according to the classical methods ($KMnO_4/H_2SO_4/NaNO_3$- Hummers' method; $HNO_3/NaClO_3$- Brodie's method). The graphene oxide (*i.e.*, the delaminated GO) could be considered "as derivatized graphene with a myriad of oxygen functionalities due to the introduction of carbonyl, hydroxyl, and epoxy groups on the planar surfaces and edges of the carbon sheets during graphite oxide exfoliation" [72]. The delaminated GO is transformed to reduced graphene oxide (r-GO), which is the most frequently used GNS in the production of supported catalysts. The GO itself can be considered as a highly functionalized starting material; during its further use (*e.g.*, platinum load from H_2PtCl_6 by ethylene glycol-$NaBH_4$ reduction method), it can also be transformed *in situ* into r-GO. In another approach, GO can be exfoliated by thermal shock at high temperatures [61]. Its functionalization was carried out using CA subsequently heat treated to

obtain functionalized graphene (indicated as FG in ref. [61]). Pt/FG, home-made Pt/G prepared from non-functionalized graphene, and commercial Pt/C electrocatalysts were utilized at the anode, as well as at the cathode side of PEMFCs. The highest P_{max} and the highest long-run stability were measured by use of the Pt/FG. Better performance of Pt/FG and Pt/G in comparison to Pt/C was assigned to the combined effect of the enhanced ORR activity, hydrogen adsorption/desorption activity, higher electrochemical surface area, along with Pt distribution [61]. Inclusion of other functional groups (e.g., –SH [62],–SO_3H [63]) into GNSs has also been mentioned in the literature. By use of diazonium chemistry and 4-aminothiophenol precursor, thiophenyl groups were grafted onto the GO (see Fig. 7) [62]. Compared to that of Pt@rGO, higher activity of Pt@SC_6H_4–rGO was observed in the ORR using acidic electrolyte, which was explained by the contribution of the thiophenol via cooperative factors such as (i) a favourable interfacial interaction among r-GO and Pt nanoparticles, (ii) the capability of the 4-aminothiophenol to generate protonated thiol groups, which function as an ionomer providing proton transport on the catalyst surface, (iii) the occurrence of sulphur, which may influence ORR adsorption processes and the electron transfer rates [62].

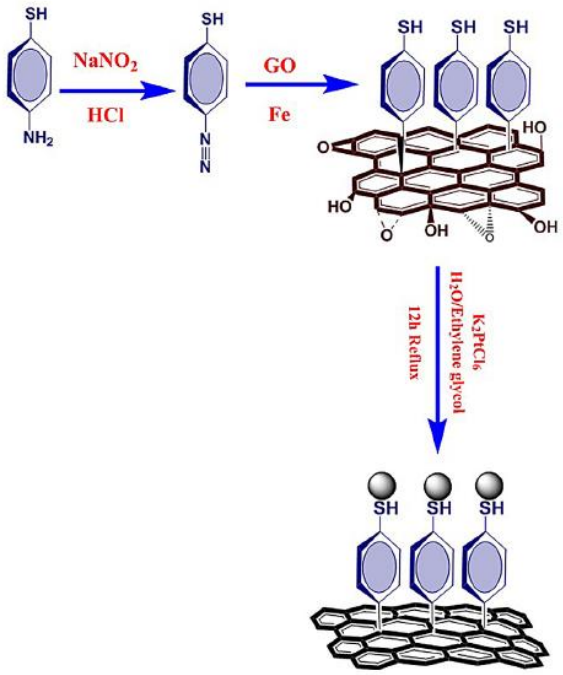

Fig. 7. Scheme of functionalization of exfoliated graphene oxide and decoration of Pt nanoparticles (Reprinted with permission from ref. [62], 2022, Elsevier copyrights 5440710521559).

SO_3H-functionalized graphene was prepared by use of $(NH_4)_2SO_4$ and GO. Better adsorption of trimetallic nanoparticles (PtCoFe) on the support and an increase in the stability of the electrocatalysts in PEMFC were achieved due to the presence of $–SO_3$ groups on the graphene material [63]. Utilising 4-aminobenzoic acid, hydrochloric acid, and sodium nitrite moderately reduced GO was exposed to diazonium functionalization in order to synthesise hierarchical PBI-grafted graphene hybrids as supports for Pt nanoparticles. Then it was transformed to benzoic acid functionalized graphene by hydrazine, followed by heating in the presence of isophthalic acid, 3,3'-diaminobenzidine and polyphosphoric acid. Pt/PBI-graphene behaved as a highly active and durable ORR catalyst in H_2/O_2 PEMFC [64].

Chemical functionalization of GNPs with hydroxyl-, amino-, and carboxylic terminal groups is also possible [73]. In addition to organic chemical procedures, ball milling is a simple but efficient approach for producing different edge-functionalized GNPs. Strong shear stresses created by fast whirling balls induced graphitic C-C bonds to break mechanically, which then allowed functional groups and/or heteroatoms to spontaneously incorporate at the impaired edges of graphitic networks and exfoliated the graphite as GNPs in the same time [74].

3.3 Functionalization of other new types of carbon nanomaterials for PEMFC catalysts

Functionalization of other, new types of carbonaceous material has also been reported. Aligned carbon nanotubes (ACNTs) were successfully used for PEMFCs. For example, growing dense ACNT layers with highly aligned structure directly on cathode materials promotes gas diffusion. Post-functionalization of ACNTs by colloidal chemistry approach with platinum nanoparticles obtained from $[PtCl_6]^{2-}$ led to improved cell performance at decreased Pt loading [75].

Highly graphitized mesoporous carbon (GMPC) was prepared through graphitizing the self-assembled soft-template mesoporous carbon under high-temperature heat treatment. GMPC was then non-covalently functionalized with PDDA and loaded with Pt nanoparticles using ethylene glycol for H_2PtCl_6 reduction. Pt nanoparticles (~3 nm) were uniformly and facilely deposited on GMPC through non-covalent functionalization. Obtained by this method Pt/GMPC catalyst exhibited high durability and higher activity towards ORR [76].

Although diamond has favourable properties such as high electrochemical stability and corrosion resistance in acidic and alkaline media, non-doped diamond is an electrical

insulator. Doping of nanodiamond makes it suitable for use as an electrocatalyst support due to improved conductivity. Along with this the frequently studied doping with B, P and N have also been mentioned as dopants of nanodiamonds [33, 49, 77, 78].

Among the carbon allotropes, fullerenes have special features such as the nanometer dimension, high electrochemical stability, high electroconductivity, special mechanical properties, which allows their application in fuel cells [79]. Although fullerenes, as specially C60 and its derivatives and carbon nano-onions have been applied for anode catalyst for the oxidation of methanol in the direct methanol fuel cells (DMFCs) several times, their use in PEMFC is mentioned rarely, connected mainly to the ORR taking place on the cathode side [79]. A solid-state mechanochemical reaction of C60 and graphite was used to prepare graphene-C60 hybrids from C60 and pristine graphite in the presence of LiOH catalyst. The connection of the fullerene and the GNP units was provided by C-C single bonds in the hybrid, which showed higher ORR activity compared to the parent carbon materials in alkali media [80]. Use of N-doped onion-like structures have been reported to show increased durability in the ORR both in acidic [81] and alkali media [82].

The study of carbon dots (CD) is an emerging new field, which has already resulted in several interesting review works [83, 84]. N-, S- and P-doped CDs and CD-graphene hybrid materials seem to be promising component of cathode catalysts, although the reported examples covered mainly results obtained the alkali media [83].

3.4 Composite type of supports for electrocatalyst via functionalization of novel carbon nanomaterials

Functionalization of new types of carbonaceous materials makes them possible to create advantageous 3-dimensional CNT-GNS composites [85]. Highly stable carbonaceous-inorganic composites can also be fabricated by the use of functional groups as they serve anchoring sites for the inorganic part during the formation of the composite (see Fig. 8) [86].

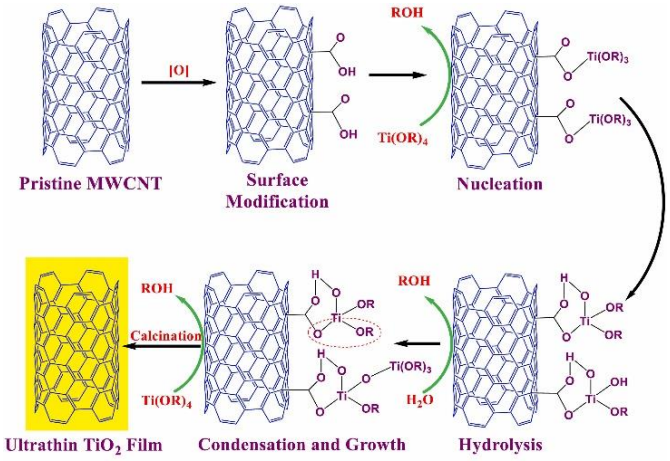

Fig. 8. Reaction scheme for the synthesis of MWCNT-TiO_2 composite (Reprinted with permission from ref. [86], 2022, Elsevier copyrights 5440710666725).

Acidic functionalization of MWCNT by means of H_2SO_4/HNO_3 mixture provided appropriate TiO_2-MWCNT composite type of supports for efficient and stable Pt electrocatalyst of PEMFC via hydrothermal [87] or sol-gel [88] synthesis. According to a non-covalent approach, TiO_2@CNT hybrid support was also prepared employing benzyl alcohol as a surfactant, which allowed TiO_2 to connect the hydrophobic surface of untreated CNTs without the necessity of covalent functionalization [88].

Preparation of GNS-inorganic oxide composite type of electrocatalyst supports has also been described in the literature. The use of TiO_2-GO derived carbon composite type of support prepared via multistep sol-gel based synthesis from GO (Hummers' method) and titanium isopropoxide precursor resulted in a stable Pt electrocatalyst [89]. We demonstrated that the Pt/TiO_2-GO derived catalyst with 20 wt.% Pt loading showed higher ORR activity than the Pt/TiO_2-C (C: Black Pearls 2000) derived one. Doping with molybdenum of the composite support containing mixed oxide-GO derived carbon, prepared in a similar way, along with improved stability, also provides a Pt/$Ti_{0.8}Mo_{0.2}O_2$-C catalyst with increased CO tolerance [39]. GO-TiO_2-Pt(x)-Nafion composites were also effectively synthesized by use of GO (modified Hummers' method) and titanium oxosulfate [90]. Besides, commercial graphene powder was also used to prepare TiO_2-functionalized GNSs by means of sodium dodecyl sulphate [91].

A special case of the inorganic-carbonaceous composites was obtained when carbonaceous part was *in situ* grown on a mixed oxide. Carbon nanostructure with helical morphology containing Fe-Sn-O (CNS-FSO) were decorated with Pt (Pt/CNS-FSO); its special

morphology, high electrical conductivity and high surface area resulted in high ECSA value. In addition, the homogeneous dispersion and strong binding of Pt nanoparticles led to good fuel cell performance [92].

4 Functionalized carbon nanomaterials as potential filler for PEMFCs membranes

Carbon nanostructure materials, their derivatives, and their functionalization version have drawn attention as inorganic fillers due to their extraordinary and outstanding properties. These additives markedly improve the proton conductivities, water retention capacities at high temperatures, and mechanical/dimensional stabilities. Moreover, functionalization enhances the chemical interactions between the organic matrix and the inorganic phase. This section will cover the most recent advancements of functionalized, carbon-based nanomaterials (CNTs, graphene oxide, fullerene, and graphene/graphite).

4.1 Functionalized carbon nanotubes for PEMFC membranes

In the past few years, significant progress has been achieved on composite membranes reinforced with CNTs for fuel cells. Nevertheless, two problems arise when CNTs and membranes are combined. First, because of their intense van der Waals forces, and since they are incompatible with dispersants they disperse insufficiently in polymer matrix. In addition, given the high electrical conductivity of CNTs, membranes containing CNTs are susceptible to short circuiting during operation. In order to fully harness the benefits of CNTs, a variety of methods for enhancing the dispersion of CNTs in PEM have been proposed. The CNTs compatibility with organic solvents and their distribution in the polymer matrices can both be enhanced by functionalising CNTs. Sulfonation, carboxylation, oxidation, alteration of surfactants, polymer absorption, and covalent grafting of small molecules or polymers to end-group processes are examples of CNT functionalization techniques [93]. Functionalized CNTs are a common type of bifunctional filler because of their distinctive nanostructure and the strength of the bonds between the carbon atoms making them highly electrically and thermally conductive and enhancing their tensile strength. In addition to being chemically modifiable, CNTs can readily bond with the constituents of other materials due to the presence of functional groups on their surface [18].

Functionalization of MWCNT with Nafion and their use as filler for Nafion membrane was reported by *Liu et al*. [94]. Nafion ionomer was first ozonated using continuous stream of O_3–

O_2, and then MWCNT in certain amount was added and reacted at 60 °C for half an hour. The resulted powder MWCNT-Nafion was obtained after washing with isopropanol and drying in vacuum oven. The filler was then employed in Nafion dispersion. The fabricated composite membrane contains 0.05 wt.% MWCNT-Nafion observed extensive proton conductivity, which is 5 times more than pristine Nafion membrane. Additionally, the membrane achieves 1.5 times higher power density and current density at 0.6 V compared to the pristine membrane.

Oxidation of CNTs was reported by Cele *et al*. [95] as a nanofiller for Nafion-based nanocomposite membranes. The oxidized-CNTs/Nafion nanocomposite membrane was prepared by melt-blending at 250 °C. Due to the interaction between the proton produced from the ion exchange and the -SO_3H group in the Nafion matrix, the incorporation of 1 wt.% oxidized-CNTs has significantly enhanced the mechanical and thermal stability of the nanocomposite membrane compared to the pure Nafion membrane. In contrast, the proton conductivity of the nanocomposite membranes has dramatically decreased.

Sulfonation is one of the most reported functionalization for the carbon nanostructure materials. Sulfonated CNTs incorporated Nafion was reported by Yin *et al*. [96]. Fig. 9 (a) shows the transportation of the protons in the hydrated Nafion based membrane enforced with sulfonated carbon nanotubes with their “highways”. While using the sulfonated CNTs and SPAES, a new hydrocarbon-based composite membrane for high temperature PEMFCs has been prepared by Yu *et al*. [97]. Fig. 9 (b) represents their sulfonation process and the preparation of sulfonated CNTs.

For both membranes, the incorporation of sulfonated CNTs shows enhanced proton conductivity due to the formation of a large number of proton-conducting channels produced from ionic water clusters resulting from the clusterization of water molecules on the sulfonated CNTs surface. The incorporation of the sulfonated CNTs with 5 wt.% with respect to Nafion has shown three times increase in conductivity compared to non-functionalized CNT/Nafion membrane of 0.03 S cm^{-1} at 50 % relative humidity (RH) and room temperature [96]. On the other side, the incorporation of the sulfonated CNTs with only 0.2 wt.% in the SPAES polymer matrix membrane shows approximately 1.5 times increase in the conductivity at a value of 0.0322 S cm^{-1} at 120 °C and 50 % RH compared to the pristine membrane [97].

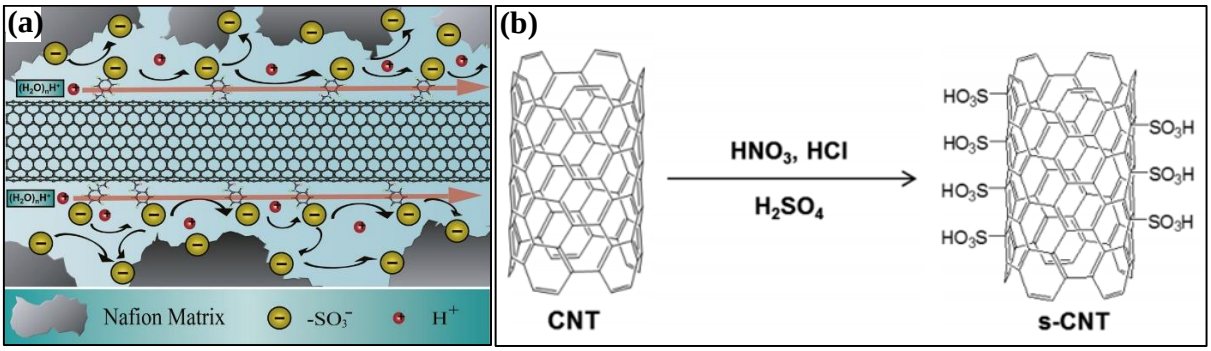

Fig. 9. (a) Proton transportation in water hydrated sulfonated CNTs/Nafion membranes with proton "highways" along sulfonated CNTs (Reprinted with permission, Copyright © 2018, American Chemical Society ref. [96]); (b) Scheme of the preparation of sulfonated CNT (Reprinted with permission from ref. [97], 2022, Elsevier 5440730654885).

Additionally, Kannan *et al*. [98] prepared Nafion based membrane using sulfonated SWCNTs. Simultaneously, Steffy *et al*. [99] prepared MWCNTs incorporated Nafion-based membranes. The sulfonation process of the MWCNTs by using sulfonic acid containing aryl radicals to insert sulfonate groups on the surface of MWCNTs is shown in Fig. 10 (a).

The results of both studies suggest that the sulfonation of the CNTs surface can enhance the fuel cell performance and improve the membrane's durability. Comparing the achievements from the papers mentioned above, sulfonated MWCNTs show higher performance due to better compatibility with the Nafion matrix. This leads to higher thermal and mechanical stability; consequently, enhancement in the water uptake and the proton conductivity has been reported due to the high hydrophilicity of the sulfonated MWCNTs. Nevertheless, 0.05 % sulfonated SWCNTs can enhance the proton conductivity under full humidification conditions by about 10 % and achieve a power density of 250 mW cm^{-2} at 700 mA cm^{-2} current density, while 0.25 % sulfonated SWCNTs achieved ~500 mW cm^{-2} at ~ 700 mA cm^{-2} under 80 % RH.

In another approach, phosphonic acid functionalized CNTs was used as filler in SPEEK [100]. The functionalization of the CNTs with phosphonic acid group consists of three steps, as presented in Fig. 10 (b). The first step is the oxidation of CNTs using Hummers' method. The resulting oxidized CNTs (indicated as CNT-COH in ref. [100]) were reacted with diethylphosphatoethyl triethoxysilane (PETES) to graft phosphonate ester on the CNT-COH. Finally, upon refluxing in H_2SO_4, the phosphonate ester groups on the surface of the CNTs were cleaved into phosphonic acid groups. The results show that the blend membrane

consisting of 2 wt.% functional CNT was found to enhance the tensile strength by ~ 75 % and improve the water uptake to double value. This results in enhancing the proton conductivity, consequently, improves the fuel cell performance [100].

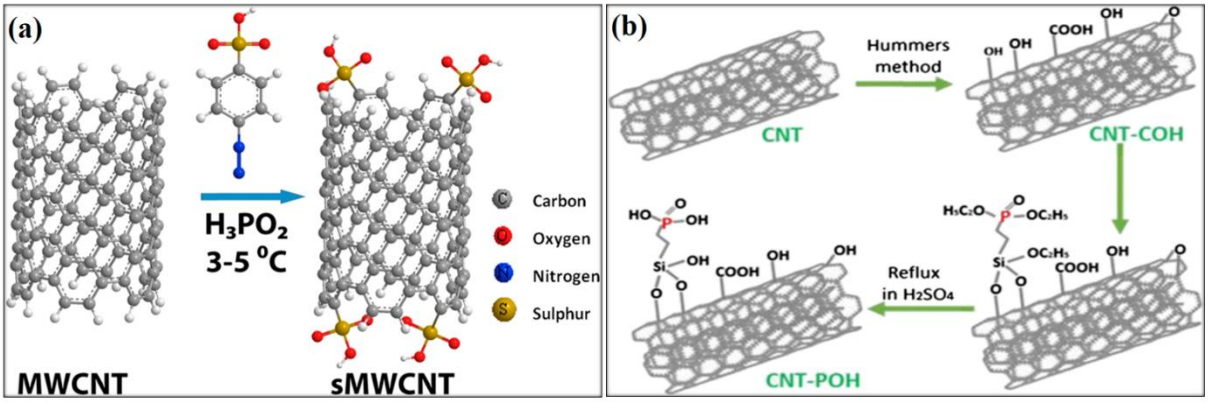

Fig. 10. (a) Sulfonating process by use of sulfonic acid containing aryl radicals (Reprinted with permission from ref. [99], 2022, Elsevier copyright 5440740595808); (b) Synthesis of phosphonic acid functionalized CNT (Reprinted with permission from ref. [100], 2022, Elsevier copyright 5440740874989).

Recently, Gao *et al*. [18] reviewed the use of different functionalized carbon nanotubes filler in proton exchange membranes. Authors reviewed the work presenting amino-functionalized CNTs (ACNT) embedded in SPEEK matrix as one example of the preparation of nanocomposite membrane. The amino functionalization proved to be more significant for proton exchange membranes at low humidity [101]. Figs. 11 (a and c) and 11 (b and d) show images of the SEM for the produced CNT and amino-functionalized CNT (ACNT), respectively. While TEM images for CNT and ACNT are presented in Figs. 11 (e) and 11 (f), respectively. Additionally, Fig. 11 (g) illustrates the functionalization process for CNTs using aminopropyl trimethoxysilane (APTES) as the amino group precursor and the preparation of the nanocomposite membranes. Authors show that water uptake and proton conductivity increase due to the formation of local proton conducting network based on the interaction between the amino group on the surface of the CNTs and the sulfonic acid group in polymer matrix. Furthermore, the durability test of the pristine SPEEK and nanocomposite membranes containing the same amount of CNTs and amino-functionalized CNTs attributed that the membrane with amino-functionalized CNTs has higher stability. This is assigned to the compatibilizing effect of amphiphilic amino-functionalized CNTs with the polymer structural domain.

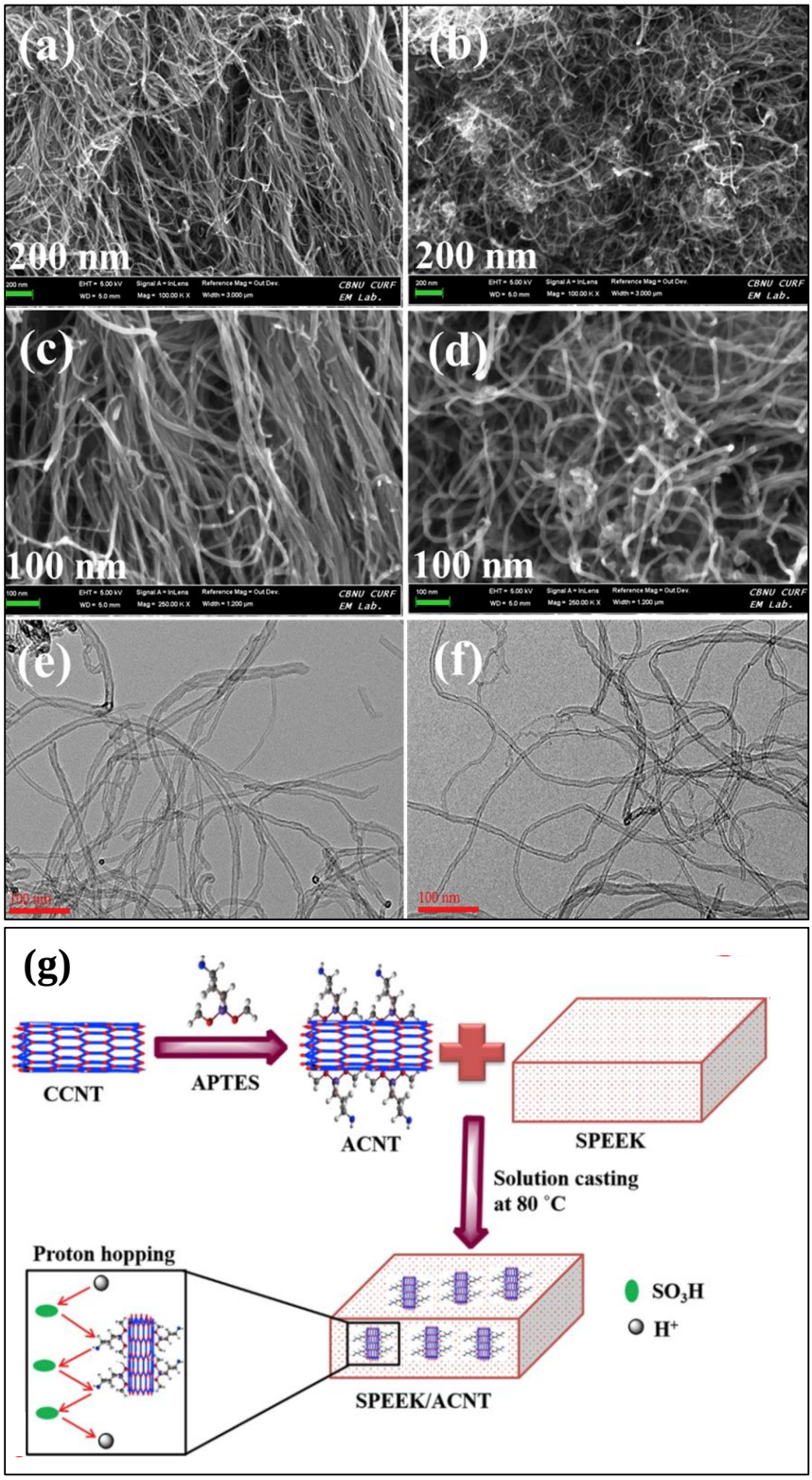

Fig. 11. SEM images of (a and c) CNT and (b and d) amino-functionalized CNT (ACNT); TEM images of (e) CNT and (f) ACNT; (g) Preparation process of SPEEK/ACNT composite membrane and its proton hopping (Reprinted with permission from ref. [101] 2022&2023, Elsevier copyright 5440741002911& 5570731133952).

In addition to the above-mentioned polymers, Gao *et al*. reviewed the use of CS as a natural polymer with good hydrophilicity at high temperatures. The preparation scheme of imidazole modified MWCNTs (MWCNT-Im) is presented in Fig. 12. The membrane containing 0.5 % MWCNT-Im shows enhanced proton conductivity. The high conductivity was achieved by creating new proton conducting channels and enhancing the Grotthuss mechanism after the incorporation of the imidazole group into the surface of the MWCNTs [18].

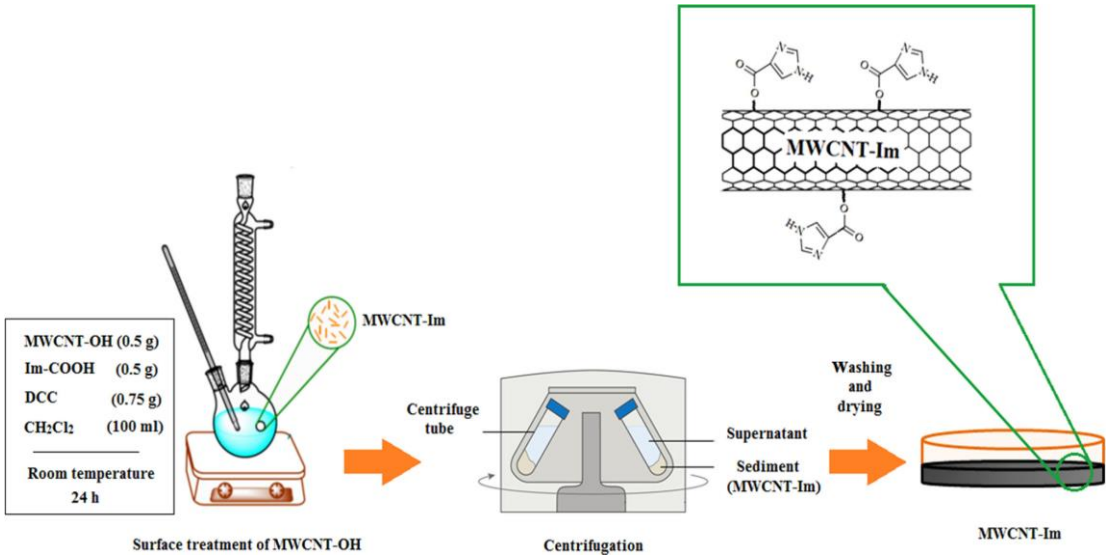

Fig. 12. Schematic diagram for the surface modification of MWCNT with imidazole (MWCNT-Im) (Reprinted with permission from ref. [102], copyright T&F af/lmsa/02801521).

4.2 Functionalized graphene oxide for PEMFC membranes

Graphene oxide is considered as one of the most attention-drawing carbon nanostructures for fuel cell applications. It has an extensive water permeability, which makes it a more suitable material for the fuel cell application. Compared to graphene, graphene oxide has different oxygen-containing functional groups on its surface, such as, for example, -OH, -C=O, and -COOH. These groups are the main reason of increased graphene oxide hydrophilicity by allowing the insertion of water molecules between them.

This exceptional property gives graphene oxide several benefits for membrane fuel cells, such as (a) higher proton conductivity due to the promotion of the H^+ transfer, (b) reduction of fuel crossover, (c) superior mechanical, thermal, and chemical stability of the PEM, and (d) higher water retention and consequently, self-humidification of the cell at low RH and even

higher temperature. It is reported that functionalized graphene oxide is achieving higher performance compared to non-functionalized [103].

Influence of highly oxidized graphene oxide (HGO) on the performance of Nafion/SPEEK blend membrane was studied and reported by Mishra *et al*. [104]. Composite membranes containing HGO demonstrated higher thermal stability compared to that containing graphene oxide with a low degree of oxidation. Moreover, the incorporation of 0.75 wt.% HGO in the membrane containing 1 wt.% SPEEK made it possible to achieve the optimum proton conductivity of 322 mS cm^{-1} at 100 % RH and 90 °C compared to 198 mS cm^{-1} for Nafion at the same conditions.

Zhang *et al*. reported that the insertion of phosphonic acid-functionalized graphene oxide (PGO) in Nafion results in higher power density. The hybrid membrane, containing 2 wt.% PGO, achieves approximately six times higher conductivity of 0.0441 S cm^{-1} at 80 °C and 40 % RH compared to the pristine Nafion membrane [105]. While Abouzari-Lotfi reported that intercalating 1.5 % of PGO in 2,6-pyridine functionalized PBI (Py-PBI) composite membranes exhibit around four times higher conductivity than that of phosphoric acid doped Py-PBI membrane at 140 °C and anhydrous condition. Compared to the pristine membrane, the 1.5 % PGO-Py-PBI exhibited 75 % higher power density of 360 mW cm^{-2} at 120 °C and dry conditions [106].

On the other hand, sulfonation is one of the most used functionalization for graphene oxide nanostructure for fuel cell applications. Beydaghi *et al*. [107] reported the incorporation of aryl sulfonated graphene oxide (SGO) in PVA matrix. It was demonstrated that the addition of 5 wt.% SGO into PVA enhanced both thermal and mechanical stability of the PVA-based membranes. Additionally, the 5 wt.% SGO has improved the proton conductivity by approximately 16 times that the non-sulfonated GO and 83 times that of the pure PVA. Moreover, sulfonation of graphene oxide was reported by Pandey *et al*. [93], using addition of both sulfonated imidized (SIGO) and sulfonated propylsilane graphene oxide (SPSGO) into sulfonated polyimide (SPI). Both membranes showed improved proton and thermal, mechanical, and chemical stabilities as well as high water retention, which help for membrane self-hydration of the membrane matrix. Regarding the SPI/SPSGO, 8 wt.% filler achieved the highest performance compared to Nafion 117 membranes. Conversely, 15 wt.% of SIGO exhibits the best performance compared to both pristine PI and Nafion 117.

Besides the above mentioned examples, nanocomposite membranes based on Nexar (non-fluorinated hydrocarbon) and sulfonated graphene oxide were reported by Ansari *et al*. [108]. The sulfonation process was done using chlorosulfonic acid in the presence of chloroform. However, the water uptake and swelling degree of the 5 wt.% loading sulfonated graphene oxide-based membrane decreased to half value compared to the bare Nexar membrane, but this value is still higher compared to Nafion membrane. On the other hand, sulfonated graphene oxide demonstrated higher ion exchange capacities compared to non-functionalized graphene oxide, but lower by approximately 10 % than pristine Nexar membrane. Moreover, proton conductivity of both 2.5 and 5 wt.% loaded membranes was found to be higher compared to non-functionalized graphene oxide and bare Nexar membranes.

In addition to sulfonated aryl, imidized and propylsilan graphene oxide, sulfonated organosilane functionalized graphene oxide (SSi-GO) was used as filler in the core for the preparation of cambiform-like core-shell SPEEK nanofiber membrane using coaxial electrospinning technique. The scheme of the unique preparation strategy of the coaxial electrospinning SSi-GO/SPEEK core-shell structure is presented in Fig. 13 (a). In comparison with the monoaxial electrospun blend membrane and the cast membrane, the measured coaxial membrane exhibited approximately 43.2 % and 33.0 % higher water uptake, respectively. Furthermore, authors reported that when compared to other membranes, co-spinning membrane with 2.5 wt.% SSi-GO showed a considerable improvement in proton conductivity, increasing it to about 156.6 mS cm^{-1}, which is 1.24 and 1.42 times better than the best mono-spinning and mix cast membranes, respectively [109].

In another work, SGO with controllable sulfonic acid group loading prepared by distillation–precipitation polymerization process was reported in ref. [110]. The synthesized SGO was incorporated in CS to prepare nanohybrid membranes. Because the acid group of the SGO and the NH_2 group of CS are strongly attracted electrostatically, the mobility of CS chain is suppressed resulting in decreasing the swelling degree and consequently improving the mechanical and thermal stability compared to pure CS membrane. At the same time, the acid-base pairs generated by the incubation of SGO in the CS polymer chain facilitate the proton transfer and therefore enhance the proton conductivity in both hydrated and dry conditions. Predominantly, in comparison with CS membrane, the 2 % SGO addition achieved the greatest improvement in the proton conductivity by 122.5 % and 90.7 % increase in hydrate and dry status, respectively [110].

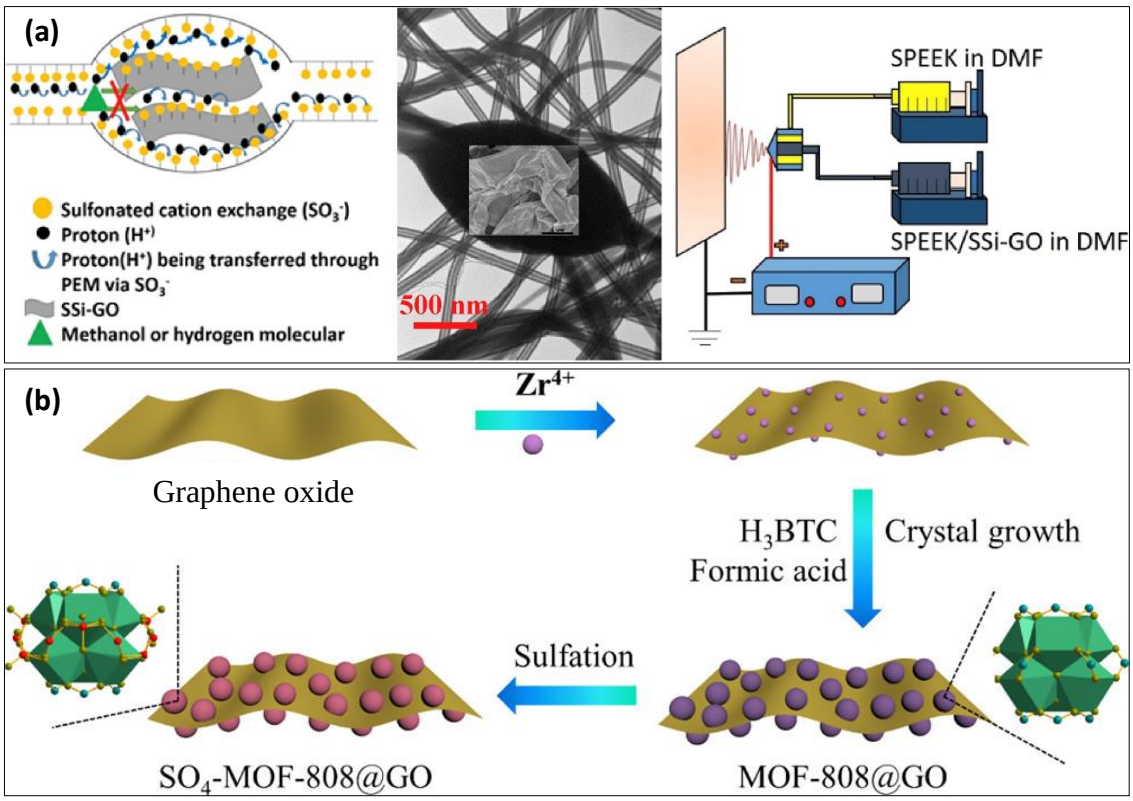

Fig. 13. Examples for unique preparation strategies of graphene oxide derived membranes. (a) Scheme of the coaxial electrospinning SSi-GO/SPEEK core-shell structure (Reprinted with permission from ref. [109], copyright 2022, Elsevier, 5442790516090); (b) Synthesis of SO_4-MOF-808@GO (Reprinted with permission from ref. [111], Copyright ©2021, American Chemical Society).

Recently, a new way of functionalization of the graphene oxide surface was reported by Cai *et al*. [111]. They functionalized the surface by incorporating a sulphated metal organic framework (SO_4-MOF-808). The preparation of the hybrid filler was done via *in situ* growth of MOF-808 on the surface of the graphene oxide using zirconium oxychloride hydrate as a precursor, and 1,3,5 benzene tricarboxylic acid, as a crystal growth agent. The produced MOF-808@GO was then sulphated using 0.1 M H_2SO_4 as shown in Fig. 13 (b). The hybrid filler was then intercalated in SPEEK, and high-performance composite membranes were fabricated. Due to the homogeneous deposition of the SO_4-MOF-808 on the surface of graphene oxide, aggregation of MOF molecules was restricted. The existence of sulphate groups on the surface enhances the water uptake and water retention properties of the fabricated membrane. Therefore, higher proton transfer ability and proton conductivity even at low humidity compared to the pristine SPEEK membrane. The observed proton conductivity of 2 wt. % of SO_4-MOF-808@GO in SPEEK is 2.63- and 7.44-fold compared to

pristine SPEEK membrane at 70 °C under 90 % RH and at 90 °C under 40 % RH, respectively. Moreover, the membrane shows a power density of approximately 70 % higher than that of pure SPEEK membrane.

4.3 Functionalized fullerenes for PEMFC membranes

Buckminster fullerene C60 is another type of carbon nanostructure with high electron affinity, perfect bucky ball structure, high density of functional groups on the surface, and radical scavenging property. Considering these features, using fullerene as an additive for the fabrication of polymeric composite membranes has attracted scientists' attention [112]. Hinokuma *et al*. studied the effect of functionalization on the proton conductivity of fullerene [113]. Authors reported that the polyhydroxy hydrogen sulfated fullerenes achieved a high proton conductivity of 10^{-3} to 10^{-2} S cm^{-1} at 23-150 °C in an anhydrous system [113]. Wang *et al*. [114] used two new fullerene derivatives, namely tri-cyanohydrofullerene ($HC60(CN)_3$), and poly{4-[2-[2-(2 methoxyethoxy) ethoxy]ethoxy]benzyl}fullerene ($C60(TEO)_n$) as additives to Nafion for the fabrication of PEM. The incorporation of the $HC60(CN)_3$ had a maximum of 2 % due to its poor dispersion, while the addition of $C60(TEO)_5$ remained constant at 0.5 %. The addition of $HC60(CN)_3$ alone or combined with $C60(TEO)_5$ enhanced the water uptake of the Nafion membrane under hydrous and anhydrous conditions. Moreover, it was shown that the addition of $HC60(CN)_3$ alone led to an improvement of proton conductivity compared to the recast Nafion. The incorporation of both $HC60(CN)_3$ and $C60(TEO)_5$ resulted in higher proton conductivity over a wide range of RH compared to most of the C60, or polyhydroxy fullerene reported Nafion membranes. On the other hand, Bhat *et al*. [115, 116] reported using sulfonated fullerene (SFu) as additive for both Nafion and SPEEK composite membranes. Composite membranes based on SPEEK polymer containing 0.5 wt.% of SFu exhibited higher proton conductivity by 1.4 times than the SPEEK in addition to double power density of 103 mW cm^{-2} at 60 °C. Meanwhile, the addition of SFu was optimized at 1 wt.% in Nafion-based composite membranes. The membrane showed power density of 146 mW cm^{-2}, which is higher than the obtained value for Nafion 117 at the same conditions.

4.4 Functionalized graphene and other carbonaceous structures PEMFCs membranes

Graphene/graphite like the previously described carbonaceous materials, possess extraordinary mechanical and thermal characteristics. However, aggregation and poor dispersion of graphene in different solvents obstruct it from further processing. Consequently,

it is necessary to eliminate these cripples. Chemical functionalization of graphene is one of the most successful methods, which makes this carbonaceous material compatible with several solvents, allowing to fabrication of membranes from it.

Graphite nanofibers (GNF) exhibit excellent fibrous structure, chemical stability, and acceptable surface area. Additionally, heteroatom engineering to GNF fundamentally changes structural transformation, configures the properties of electron donors and acceptors, and subsequently adjusts their electrochemical activity. Furthermore, chemical functionalization by sulfonation is considered one of the possible ways to introduce GNF to fuel cell applications. Inspired by the aforementioned reasons, the impact of the sulfonic acid-functionalized, unzipped graphite nanofiber (SO_3H-UGNF) as a promising filler for Nafion composite membrane of PEMFC was investigated by Vinothkannan *et al*. [117]. Because the dense functionalization of -SO_3H groups may be significantly limited because of the closed fibrous frameworks of GNF, the unzipping process was chosen to enhance the density of surface functionality of the GNF. The process of unzipping was done using NH_4F via pyrolysis from room temperature to 900 °C under N_2 atmosphere after purification by HCl. Then, the SO_3H-UGNF was prepared by using 4-benzene-diazonium sulfonate (BDS) as a sulfonating agent. Figs. 14 (a-c) represent SEM images and Fig. 14 (d-f) show TEM images for the GNF, unzipped-GNF, and sulfonated-GNF, respectively. The scheme of the synthesis of SO_3H-UGNF and its composite membrane is presented in Fig. 14 (g). Compared to the membrane obtained from the pristine Nafion, to that obtained from nanocomposite contained GNF, and even to that obtained from nanocomposite contained UGNF, the membrane contained SO_3H-UGNF showed more advantageous chemical, thermal and electrochemical properties. The upsurge in the membrane efficiency were credited to the better distribution of the SO_3H-UGNF in the polymer matrix due to the existence of a large density of –SO_3H on the surface. Among different concentrations of SO_3H-UGNF (0.5, 1, or 1.5 wt.%), the incorporation of 1 wt.% showed an optimum power density of 0.226 W cm^{-2} and durability of over 129 h at 120 °C at 18 % RH [117].

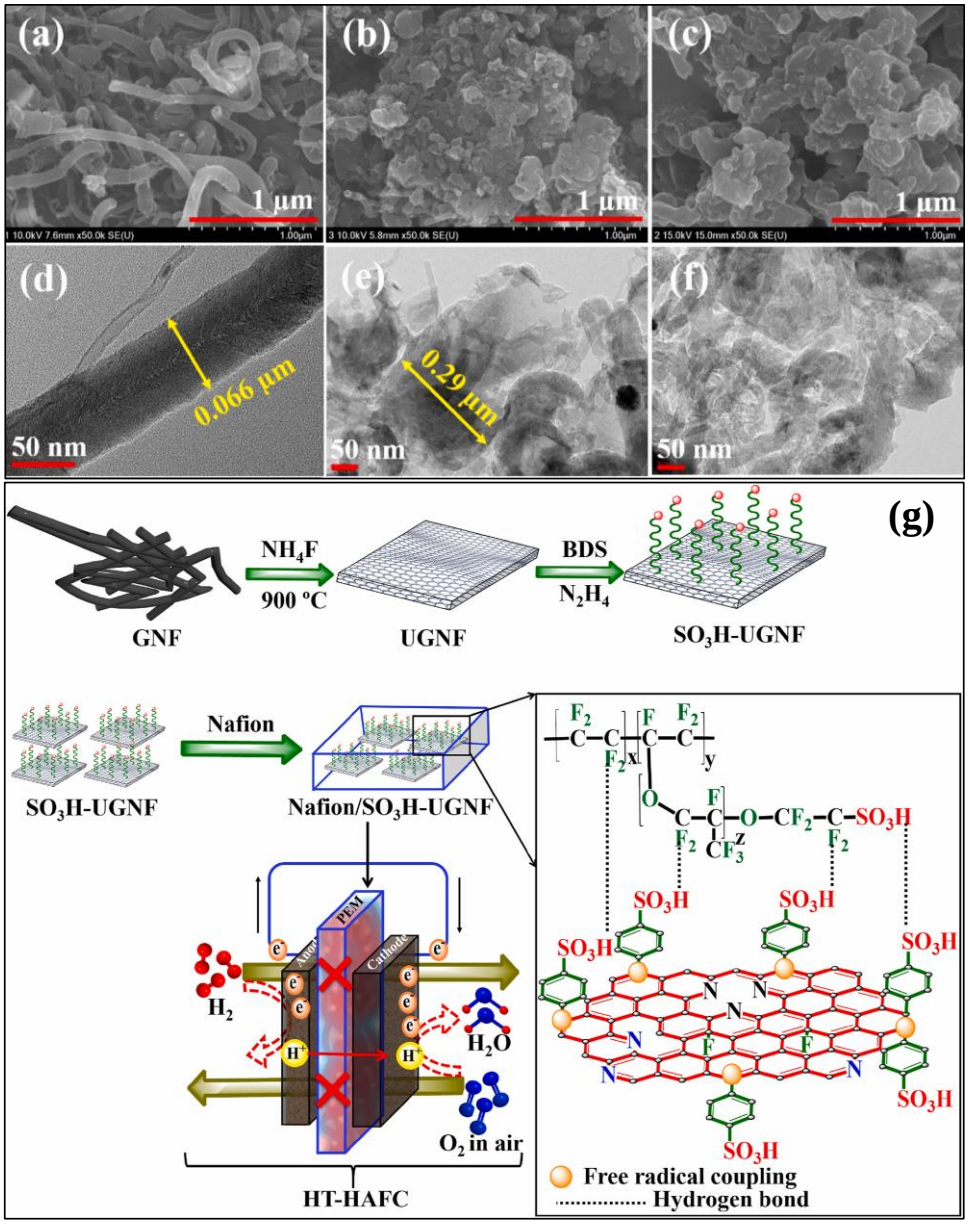

Fig. 14. (a-c) SEM images and (d-f) TEM images of GNF, unzipped-GNF and sulfonated-UGNF; (g) Synthesis of SO_3H-UGNF and its composite membrane with Nafion (Reprinted with permission from ref. [117], copyright 2023& 2022 , Elsevier 5570760204036 & 5442790723914).

In addition, Shukla *et al*. [118] have chosen sulfonated graphene nanoribbons-sulfonated graphene quantum dots (sGNR-sGQD) nanohybrids as additive for SPEEK membrane. The aim of using sGNR-sGQD was to form chemically functionalized graphene in the form of nanohybrid, which is more dispersible in different solvents for forming nanocomposite membranes. Additionally, the interaction between the graphene nanoribbon (GNR) and the graphene quantum dot (GQD) as well as the charge transfer may show excellent properties. Furthermore, the functionalization with sulfonic group could help to add more hydrogen

bonding interaction between the sulfonic acid group of GNR and GQD. Thus, the intercalation of the produced sGNR-sGQD nanohybrid could help to reduce the ionic channel in the SPEEK membrane and keep the high proton conductivity. Therefore, the produced nanocomposite membrane is able to eliminate the fuel crossover in the fuel cell. The full scheme of the sGNR-sGQD synthesis, *i.e.*, starting formation of the GNR-GQD hybrid using chlorosulfonic acid via an epoxy intermediate, followed by the sulfonation process using DBS precursor, is presented in Fig. 15 (a). Hence, the nanohybrid filler improves the dispersion in SPEEK membrane, and better water uptake, ion exchange capacity and proton conductivity have been observed. Moreover, the introduction of 1.5 wt.% sGNR-sGQD shows a significant increment of the peak power density by approximately 40 % compared to Nafion 117 and bare SPEEK membrane. Additionally, the structure-dependent effect on the sGNR-sGQD showed higher durability up to 100 hours of operation.

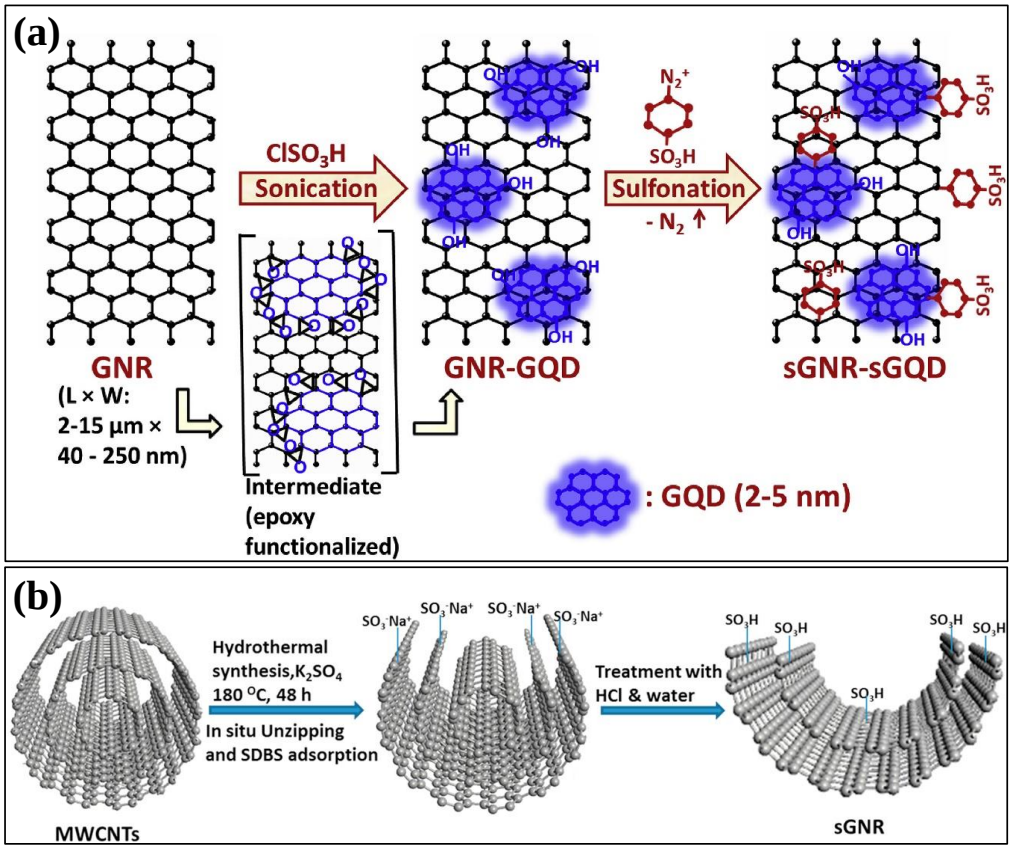

Fig. 15. (a) Preparation of graphene nanoribbons- graphene quantum dots (GNR-GQD) and sulfonated graphene nanoribbons-sulfonated graphene quantum dots (sGNR-sGQD) nanohybrids (Reprinted with permission from ref. [118], copyright 2022, Elsevier 5442790838581); and (b) Simultaneous unzipping

process of MWCNTs and sulfonation of produced graphene nanoribbons (sGNR) (Reprinted with permission from ref. [119], copyright 2022, Elsevier 5442790923233).

The same research group worked on converting the MWCNTs to GNR by sequential unzipping followed by a sulfonation process to the open edges to augment the density of ionic groups (sGNR) [119]. Afterward, they coupled sGNR with SPEEK and employed the resulting sGNR/SPEEK composite membrane in PEMFCs. The unzipping and sulfonating process was carried out in two steps, as shown in Fig. 15 (b), starting with the hydrothermal treatment using K_2SO_4 and sodium dodecyl benzene sulfonate (SDBS) followed by treatment with diluted HCl. In addition to the higher mechanical stability, the nanocomposite membranes boosted the water uptake, ion exchange capacity, and, most importantly, the proton conductivity compared to the bare SPEEK membrane. These features facilitated the proton transport through the membrane; therefore, higher power output was obtained. The composite membrane of 0.1 wt.% sulfonated GNR exhibited a current density of 840 mA cm^{-2} compared to 480 mA cm^{-2} for bare SPEEK membrane at 0.6 voltage as long with approximately 1.7 times more peak power density at the same conditions. Interestingly, the accelerated durability test showed that the aforementioned nanocomposite membrane has high durability even after 200 hours [119].

5 Conclusion and Future Prospects

Due to their advantageous properties, such as good electrical conductivity and high SSA, carbonaceous materials are of great interest as promising candidates for electrocatalyst supports and membrane fillers. In case of the catalysts, the role of carbon functionalization is 3-fold: (i) ensuring deposition conditions on molecular level (anchoring sites), (ii) ensuring deposition conditions on macroscopic level (wettability, hydrophilicity, surface charge), and (iii) ensuring good contact between the support and deposited particles. Although the presence of a large number of functional groups leads to a small size of metal particles, an increase in the ECSA and in electrocatalytic activity, it decreases the electrical conductivity and corrosion resistance. Thus, the balance between high electrocatalytic activity and high corrosion resistance has to be achieved.

Although novel carbonaceous materials (CNTs, graphene) offer new solutions for the catalysts of PEMFCs, their use as catalyst support in pristine form is cumbersome because of their highly hydrophobic character. Deposition of stable metal nanoparticles on their surface

is difficult; furthermore, graphene layers tend to stick together, thereby reducing the accessibility of the active metal supported by them. Both covalent and non-covalent functionalization helps to overcome the aforementioned difficulties resulting in an active and stable electrocatalyst.

Regarding the membranes, functionalized nanostructured carbonaceous material-polymer membranes have higher mechanical, thermal, and chemical stability as long with higher proton conductivity compared to non-functionalized and pristine membranes. Among the various functionalization methods, sulfonation is an easy way to prepare PEMs with significant proton conductivity. Heteroatom engineering for the unzipping process for CNTs, GNF, etc., is a skilful method to increase the density of the functional groups on the surface and enhance their dispersion in different solvents. Formation of functionalized hybrid filler either between two carbon nanostructures (sGNR-sGQD) or with different materials (sMOF-808@GO) might be a promising technique to fabricate new effective nanocomposite PEMs.

Although a large number of diverse functionalization methods have already been available, the optimal one must be selected considering the given system.

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List of abbreviations:

AB	Acetylene Black
ACNT	Amino-functionalized Carbon Nanotube
ACNTs	Aligned Carbon Nanotubes
ADT	Accelerated Degradation Test
AEPTMS	3-[2-(2-Aminoethylamino) ethylamino]propyltrimethoxysilane
APTES	Aminopropyl trimethoxysilane
CA	Citric Acid

CATB	Cetyltrimethylammonium bromide
CB	Carbon Black
CB_O	Oxygen-functionalized carbon black
C-CSA	Chlorosulfuric acid functionalized carbon
CNS-FSO	Fe-Sn-O containing carbon nanostructure
CNT	Carbon Nanotube
CS	Chitosan
C-SA	Sulfuric acid modified carbon
$C60(TEO)_n$	Poly{4-[2-[2-(2 methoxyethoxy) ethoxy]ethoxy]benzyl}fullerene
DBS	4-Benzene-diazonium sulfonate
DETA	Diethylenetriamine
DMFC	Direct Methanol Fuel Cell
DMF	N, N'-dimethylformamide
DoE	Department of Energy
Dual-CL	Dual Catalyst Layer
ECSA	Electrochemical Surface Area
f-AB	Functionalized Acetylene Black
FCB	Negatively charged SO_3H-carbon black in Ref. [64]
FCNT	Functionalized Carbon Nanotube
FG	Functionalized Graphene
GMPC	Graphitized Mesoporous Carbon
GNF	Graphite Nanofibers
GNR	Graphene Nanoribbons
GNP	Graphene Nanoplatelet
GNS	Graphene Nanosheet
GO	Graphite Oxide
GQD	Graphene Quantum Dots
$HC60(CN)_3$	Tri-cyanohydrofullerene
HGO	Highly Oxidized Graphene Oxide
HOR	Hydrogen Oxidation Reaction
KB	Ketjen Black
MEA	Membrane Electrode Assembly

MN	Malononitrile
MOF	Metal Organic Framework
MWCNT	Multi-Walled Carbon Nanotube
MWCNT-Im	Imidazole modified Multi-Walled Carbon Nanotube
NCNT	N-doped carbon nanotube
NG	Natural graphite
NT	Multi-Walled Carbon Nanotube in Ref. [13]
O-FGs	Oxygen-containing functional groups
OMC	Ordered Mesoporous Carbons
ORR	Oxygen Reduction Reaction
$\mathbf{P_{max}}$	Maximum value of power density
PANI	Electron-conductive polyaniline
PBI	Polybenzimidazole
PDDA	Poly(diallyldimethylammonium chloride)
PEM	Proton Exchange Membrane
PEMFC	Proton Exchange Membrane Fuel Cell
PETES	Diethylphosphatoethyl triethoxysilane
PFSA	Perfluorosulfonic acid
PGO	Phosphonic acid-functionalized graphene oxide
pPDA	Para-phenylenediamine
PVA	Poly (vinyl alcohol)
Py-PBI	2,6-pyridine functionalized polybenzimidazole
r-GO	Reduced Graphene Oxide
RCNT	Raw carbon nanotube
RH	Relative Humidity
SDBS	Sodium dodecyl benzene sulfonate
SFu	Sulfonated Fullerene
SGO	Sulfonated Graphene Oxide
sGNR	Sulfonated Graphene Nanoribbon
sGNR-sGQD	Sulfonated graphene nanoribbons-sulfonated graphene quantum dots
SCE	Saturated Calomel Electrode
SIGO	Sulfonated Imidized Graphene Oxide

SMSI	Strong Metal-Support Interaction
SO_3H-UGNF	Sulfonic acid-functionalized, unzipped graphite nanofiber
SO_4-MOF	Sulfated Metal Organic Framework
SPAES	Sulfonated poly (aryl ether sulfone)
SPEEK	Sulfonated poly (ether ether ketone)
SPEES	Sulfonated poly (ether ether sulfone)
SPES	Sulfonated poly (ether sulfone)
SPI	Sulfonated Polyimide
SPSGO	Sulfonated Propylsilane Graphene Oxide
SSA	Specific Surface Area
SSi-GO	Organosilane functionalized Graphene Oxide
Sulfanilic acid	4-Aminobenzenesulfonic acid
SWCNT	Single-Walled Carbon Nanotube
SWNT-NF	Non-functionalized single wall carbon nanotubes
SWNT-MF	SWCNT of medium -COOH functionality
SWNT-LF	SWCNT of low -COOH functionality
SWCNT-HF	SWCNT of high -COOH functionality
PETES	Diethylphosphatoethyl triethoxysilane
UGNF	Unzipped Graphite Nanofiber
TEA	Triethyl amine
TETA	Triethylenetetramine
THF	Tetrahydrofuran
PtNW	Platinum Nanowire
VC	Vulcan XC-72R in Table 1.

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