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# Advanced Supporting Materials for Polymer Electrolyte Membrane Fuel Cells

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## Abstract

Among the various kinds of fuel cell, polymer electrolyte membrane fuel cell (PEMFC) is the most prominent energy conversion device for portable applications. The catalyst-supporting materials provide active triple phase boundary for electrochemical reactions where the reactant molecules can easily interact with the catalyst surface. Catalysts play a vital role for improving the overall efficiency of the fuel cells through the advancement in the catalyst and their supporting materials for cathodic oxygen reduction reaction (ORR) in PEMFCs. The supporting materials mainly contribute to increase the electrocatalytic activity of the catalysts by providing more active surface area and extended life-time. The major roles of supporting materials are (i) they act as electron source with improved conductivity; (ii) they hold the metal nanoparticles; (iii) they possess higher surface area and (iv) they should have better stability under operating conditions. In this chapter, the various supporting materials were reviewed carefully based on their nature and performance toward the electrochemical reduction of oxygen for PEMFCs. They are classified into three major categories as (i) carbon supports; (ii) carbon-free supports, and (iii) polymer nanocomposites. In summary, the overall view on support materials and their role on electrocatalysis for fuel cell reactions is provided.

**Keywords:** oxygen reduction reaction, carbon supports, graphene, clay minerals, metal oxides, support-free catalysts

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## 1. Introduction

In order to move toward a sustainable existence in our extreme energy-dependent society, there is a convincing need to adopt environmentally sustainable methods for energy production, storage, and conversion [1]. A significant task is being placed to produce power without damaging our ecological system. The fossil fuels such as coal and petroleum products are

nonrenewable, and burning of these fuels increases the level of pollution and leads to global warming. Nowadays, many eco-friendly alternatives are explored as possible renewable energy sources such as solar, wind, tidal, and hydrothermal power but can be availed only at a particular climatic season. Till date, the internal combustion engines (ICEs) are used as major energy source to meet the global energy demand in wide range of applications [2]. ICEs are involved in the conversion of heat energy to mechanical energy and further used to generate the electrical energy, and this combustion process emits harmful greenhouse gases such as carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), etc. The limited availability of fossil fuels and emission of pollutant gases propel the search of alternative and sustainable clean energy sources [1–3].

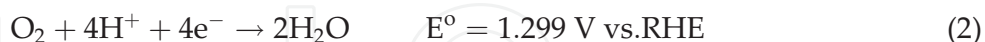
Among the various alternative energy sources, fuel cell is the most reliable choice with efficient energy conversion technology which converts chemical energy into an electrical energy through electrochemical reactions namely anodic oxidation and cathodic reduction reactions. Fuel cells are clean energy conversion device, where the oxidant and reductant are continuously supplied to produce electricity, unlike primary batteries that contain pre-packed chemical components. Fuel cells can provide long-term solutions as sustainable and efficient energy conversion devices with minimum or zero emission of greenhouse gases [4]. Significant environmental benefits are expected on fuel cells, particularly for automobile sector and power generation for stationary and portable applications.

Basically, fuel cell is an electrochemical cell, which continuously converts the chemical energy of a fuel and an oxidant to electrical energy in an electrode-electrolyte system, designed for continuous feeding of reactants at a high temperature in the presence of an electrocatalyst to catalyze the oxidation and reduction reactions [5].

(i) Hydrogen at the anode undergoes oxidation to form protons as shown below.



(ii) Oxygen at the cathode undergoes reduction to form water as given below [6].

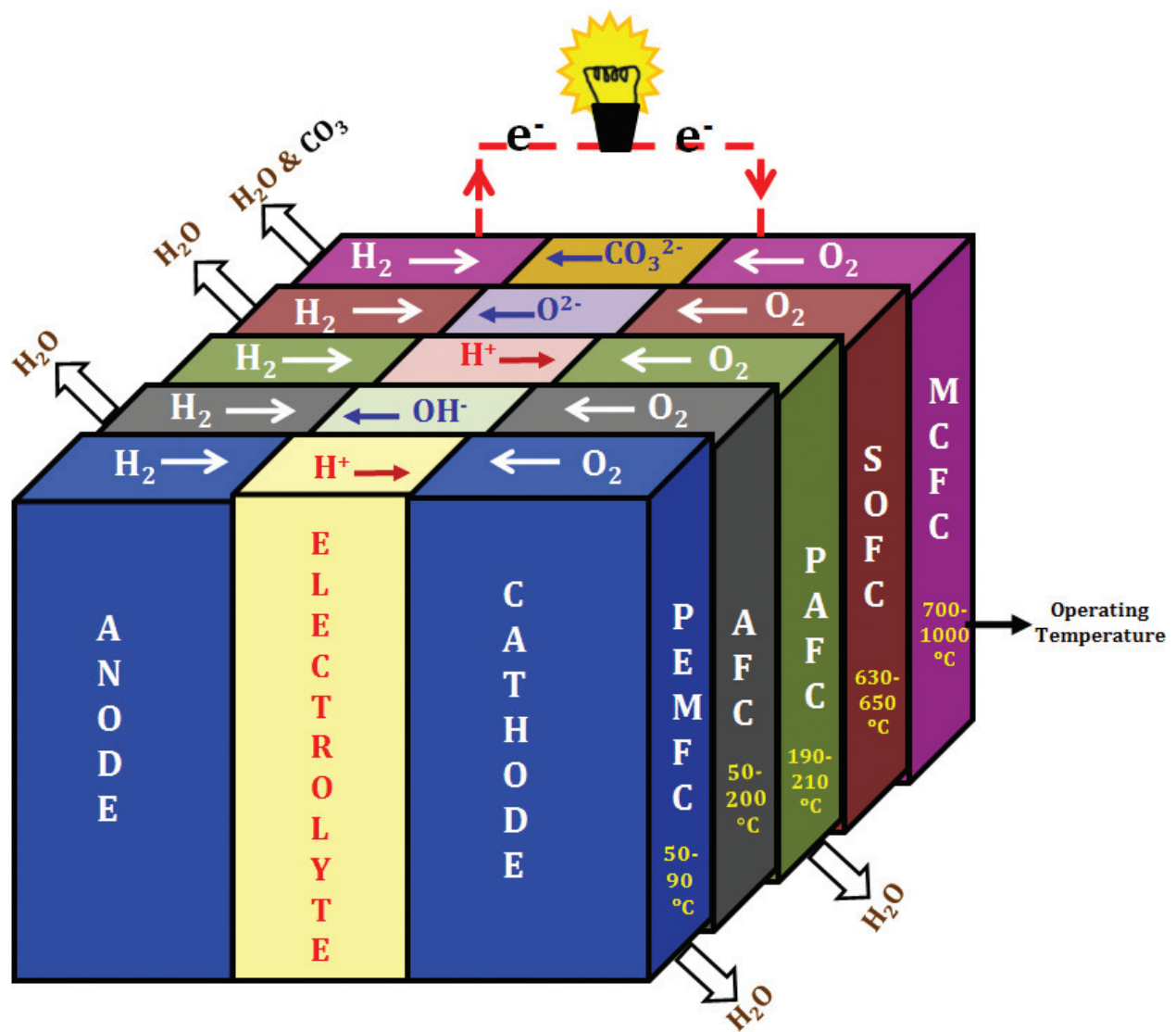


Generally, pure hydrogen, methanol, ethanol, etc., can be taken as a fuel that can be oxidized at the anode, while the oxygen or air is taken as the oxidant and get reduced at the cathode. Here, the oxygen reduction reaction (ORR) has sluggish reaction kinetics due to a complex multistep reaction mechanism, which can be catalyzed by electrocatalysts. Electrocatalysts are mostly the metal nanoparticles embedded or decorated over the supporting materials, which provide uniform dispersion to the metal nanoparticles, stability by physical intact, higher surface area, and good electron/proton conductivity that helps to construct three phase boundary. This chapter deals about the role and importance of advanced supporting materials such as various kind of carbon materials, noncarbonaceous supports like inorganic materials, and conductive polymeric supports for cathodic oxygen reduction in polymer electrolyte membrane fuel cells (PEMFCs).

## 2. Types of fuel cells

Fuel cells are classified in many ways as direct and indirect fuel cells based on operating temperature, the state of matter of the elements of the fuel cell, and the type of electrolyte used. As shown in **Figure 1**, the fuel cells are classified based on their operating temperature such as low-temperature fuel cells and high-temperature fuel cells. Proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), and alkaline fuel cell (AFC) are placed under the category of low-temperature fuel cells.

Solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), and phosphoric acid fuel cell (PAFC) are placed under the category of high-temperature fuel cells. Among this classification, PEMFCs are more attractive and reliable than other fuel cells due to the wide range of application,



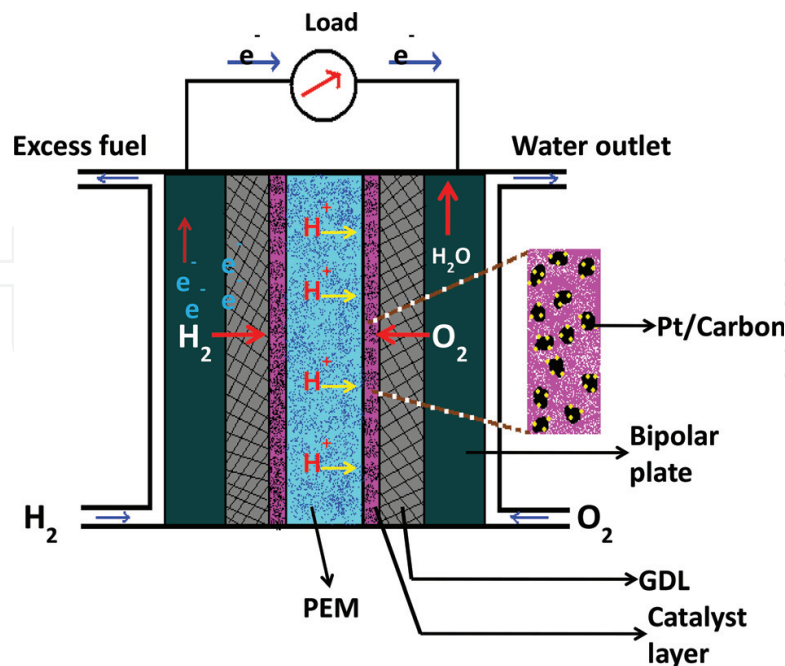
**Figure 1.** Schematic representation of various types of fuel cells with anodic and cathodic feeds and the corresponding electrolyte charge carriers and byproducts.

high efficiency, and near zero emission of pollutants, and it could be a basic system for DMFC and AFC. The alkaline or acidic solutions are used as electrolytes in fuel cells called *mobile electrolyte system*. If the electrolyte is soaked up in a porous material such as asbestos, it is called as an *immobile electrolyte system or matrix system* [5–8].

### 3. Proton exchange membrane fuel cell (PEMFC)

The proton exchange membrane fuel cell also known as the polymer electrolyte membrane fuel cell works at typically less than  $100^{\circ}\text{C}$  with special polymer electrolyte membranes. This lower temperature fuel cell is the preferred choice for transportation vehicles, portable applications like hand held devices because of its quick start-up, low operating temperature, and excellent energy efficiency. The electrolyte in this fuel cell is an ion exchange membrane—perfluorinated sulfonic acid polymer—commercially sold as Nafion, a good proton-conducting ionomer [5, 9]. The only byproduct in this fuel cell is water, and the water management in the PEMFC is critical for efficient performance. The fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced, because the membrane should be kept under hydrated conditions.

**Figure 2** shows the schematic representation of cross sectional view of PEMFC. The low operation temperature of PEMFC requires active electrocatalysts such as Pt. The hydrogen oxidation reaction (HOR) is relatively facile and requires low Pt loading of ca.  $0.05\text{ mg/cm}^2$  [10]. However, the oxygen reduction is sluggish, and the rate of ORR is most critical at the



**Figure 2.** Cross-sectional view of polymer electrolyte membrane fuel cell.

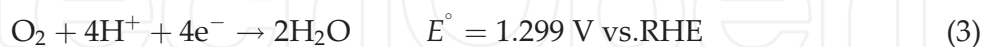
cathode and requires more active element like platinum (Pt). Typically, the carbon-supported Pt nanoparticles (Pt/C) having ~2–3 nm size and high Pt surface area (~100 m<sup>2</sup>/g) is ideal to enhance the reaction rate. Although the use of Pt/C is preferred compared to other catalysts due to the acid resistant property of Pt, corrosion of carbon support and the loss of expensive electrocatalyst push the research community to find the other alternative solutions in terms of advanced supporting materials to increase the activity by higher surface area and life time of Pt, Pt-M alloy, and non-n Pt catalysts without compromising the fuel cell efficiency [11].

Among the fuel cells, PEMFCs have got huge attention due to

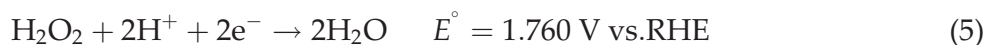
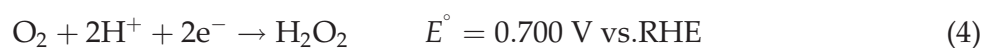
- a. high energy conversion efficiency,
- b. low operating temperature (around 100°C),
- c. quick startup,
- d. almost zero emission of pollutants with water as the only byproduct, and
- e. can be used for automobile applications because of its portability and easy to operation.

Although PEMFC has many advantages as stated above, the wide spread usage and commercialization are not realized due to the *kinetically sluggish cathodic reduction of oxygen*. The two major electrochemical reactions occur in PEMFC, whereas hydrogen oxidation at anode is intrinsically faster than cathodic oxygen reduction on catalyst surface, because the O—O bond dissociation energy (494 kJ/mol) in O<sub>2</sub> molecule is higher than H—H (433 kJ/mol) [12, 13]. The ORR is a complex multistep reaction involving many electron transfer process with the formation of different intermediates depending on the pH of the electrolyte. In PEMFC, the ORR mechanism can proceed by two different reaction pathways. They are: (i) direct four electron transfer leading to water formation as the only byproduct and (ii) two electron transfer mechanism leading to the formation of H<sub>2</sub>O<sub>2</sub> intermediate which again undergoes reduction in a series of electron transfer steps to form water. The reduction of the molecular oxygen in aqueous acid electrolyte solutions in PEMFC (particularly in sulfuric or perchloric acid medium) is assumed to proceed through either of the two major pathways as shown below [11, 14].

(i) The direct 4-electron transfer reduction reaction to H<sub>2</sub>O.



(ii) The parallel 2-electron transfer reduction reaction to form H<sub>2</sub>O<sub>2</sub>.



where  $E^\circ$  is the thermodynamic standard electrode potential at 298.25 K and 1 atm. In 2-electron transfer pathway, two possible products are formed either the reaction stops with the production of H<sub>2</sub>O<sub>2</sub> as an intermediate or it is further reduced by another 2-electron transfer to produce

H<sub>2</sub>O as the final product. The extent of reduction reaction appears to depend on the chosen catalyst material; thus, it confirms the role of the electrocatalyst on overall efficiency of fuel cell, which includes the choice of catalyst and its supporting material. The 4-electron route is the most favored reaction pathway, since it produces a high voltage for a H<sub>2</sub>-O<sub>2</sub> PEM fuel cell. For better performance and efficiency, fuel cell requires the sufficient *three phase boundary* (fuel cell reactions occurs in electrode-electrolyte interface) in membrane electrode assembly, which consists of reactant gas molecule, electron conduction over solid catalyst surface (either metal or nonmetal nanomaterials with supports), and proton conduction through polymer electrolyte (conducting polymeric materials) [15, 16]. It seems that the catalyst, catalyst supports, and the conducting polymers are playing a key role in acceleration of kinetics of fuel cell reaction, peculiarly for cathodic dioxygen reduction.

#### 4. Catalyst supports

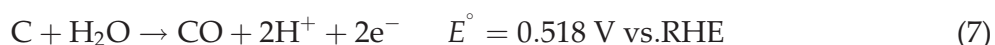
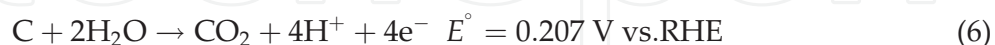
Catalysts are supported on high surface area materials which are playing a major role to increase electrochemically active surface area of electrocatalysts by providing uniform dispersion and accessibility of active sites for fuel cell reactions. The electrocatalyst with active surface area must be intact directly with electronic and ionic conducting materials, and hence, it is named as *three phase boundary* [16]. The major role of supporting materials is (i) to act as electron source with improved conductivity; (ii) to hold the metal nanoparticles (physical interaction); (iii) to possess higher surface area; (iv) to provide better stability; (v) to provide porosity; and (vi) to have higher corrosion resistance under fuel cell operating conditions [17, 18]. Many forms of carbonaceous materials are available, which vary based on its structure, conductivity, thermal stability, surface area, etc., which include the preparation procedure with different physiochemical approaches [19]. Even though, some certain number of carbon materials have got huge attention for various applications in wide range of fields such as sensor, medicine, and especially for energy materials.

#### 5. Carbon supports

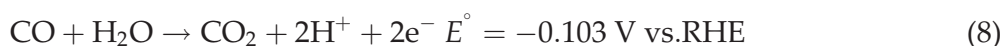
Carbon materials are widely employed catalyst support for energy applications, and its multidimensional structure provides high electrical conductivity and surface area with greater chemical and electrochemical stability. Carbon supports are the major choice of catalyst support for fuel cell reactions in both anode and cathode electrocatalysts to conduct electrons and heat in [20, 21]. A common choice of carbon support material is Vulcan Carbon XC-72 (VC, BET specific surface area 254 m<sup>2</sup>/g), due to low cost, high-specific surface area, adhesion properties with catalyst particles and distribution, better interaction with the polymer, and high conductivity [21–23]. It has noticeable disadvantages such as carbon corrosion owing to its surface oxidation to produce CO<sub>2</sub> during fuel cell operation and results in dissolution of Pt nanoparticles from the carbon support leading to low Pt utilization and less performance [24].

Carbon corrosion is one of the key factors inducing cathode electrocatalyst (Pt/C) degradation in PEM fuel cells. It is electrochemical oxidation and thus needs to be investigated *in situ* with potential imposed because the ORR occurs at potentials closer to those where oxidation of carbon can also happen [25]. Carbon is not thermodynamically stable at higher potentials in the fuel cell environment, which is problematic for long-time durability of the electrocatalysts. Carbon corrosion depends on the operating temperature, high potentials (above 0.5 V vs. RHE), low pH, and high humidity. During oxidation, the major product formed is CO<sub>2</sub> with trace amounts of CO [24–26].

Typically, the electrochemical oxidation reaction of carbon takes place as follows [23–25],



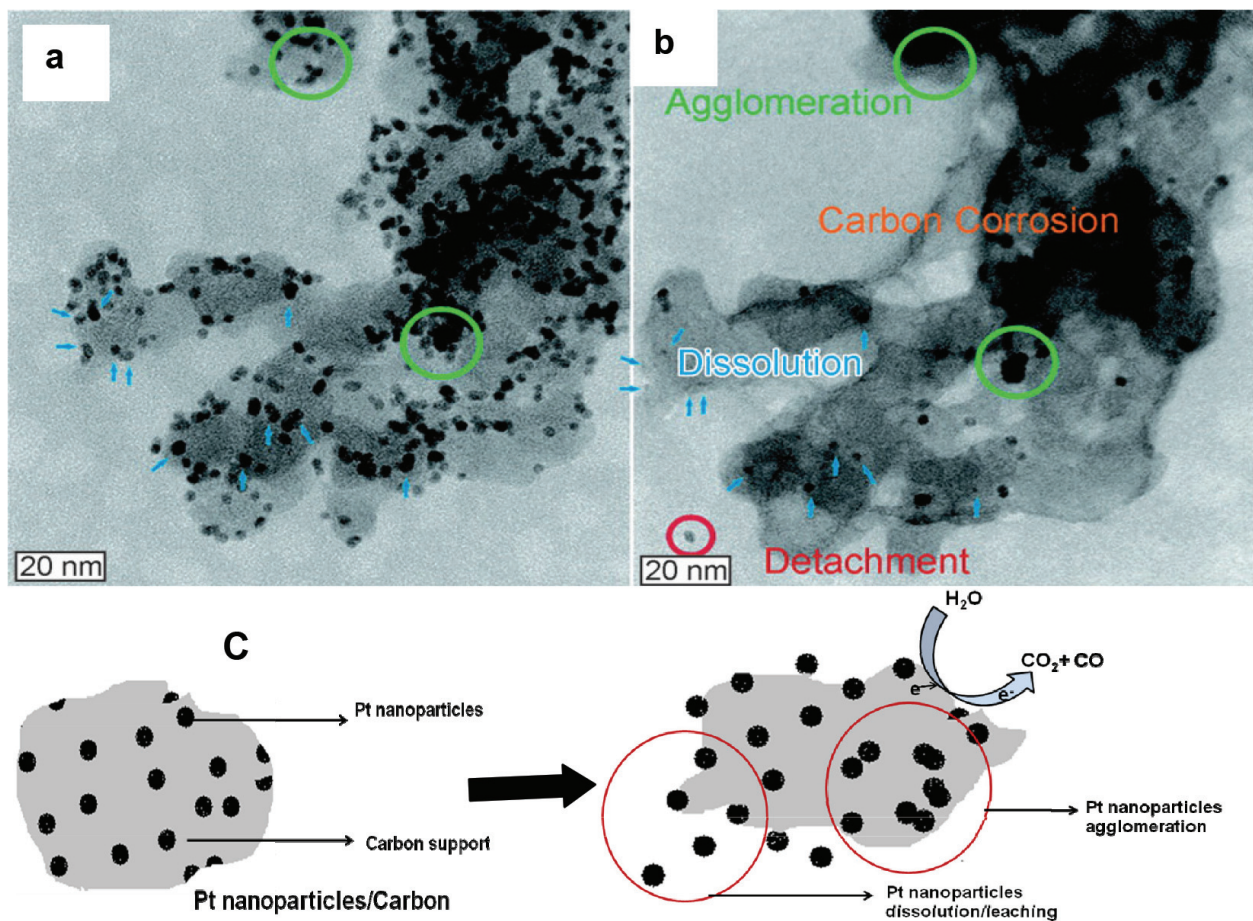
Carbon monoxide (CO) is thermodynamically unstable and therefore slowly converted to CO<sub>2</sub>.



Pt is also found to catalyze the carbon oxidation [23]. Under fuel cell operating conditions, the corrosion rate is significant, leading to large voltage degradation, and further, the CO formed deactivates the Pt catalysts. Several reports reveal that the corrosion of carbon support reduces the integrity of the catalyst layer and enhances Pt dissolution [25–28]. **Figure 3** shows the TEM images (**Figure 3a** and **b**) of Pt/C captured before and after the durability test, and **Figure 3c** depicts the same as a schematic representation [29]. Wang et al. have reported the effect of carbon support corrosion on the stability of Pt/C using two different carbon support materials such as Vulcan carbon XC-72 (VC) and Black Pearls 2000 (BP-2000). They have concluded that the decrease in ECSA of Pt embedded carbon support materials reveals the loss of Pt nanoparticles during the accelerated durability test due to surface oxidation of carbon supports.

Among these conventional carbon supports, carbon nanotubes and graphene derivatives have got huge attention and employed as major catalyst supports for fuel cell applications due to its excellent physiochemical properties. Carbon nanotubes (CNTs) are the family of carbon allotropes consist of *sp*<sup>2</sup> hybridized carbons bonded in a hexagonal lattice arrangement [30]. They are described as cylindrical hollow natured materials formed by the rolling of single or multi layers of graphene sheets called single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), respectively. SWCNTs and MWCNTs are typically 0.8–2 nm and 5–20 nm of diameters, respectively, while MWCNT can exceed 100 nm of diameters. The lengths of CNTs range from less than 100 nm to several centimeters and are considered to be one dimensional (1D) structure [31, 32]. CNTs are possessing good electronic conductivity, thermal conductivity, and mechanical stability than conventional carbon supports. In recent days, surface functionalized CNTs [32–35], N, S, B, and halogens-doped CNTs [36, 37] and hybrid CNTs [37, 38] were prepared and employed as catalyst support for ORR in PEMFC.





**Figure 3.** Carbon support corrosion during potential cycling on Pt/C lead catalyst dissolution and agglomeration observed from same location TEM images (a and b) [34]; (c) schematic representation.

An exceptionally outstanding performance was derived from the new carbon supporting material for ORR namely graphene, an iconic carbon form in the history of material sciences. It is a single-layer  $sp^2$  bonded carbon with 2-dimensional (2D) honeycomb structure. It exhibits high crystalline nature, and electronic conductivity explores a new looks to the carbon chemistry especially for energy applications [37–39]. Generally, the physiochemical properties of the graphene materials are related to its synthesis approach and surface treatment. It is a building block of all graphitic materials when it wrapped into 0-dimensional fullerene, 1-dimensional carbon nanotubes, and 3-dimensional graphite. The physical properties of graphene can be defined through preparation method. Especially, the porosity of graphene may be either mesoporous or microporous, and hence, it is one of the critical properties which contribute to accelerate the kinetics of electrochemical reactions in PEMFC. Usually, the carbon supports are the prime choice as catalyst support for cathodic ORR in PEMFC providing high surface area and conductivity, whereas the surface oxidation of carbon supports suppresses the performance of catalyst through surface masking, leading to poor ORR kinetics. The physical properties such as porosity, specific surface area, and conductivity of various carbon supports are summarized in **Table 1**.

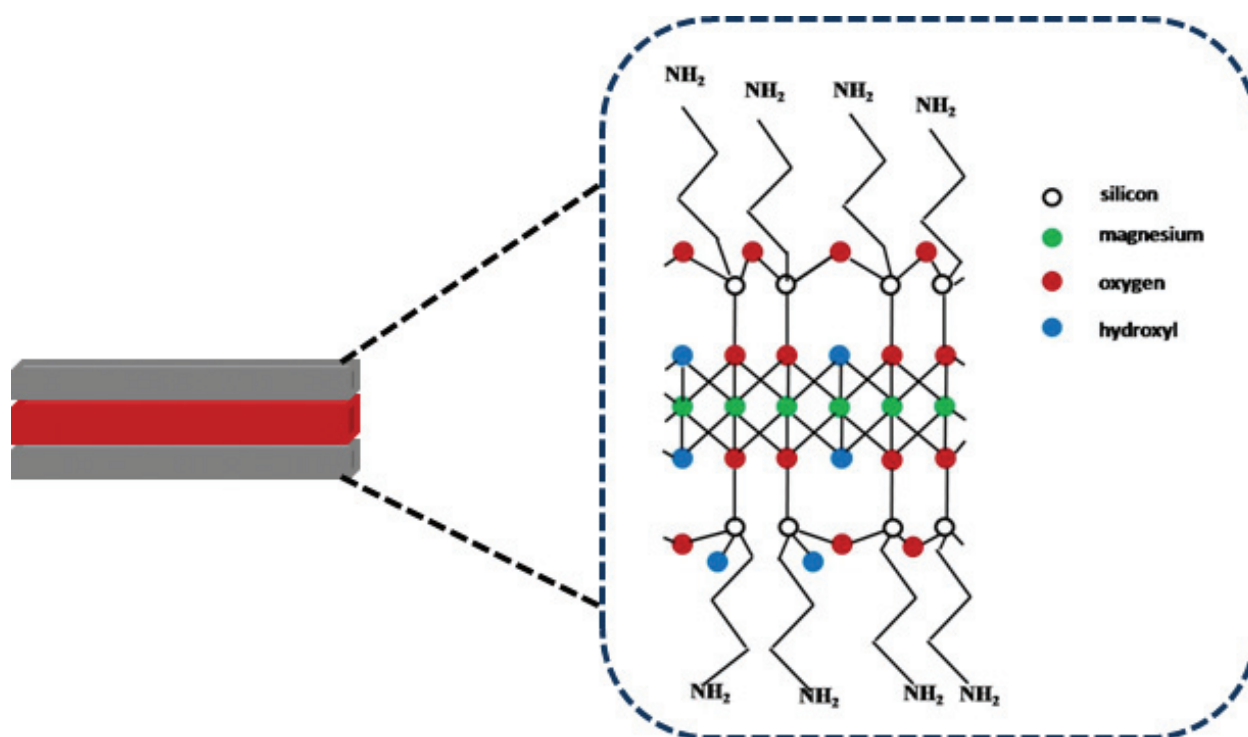
Name of the material	Nature of porosity	Specific surface area (m <sup>2</sup> /g)	Electrical conductivity (S/cm)	Ref. no.
Vulcan carbon	Micro porous	254	4.0	[20]
Carbon black	Micro porous	475	1.4	[20]
Carbon nanotube				
Single-walled carbon nanotube	Micro porous	400–900	10 <sup>2</sup> –10 <sup>6</sup>	[34]
Multi-walled carbon nanotube	Mesoporous	200–400	10 <sup>3</sup> –10 <sup>5</sup>	[34]
Graphite	Meso-/microporous	10–20	2–3 × 10 <sup>4</sup>	[35]
Graphene		1500	~2000	[35]

**Table 1.** Various carbon materials and their physical properties.

## 6. Carbon-free catalyst supports

In general, carbon-free supports are mostly inorganic metal oxides, and other mineral oxides possess better corrosion resistance, improved interaction with metal nanoparticles, and stable morphology. However, these materials are poor in electrical conductivity, and low porosity leads to less specific surface area than highly porous supporting materials. The major inorganic additives are metal oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, etc., [40, 41]), some of the carbides (WC, VC, etc., [42, 43]), and layered silicate materials such as clay minerals [44, 45], which are increasingly used as catalyst supports for PEM fuel cells. Clay minerals belong to a subtype of phyllosilicates with characteristic layered structures. Two basic layered structural units are important in the formation of the clay-structured materials: the tetrahedral structure formed by silicon and oxygen atoms and the octahedral structure formed by aluminum/magnesium and oxygen atoms. The tetrahedral units are linked through their corners, forming a tetrahedral sheet, whereas the octahedral units are edge-linked, resulting in an octahedral sheet. The structural framework of the clay platelets is basically composed of these two kinds of sheets joined together to form layers.

Layered silicates are clay minerals built of two structural units. The simplest form of clay minerals is the 1:1 structure (e.g. *kaolinite*) where a silica tetrahedral sheet is fused to an aluminum octahedron, sharing the oxygen atoms. However, commonly employed layered silicates for the preparation of polymer nanocomposites, such as montmorillonite (MMT), belong to the family of 2:1 phyllosilicates, more specifically *smectites* [46]. Their crystal structure consists of stacked layers made of two silica tetrahedrons fused to an edge-shared octahedral sheet of alumina. The layer thickness is approximately 1 nm, and the adjacent layers are separated by a regular van der Waals gap called the interlayer or gallery. Clay layers carry negative charges due to the replacement of some Si<sup>4+</sup> ions in the tetrahedral sheets or some Al<sup>3+</sup> or Mg<sup>2+</sup> ions in the octahedral sheets. To compensate the negative charges created, cations (Na<sup>+</sup> or Ca<sup>2+</sup>) are usually present in the interlayer domain. When clays are dispersed in aqueous solution, these charge-compensating cations can be exchanged and replaced by others present in the bulk solution. Although smectite types of clays have substantial importance in



**Figure 4.** Schematic representation of amino propyl functionalized Mg-phyllsilicate clay.

multidisciplinary applications, they require surface modification by covalent functionalization to improve the dispersing ability in aqueous or organic media [46–48].

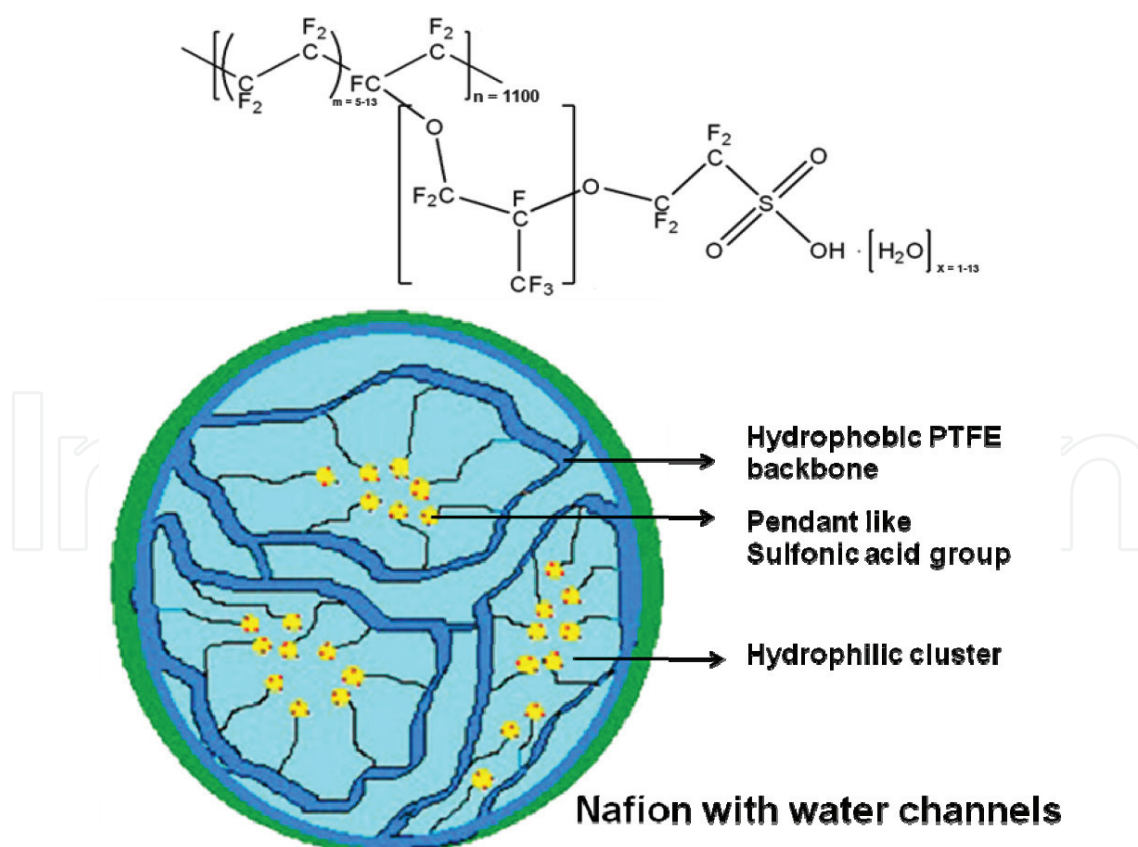
Like naturally occurring clay minerals, synthetic clay also employed as catalyst support for cathodic oxygen reduction in PEM fuel cells. Amino propyl functionalized Mg-phyllsilicate clay employed as catalyst support for ORR in PEMFC [49, 50]. The amino groups of synthetic clay hold metal nanoparticles by physical interaction and increase the stability of the catalyst than conventional carbon supports. In **Figure 4**, the layered structure of aminoclay is schematically presented. The structure of aminoclay contains 2:1 Mg-phyllsilicate layer with surface functionalized arm-like amino propyl groups. Hence, the amino groups can hold the metal nanoparticles and provides uniform distribution for the preparation of polymer nanocomposite membranes.

## 7. Polymer nanocomposites

The proton conducting membranes are inserted between the anodic and cathodic compartments to prevent mixing of reactants and to conduct protons formed due to the oxidation of hydrogen at the anodic compartment to cathodic side. The polymer electrolyte membrane should possess high proton conductivity, low fuel permeability, good thermal stability, and better film forming ability, and more importantly, it should be of low cost and should have high durability. Under fuel cell-operating conditions, it should have sufficient water uptake and moderate swelling, excellent electrochemical stability in an aggressive environment like

low or high pH solutions, and good mechanical strength, i.e., significant stability in structure and morphology [15]. Nafion is a perfluorinated ionomer containing hydrophobic polytetrafluoroethylene (PTFE) backbone with pendant-like side chains of perfluorinated vinyl ethers terminated by perfluorosulfonic acid groups as shown in **Figure 5**.

Nafion has many key properties such as thermal, mechanical, and chemical stability and, most importantly, high water-saturated proton conductivities during long-term fuel cell operation. Teflon-like PTFE backbone provides the long-term durability during the oxidative and reductive fuel-cell operating conditions [9]. But the drawbacks of Nafion membrane include low conductivity under low humidification, poor performance at elevated temperatures (above 90°C), and high cost. Therefore, in order to improve the properties of Nafion under fuel cell working conditions, some nanoscale additives are usually added to obtain Nafion nanocomposites [17, 51, 52]. Therefore, an extensive research has been attempted by many researchers to synthesize novel polymer nanocomposite materials by blending with suitable polymers and organic/inorganic additives with improved physicochemical properties. Many conducting polymers were used such as poly(aniline), poly(ethylene oxide), poly(styrene), poly(vinyl alcohol), poly(propylene), poly(vinylpyrrolidone), and poly(3,4-ethylenedioxythiophene), etc., along with Nafion to form polymer blends. In polymer nanocomposites, inorganic additives such as quaternary ammonium salts, SiO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>2</sub>, etc. [40, 41, 52, 53] and layered silicate minerals such as clay minerals [50] are used as fillers



**Figure 5.** Chemical structure and pictorial representation of Nafion ionomer with hydrophilic clusters and hydrophobic backbone units.

and used as catalyst supports for energy applications. Aminoclay/Nafion nanocomposite membranes were prepared through sol-gel approach with embedded Pt nanoparticles by simple chemical reduction method. The electrocatalytic performance and durability of Pt nanoparticles-embedded Aminoclay/Nafion toward ORR were studied for PEMFC [49, 50].

In electrochemical processes, the electron transfer between solid-liquid interfaces is the elementary step, and the interfacial properties such as conductivity, surface area, etc. have significant influence on electron transfer [54]. In contact with electrolytic solution, electrodes (catalyst materials) can act as a source or a sink for electrons to change the electroactive species according to classical voltammetry. The nature of the electrode surface can alter the efficiency of the electron-transfer process and mass-transport regime. Therefore, it is extremely important to obtain the desired electrochemical properties at the interface between the electrode and the electrolytic solution by modifying the electrode surface. In conventional electrochemical cells, bulk Pt was employed as electrocatalyst to catalyze the fuel cell reactions and thus have disadvantage of low surface area and poor utilization [54–56]. Later on, the nanosized electrocatalysts got more attention especially in energy applications due to their unique physical and chemical properties. Nanomaterials show size, shape, and composition-dependent properties, and a single material can show a wide range of properties and applications depending on the size [57–59]. As the dimensions of a particle decrease, the surface-area/volume ratio drastically increases. When this ratio is large, the low-coordinate atoms on the particle surface predominate and dominate the particle properties called as *surface effects*. Surface effects make the properties of nanoparticles different from those of the corresponding bulk materials [56, 60–62]. Thus, the surface activity can be further enhanced by the proper choice of supporting materials, which meet the requirements to provide *three phase boundary* for electrochemical reactions in fuel cells.

## 8. Conclusion

In conclusion, catalyst-supporting materials are playing a crucial role for improving the overall efficiency by enhancing the activity and stability for PEMFCs. The major requirements of promising supporting materials for fuel cell catalysis are high surface area, good electrical conductivity, porosity, and better stability under fuel cell operating conditions. Carbon supports are widely used supporting materials for ORR in PEMFC. Due to the surface oxidation, conventional carbon supports diminish the activity of catalysts under fuel cell operating conditions. In order to overcome these issues without compromising the performance of catalysts, novel carbon materials such as CNT, graphene and its derivatives, noncarbon supports, and conducting polymers are used as catalyst supports for ORR. Hence, the overall efficiency and performance of the fuel cell are laid on nature of the catalysts and their supporting materials, which can provide sufficient *triple phase boundary*, where the reactant gas molecule undergoes electrochemical reaction over the catalyst surface. The result of this study describes the development of novel nanostructured catalysts with hybrid supporting materials is still en route to attain better fuel cell performance and efficiency, which make the technology as commercially viable.

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