Review

Catalysts for Oxygen Reduction Reaction in the Polymer Electrolyte Membrane Fuel Cells: A Brief Review

Martin Tomas ^{1,*} , Fatemeh Gholami ¹ , Zahra Gholami ² and Jan Sedlacek ¹

¹ New Technologies-Research Centre, University of West Bohemia, Veleslavinova 42, 301 00 Plzen, Czech Republic; gholami@ntc.zcu.cz (F.G.); sedlacek@ntc.zcu.cz (J.S.)

² Unipetrol Centre of Research and Education, a.s., Areal Chempark 2838, Záluží 1, 436 70 Litvinov, Czech Republic; Zahra.Gholami@unicre.cz

* Correspondence: mtomas@ntc.zcu.cz

Abstract: This mini-review presents a short account of materials with exceptional activity towards oxygen reduction reaction. Two main classes of catalytic materials are described, namely platinum group metal (PGM) catalyst and Non-precious metal catalyst. The classes are discussed in terms of possible application in low-temperature hydrogen fuel cells with proton exchange membrane and further commercialization of these devices. A short description of perspective approaches is provided and challenging issues associated with developed catalytic materials are discussed.

Keywords: PEMFC; catalyst; ORR; platinum

Citation: Tomas, M.; Gholami, F.; Gholami, Z.; Sedlacek, J. The Catalysts for Oxygen Reduction Reaction in the Polymer Electrolyte Membrane Fuel Cells: A Brief Review. *Electrochem* **2021**, *2*, 590–603. <https://doi.org/10.3390/electrochem2040037>

Academic Editor: Masato Sone

Received: 29 September 2021

Accepted: 19 October 2021

Published: 22 October 2021

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1. Introduction

Fossil fuel generation is gradually replaced with renewable energy generation to decrease the CO₂ emission of the power system. Electrical energy storage (EES) is one of the required new technologies for the energy generation industry [1–3]. The efficiency and operation cost of the EES system is determining by their performance. The critical goal of using EES is reducing the negative impact on the environment, capital and operating cost and ensuring durability. The type of the storage device depends on the energy being stored. Electrical storage systems can be classified into mechanical, electrochemical, chemical and thermal storage systems [4].

Chemical energy storage systems is classified into hydrogen and biofuels. The hydrogen storage systems include different categories: hydrogen pressurization and absorption of metal hydrides, adsorption of hydrogen on carbon nanofibers and liquefaction of hydrogen. Low pressure, compatibility and high absorption rate are the advantages of this storage system [5].

Another way of producing hydrogen is electrolysis of water and use with a fuel cell. The stored hydrogen gas can be used in a fuel cell where oxygen and air are oxidants. Fuel cells are energy converting devices that produce electrical energy directly from the chemical energy in the fuel. Water and thermal management of fuel cells are critical, as they control the cell's overall performance. The required reactant for electricity generation is externally supplied. Fuel cells are environmentally friendly and usually produce electricity without noise due to the absence of moving parts. Fuel cells are ideal for energy management and power quality, making them suitable in the automotive industry. The various types of fuel cells are based on the type of electrolyte, cell operating temperature and the fuel used in its operation, e.g., phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEMFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) [4,6].

The fuel cells provide a clean, efficient and probably the most flexible conversion of chemical energy to electricity [7–10]. Proton exchange membrane fuel cells (PEMFCs) are generally considered to be one of the most promising types of renewable energy sources

which allow an emission-free conversion of chemical energy into electrical power [11,12]. In the last two decades, a tremendous effort has been made in order to radically decrease the amount of platinum group metals (PGM) loading on the cathode side of the PEMFCs [13]. A sluggish kinetics of oxygen reduction reaction (ORR) at the cathode side—difficult O₂ activation, O-O bond cleavage and oxide removal—is limiting the further development of PEMFCs and other types of fuel cells such as direct methanol fuel cells (DMFCs) [14]. This well-known issue was addressed by many groups of researchers, thus the developed catalysts advance the path towards the process of fuel cell commercialization. So far, the fuel cells are successfully used as energy sources for backup power supply, material handling (forklifts) and portable applications. However, the breakthrough in automotive industry is yet to come.

The ORR proceeds in two ways. One of them is direct four-electron transfer which results in the formation of the water molecule, see Figure 1. This pathway is favourable, however, the series of two-electron transfers can occur and leads to formation of hydrogen peroxide [15]. Some other intermediates are produced too, namely O•, OH• and OOH•, which cause the membrane degradation [16]. The reaction pathway depends on the oxygen coverage of the catalyst; high coverage induces higher hydrogen peroxide production [14]. Then, the formed H₂O₂ causes the carbon support corrosion or bipolar plates degradation. In the case of non-fluorinated membranes, the H₂O₂ causes membrane thinning and creates pinholes or cracks. The direct four-electron transfer in acidic electrolyte can be expressed as [17]

and the indirect two-electron transfers proceeds as follows

The kinetics of ORR is approximately 5 orders of magnitude slower compared to hydrogen oxidation reaction (HOR) occurring at the anode.

On the other hand, the loading of platinum-based or PGM catalysts in the fuel cell decreased significantly [18]. Nowadays, the units with a total amount of PGM of around 10 g are produced [19]. So that, the amount of precious metals is comparable to the amount of these metals used in vehicles with internal combustion engines (ICE), where the PGM is needed for catalytic reduction of flue gas (exhaust gas converter for cleaning duty). Obviously, the cost of a fuel cell unit in the car is mostly related to other components namely bipolar plates. As commercialization through mass production proceeds, the cost of fuel cell components is ought to decrease with exception of platinum catalysts.

On account of the low earth abundance of platinum and related cost volatility, the research of catalysts for the hydrogen fuel cells is focused on the platinum replacement and the decrease of loading. Many types of catalysts have been proposed as promising candidates for commercial fuel cell units. The main problem of these materials is the difference between in-situ and ex-situ properties. Many of these materials demonstrated extraordinary mass activities, but after the fabrication of membrane electrode assembly (MEA), lower than expected performance was observed. Moreover, a remarkable Beginning of Life (BoL) performance quickly decreased and the stability/durability problem seems to be crucial for many of these catalysts [14]. So far, the research activities in catalyst development may be divided to two broad groups: Platinum group metal catalysts (PGM) and Non-precious metal catalysts.

Figure 1. Illustration of a hydrogen fuel cell depicting main components, namely: (a) A bipolar plate with ribs feeding the fuel cell with the reactants. (b) A gas diffusion layer (GDL) providing homogeneous distribution of the reactants. (c) An anodic catalytic layer. The central part of the fuel cell is a membrane with proton conducting channels. The polymer electrolyte used in fuel cells acts as a semi-permeable membrane allowing protons to pass through to the cathodic side. But the electrical conductivity of the membrane is low, so the electrons liberated at the anodic side generate work in the external circuit. The cathodic side of the fuel cell is symmetrically arranged, so the cathodic bipolar plate, GDL and catalytic layer are depicted in the same manner. The ORR takes place in cathodic catalytic layer. The symbol R_z denotes an electrical load.

2. Platinum Group Metal Catalyst (PGM)

Limiting factor of PGM catalyst is interaction of the metal alloys and supporting material. The performance loss caused by fading of catalyst nanoparticles can be observed after a few hundred hours of fuel cell operation. To overcome this problem, the promising catalyst surface modifications, e.g., highly ordered core-shell structure, in-situ carbonized carbon and organic functional groups, have been proposed. The synergic effects between platinum and other metals provides improved catalytic activity and CO tolerance. The effect is based on higher CO desorption rate and specific open structure with more active sites exposed to fuel [20]. The structures involve nanowires, nanoplates, nanoframes and other 3D structures, e.g., concave polyhedrons prepared by capping agents and selective corrosion [21]. The synthesis methods include colloidal deposition, co-reduction, galvanic replacement reaction, seeded growth and pyrolysis.

2.1. Platinum and Pt-Based Catalysts

Generally, the platinum in a form of nanoparticles dispersed at the surface of the carbon support, e.g., carbon black, carbon nanotubes or graphene, is the most widely used material for hydrogen fuel cell catalyst [22,23]. The carbon support possesses excellent electrical conductivity, high surface area, satisfactory porosity and low cost. The stability in acidic electrolytes and high mass activity make the platinum suitable for cathodic and anodic catalytic layer of the membrane electrode assembly (MEA). However, the carbon support can suffer from electrochemical oxidation and the platinum particle agglomeration was observed, which leads to the loss of superior activity. Moreover, a homogenous dispersion of platinum nanoparticles (and other delicate catalyst nanostructures) is distorted

by Ostwald ripening and that results in further loss of active surface [20]. At higher performances of a fuel cell, the generated water can wash out the catalytic material causing the migration of particles out of the desired location. These types of the degradation are inevitable in fuel cell cars, where the high current density needs to be produced. Furthermore, the high purity hydrogen is needed for optimal operation of the fuel cell. A contamination of reactants by carbon oxides, nitrogen oxides, sulfur oxides, ammonia or hydrogen sulfide steeply decreases the performance of a fuel cell. The platinum particles can be blocked by carbon monoxide or poisoned by adsorption of sulfur-based moieties and no longer contribute to electrochemical reactions. Lower concentrations of contaminants cause reversible performance decrease, but the high concentration of carbon monoxide leads to irreversible diminution of catalytic performance.

The mass activity of the Pt catalyst can be enhanced by two main factors—the particle size and the particle shape. A maximum dispersion of platinum is obtained if the single atom acts as an active site. This single-atom catalyst was successfully prepared by several groups, but the issues related to stability and deactivation remain [17,24]. The shape of the many-atoms particles seems to be crucial too. The investigation of the particle shape was focused mainly on the facets with low Miller indices, i.e., Pt(100), Pt(110), Pt(111), but some other forms of platinum were prepared as well [25]. However, the particles with higher Miller indices are difficult to prepare in some reasonable amount [14].

Alloying Pt with transition metals (M) has attracted attention recently as promising materials to reduce the use of Pt. Studies have shown that combining Pt with transition metals affects the position of the d-band center of Pt, d-bandwidth and influences the interaction between the electrocatalyst surface and adsorbed intermediates results in optimized electrocatalytic activity. However, the catalytic activity by alloying Pt with transition metals is remarkable, but the leaching of transition metals under strong-acid and high-potential operating conditions of PEMFCs would considerably reduce the ORR performance. In addition, the dissolved transition metals, such as Fe and Co, in the electrolyte would contribute to the Fenton reactions and degrade the ionomers of the PEMFC. Based on the crystal structure, the alloys of Pt–M can be categorized into disordered phase (solid solution) and ordered phase (intermetallic compound). The disordered phases have varying surface compositions and randomly distributed active sites because the atomic positions are occupied randomly by Pt and M. Ordered phase or intermetallic compounds have a uniform distribution of active sites on the surface plane due to their well-defined stoichiometry and better control of local geometry of metal atoms [26,27].

The bimetallic alloys of platinum can decrease the amount of scarce platinum and enhance the stability of the catalyst [28,29]. The alloys of Pt with metals such as Ni, Fe, Co, Pd, Ru, W and Ti were prepared and their properties were examined [30,31]. Some of the alloys have been used in fuel cell cars, e.g., PtCo in Toyota Mirai [32]. So far, the promising results were achieved when Pt is alloyed with iron or nickel [33–36]. In the fuel cell, iron acts as a Fenton reagent, so the presence of this element should be restricted to catalytic layer. Otherwise, the serious damage of the membrane and other components is caused by harmful by-products (hydrogen peroxide) of undesired reactions. In addition, the transition metals alloyed with platinum are prone to leach or dissolve in relatively harsh environment of a fuel cell [37]. On the other hand, Pt–Ru and Pt–Cr alloys are more immune to the CO poisoning [38,39]. The alloys of platinum and gold were also investigated and the samples exhibited higher mass activity and stability compared to pure platinum [20].

2.2. Core-Shell Catalysts

A sophisticated step towards the better utilization of platinum has been achieved by deposition of this expensive metal on a cheaper core (core-shell nanoparticles), see Ref. [40] and references therein. The high surface area of active catalyst can be realized by layering the platinum on the core made of metals such as palladium, yttrium, scandium, chromium or titanium (Figure 2) [41]. Single metals as well as binary or ternary alloys can be employed as core materials. The metallic core also influences the electronic structure of the Pt atom

and improves the electrocatalytic performance of the material. The core-shell nanoparticles are known for their capacity to weaken the Pt–O bond, so that, the electrocatalytic activity of these materials may be extraordinary. Additionally, the durability of the catalysts can be further increased by incorporating non-metals or polymers in the core [42,43]. The attention of the research groups is not limited to the conventional spherical shape of nanoparticles, other structures such as nanorods, nanowires, dendrites, star-like or tree shapes have been investigated too [44].

Figure 2. An illustrative depiction of the carbon support with the core-shell nanoparticles (Pt@Pd). The cross-section of the nanoparticle is showed indicating layered platinum (red) on the palladium shell (blue).

The activity of core-shell nanoparticles and the elegance of the catalyst structure have attracted many research groups [45–49]. It has been reported, that a monolayer of Pt atoms can be formed on the surface of the core [50]. Thus, the maximum utilization of the platinum can be achieved. Moreover, the solid core can be dissolved and a hollow core-shell particle can be formed [51]. However, the remarkable activities of hollow core-shell nanoparticles steeply decrease by voltage cycling. Furthermore, the collapse of the core or the dissolution of shell material have been observed, so the stability remains the main issue in the research of core-shell catalysts [52,53].

2.3. Nanocrystals

The activity of platinum nanoparticles increases with increasing surface area, so smaller particles with high specific surface should be very active towards ORR. This is true up to the particle size of about 2 nm, smaller particles are less active because of the presence of edges and vertices which do not allow efficient four-electron transfer [54]. The problem can be solved by synthesizing atomic planes tuned for desired ORR activity.

It is well-known fact that the catalytic activity of open structured surfaces exceeds the activity of densely packed surfaces [55]. So, the high-index planes are promising geometry for ORR catalyst, but the successful synthesis of desired shape, e.g., tetrahedral Pt nanocrystals, remains difficult. One of the perspective shapes is the Pt₃Ni octahedral nanocrystal catalyst with remarkable specific and mass activity of about 90-fold more than the activity of commercial Pt/C catalyst [56]. Moreover, a controllable Pt₃Ni synthesis leads to the creation of highly porous nanocrystals with large specific surface areas and interconnected branches [57,58]. In general, Pt-based bimetallic and trimetallic nanocrystals with the same polyhedral type exhibit better ORR activities owing to the addition of another component active for oxygen kinetics in electrocatalysis [59]. Recently, the highly active Pd@Pt-Ir icosahedral nanocrystals were prepared by Zhu and co-workers [60].

All of the above-discussed categories of platinum PGM catalysts demonstrated high activities towards ORR, however, the stability and durability of developed materials remain problematic. Platinum and Pt-based materials are expensive despite their excellent catalytic properties. The core-shell catalysts are often unstable under long-term testing

conditions and the shape-controlled nanocrystals are difficult to synthesize with well-defined morphology.

2.4. Carbon and Non-Carbon Supports for PGM Catalyst

Catalyst support strongly influences the performance of fuel cell membrane electrode assembly as it significantly contributes to key factors such as catalyst utilization, mass transfer, charge transport and durability. The most commonly used support for PGM catalyst are Vulcan XC-72 and Ketjen black. It has been established that spherical carbon particles undergo corrosion at high potentials (>1.5 V) resulting in the aggregation of Pt nanoparticles and gradual decrease in the electrochemically active surface area of Pt. Highly graphitized carbon supports are known to be less prone to corrosion at high operating potentials. High surface area, corrosion resistance and suitable morphology to anchor catalytic particles are key attributes of ideal catalyst support. The US DOE support stability target at the MEA level requires less than 30 mV voltage decrease at a current density of 1.5 A/cm^2 after 5,000 cycles from 1.0 to 1.5 V. Many carbon and non-carbon containing catalyst support have been studied to achieve the support stability target set by US DOE. Ceramic supports based on carbides, oxides, nitrides, borides have been studied as catalyst support [61]. However, they offer intrinsically high corrosion resistance, their poor electrical conductivity and low surface areas have prevented their practical use in fuel cell cathodes. The preferred choice of support is still carbon based porous materials. Chen et al. have studied the activity and stability of Pt alloy nanoparticles supported nitrogen doped graphitized carbon nanotubes. These advanced carbon supports exhibited favourable metal-support interaction and after 20,000 potential cycles (0.6–1.0 V vs. RHE), the retained electrochemical surface area (ECSA) is more than 2 times larger than that of the Pt/C catalyst [62]. Achieving a balance between high degree of porosity and graphitization is crucial to develop ideal catalyst support materials. Therefore, more careful design, synthetic strategies and testing in fuel cell cathodes are needed to move towards the US DOE support stability target.

3. Non-Precious Metal Catalyst

To avoid the usage of precious metals such as platinum, many research groups focused on catalysts based on other materials [63–65]. One of the reasons is the expected reduction in cost of the MEA [66]. For example, in the case of $\approx 500,000$ units produced per year, the estimated cost of catalyst, membrane, gaskets and GDLs might exceed 62% of the total cost of a fuel cell stack [67]. Catalyst alone is estimated to be 41% of the total cost, see Figure 3a.

Figure 3. (a) Estimated costs of fuel cell stack components [67]. (b) The illustrational structure of transition metal macrocyclic compound.

A detailed cost analysis of the most promising PGM-free M-N-C type catalyst suggested that a PGM-free Fe-N-C catalyst costs 200 times less than a Pt-based catalyst (a comparison made using electrodes with the Pt loading of 0.142 mg/cm^2) [68]. The elimination of Pt from the fuel cell cathode catalyst layers would allow realization of stack cost reduction by 6 \$/kW (assuming comparable durability)—an important step in a pathway to meet the 30 \$/kW US DoE target that would boost cost competitiveness of fuel cell electric vehicles. However, at present, the non-precious metal catalysts (NPMCs) are considered furthest from commercialization, because their performance significantly drop after voltage cycling or potentiostatic/galvanostatic experiments [69]. Moreover, the fuel cells used in automotive industry must provide high power density to meet the criteria of the market. The NPMCs exhibit low power density when implemented in the fuel cell, so that, the potential application of these materials is limited to portable applications or backup power sources.

The NPMCs are based on transition metals dispersed on nitrogen-doped carbon [70,71]. Generally, the structure of NPMCs can be expressed as $\text{M} - \text{N}_{(2 \text{ or } 4)} - \text{C}$, where M denotes the transition metal [72]. The typical structure is depicted in Figure 3b, the metal atom is coordinated into four nitrogen atoms (metal chelate). The central atom determines the catalytic activity and the surrounding ligand structure can be used for tuning the selectivity, reactivity and other parameters [73]. Moreover, the NPMCs are able to catalyse the ORR in both acid and alkaline media [74]. The Co porphyrin, see Figure 3b, has catalytic activity towards the two-electron process, i.e., reactions (2) and (3), however, the iron-based structures allow the four-electron process [75]. Recently, Banham and co-workers have reported the high performance NPMC, which represent an important step in the commercialization of this group of materials [76]. A single atom Fe-N-C catalyst with promising volumetric current density was synthesized by Liu and co-workers [77]. The FeCo-N-C catalyst has been studied by Liang and co-workers and the developed material has been incorporated into the MEA with loading of 4 mg/cm^2 [78]. The group obtained an impressive performance of 575 mA/cm^2 at 0.7 V and remarkable stability. Other types of NPMCs are based on metal oxides, metal nitrides or metal chalcogenides [79].

The synthesis of M-N-C catalyst usually involves few high temperature treatment steps leading to the formation of highly heterogeneous material composed of multiple carbon phases, metal species, limiting our ability to identify the active site and to further discover synthetic strategies to increase the active site density. To overcome this issue and subsequently increase the density of active M (Fe/Co/Mn)-N₄ sites, support-free synthesis methods from metal-organic framework type precursors consisting of metal, nitrogen, carbon bonds have been developed. Wu et al. have prepared an atomically dispersed Mn-N-C catalyst with high-density MnN₄ sites by using Mn-doped zinc imidazolate framework (ZIF-8) as precursors. The optimized Mn-N-C catalyst exhibits high current densities of 0.35 and 2.0 A/cm^2 at 0.6 and 0.2 V, respectively, in PEM fuel cells under H₂/O₂ condition [80]. By elimination of the inactive carbon phases ORR activity in acid can be significantly increased, Wan et al. have reported an atomically dispersed single Fe site based Fe-N-C catalyst that exhibits a power density of 1.18 W/cm^2 under 2.5 bar H₂/O₂ and an activity of 129 mA/cm^2 at $0.8 V_{\text{IR-free}}$ under 1.0 bar H₂/air in PEM fuel cell configuration. It is well documented in literature that the presence of Fe and peroxide promotes Fenton reaction in fuel cell cathodes generating free radicals resulting in serious degradation of the organic ionomer and the membrane. To address this challenge, nitrogen-coordinated single cobalt atom catalysts for oxygen reduction in PEM fuel cells was developed and reported by Wu et al. The atomically dispersed Co-N-C catalyst were prepared from Co-doped ZIF-8 and the optimized catalyst exhibited the power density of 0.56 W/cm^2 in H₂/O₂ fuel cell and 0.28 W/cm^2 in H₂/air fuel cell [81]. Besides transition metals such as Fe, Co and Mn that are widely used as active component in M-N-C catalyst, a Fenton inactive tin/nitrogen-doped carbon fuel cell cathode catalyst has been reported to exhibit a 40–50% higher current density than Fe-N-C type catalyst at cell voltages below 0.7 V by Luo et

al [82]. It is worth noting that a hybrid catalyst composed of both Fe-N-C type NPMC and Pt/C is found to exhibit enhanced stability and activity in PEMFCs (Table 1).

Table 1. The area specific ORR activity and mass activity of selected catalysts measured at 0.9 V_{RHE}.

Catalyst	Surface Activity/ mA/cm ²	Mass Activity/ A/mg	Ref.
commercial Pt/C	0.23	0.15	[83]
DoE 2020 target	-	0.44	[83]
Pt ₃ Ni{111}	18	-	[84]
Pt _{1.5} Ni	3.99	1.96	[85]
Pt _x Gd alloy	-	3.6	[86]
Pt ₃ Y thin layer	13.4	3.5	[87]
Pt/NiO core-shell nanowires	11.5	13.6	[88]
PtFe N-doped carbon shell	-	1.6	[89]
Pt ₂ CuNi octahedrons	-	2.35	[89]
Pt-Ni octahedrons	-	3.3	[90]
Au-7.7 nm@Ni ₂ Pt ₂ /C	1.6	0.496	[91]
Ru@Pt/C	0.7	0.5	[92]
NCs/CNTs (Pt loading 10%)	0.194	0.167	[93]
Fe-containing nanocrystals	6.18	-	[94]
PtFe nanowires	-	3.4	[95]
TiCoN _x /N-rGO	2.51	-	[96]
magnet core-shell L ₁₀ CoPt/Pt	-	2.26	[97]
tetrahedral YBaCo ₄ O _{7.3}	2.76	-	[98]
Fe-N-C+Pt/C	-	0.22	[99]

The performance comparison with Pt/C has been reported by Proietti et al. [100]. The maximum performance of 0.91 W/cm² represents approximately 75% of the performance achieved with Pt/C catalyst in the same experimental set-up.

4. Perspectives on Stability of PGM Catalyst and NPMC

The PGM based cathode catalyst is the technically feasible option for a commercial PEMFC stack. The durability becomes an issue only when the Pt loading is decreased in the cathode. The stability of catalyst is further strongly affected by conditions in operating PEMFC, see Figure 1. These conditions include (a) excess water flooding in electrode, (b) oxygen permeability through ionomer phase in catalytic layer, (c) pressure of the reactants, (d) start-up and shut-down conditions, (e) fuel deficiency at high performance conditions [101]. The continuous potential fluctuations experienced by the Pt nanoparticles in the cathode triggers onset of Pt dissolution and carbon corrosion. The electrochemical active surface area (ECSA) of Pt nanoparticles decreases over long-term operation due to collapse of the carbon support and subsequent aggregation of Pt nanoparticles and dissolution of base metals in the case of Pt alloy nanoparticles. The base metal dissolution, difficulty in maintaining the geometry of particles makes the use of shape-controlled Pt alloy catalyst extremely difficult. Therefore, it is necessary to optimize the activity and durability of catalyst particles recognizing the existence of trade-offs. Several approaches such as doping rhodium or nitrogen have been effective to reduce the dissolution of base metal Ni from the core in the case of PtNi nanoparticles. Preparation of Pt-Ni catalyst covered with Pt skin layer has also been reported to improve durability [102]. Stamenkovic et al. proposed that the utilization of a gold (Au) underlayer promotes ordering of Pt surface atoms towards a (111) structure, whereas Au on the surface selectively protects low-coordinated Pt sites [103]. This mitigation strategy was applied towards 3 nm Pt₃Au/C nanoparticles and have shown the elimination of Pt dissolution in the liquid electrolyte in addition to 30-fold durability improvement versus 3 nm Pt/C over an extended potential range up to 1.2 V. However, these materials have to be tested at the MEA level and the improvement in durability must be demonstrated at the same level reported in liquid electrolytes.

The PGM-free NPMC is still under its earlier development stage, some M-N-C type electrocatalysts may demonstrate the similar ORR activity as Pt under rotating disc electrode (RDE) conditions but none of them could reach a similar PEMFC performance. The durability issues associated with NPMCs, specifically M-N-C, has not yet been clearly identified due to the efforts so far devoted mostly to the identification of the structure of active sites present in these types of composite catalysts. In an attempt to solve the activity-stability trade-off riddle associated with Fe-N-C catalyst, Jaouen et al. have identified durable and non-durable FeN_x sites in Fe-N-C catalyst materials and described the two distinct degradation pathways. They show that Fe-N-C catalysts initially comprising two distinct FeN sites, namely, high-spin S1 site and the low- or intermediate-spin S2 site, both assigned to FeN₄ moieties but embedded in different ways in the carbon matrix [104]. Among these two sites, S1 is not durable in operating PEM fuel cells, quickly transforming to ferric oxides. In contrast, S2 is shown to be more durable, with no measurable decrease of the number of active sites after 50h operation at 0.5 V. The authors advocate further studies with a focus on increasing the site density of S2 sites and/or stabilizing S1 in acidic and oxygenated environments. There is still some distance to cover to make the Fe-N-C material desirable for direct application and continuous testing in PEM fuel cell stacks.

5. Conclusions

In recent years, significant progress in the development of the ORR catalyst has been made. In the field of theoretical research, a deep understanding of ORR has been achieved. From the point of view of experimental research, an immense effort has been spent in catalyst design, catalyst support development and tuning of electrochemical activity.

In terms of fuel cells commercialization, there is a desperate need for efficient ORR catalyst. The main obstacles are the activity, stability and the cost of developed materials. Nowadays, the state-of-the-art catalyst is based on platinum particles dispersed on the carbon support. In last decades, the platinum loading of the developed catalysts has been significantly decreased. On the other hand, the remarkable activities of low-loading catalysts suffer from voltage cycling and other real-life conditions.

The catalysts performance and stability can be improved by adjusting parameters of the operating fuel cell, i.e., humidity, temperature and flow of reactants. The future research should be focused on optimization of these parameters to overcome the stability issues. The properties of the catalysts can be also improved by homogenous deposition of the catalytic material within the MEA or by optimizing the catalyst loading. Furthermore, by employing advanced support materials like carbon nanotubes, graphene or carbon nanowalls, the durability of the catalyst can be increased [105].

The outstanding activity of core-shell nanoparticles, nanowires or nanorods has been demonstrated by many research groups. At the current stage for those well-shaped and core-shell Pt nanoparticles, the major challenge still concentrates on how to successfully transfer their high RDE activity to PEMFC performance.

In the case of further improvement of ORR catalyst activity, stability and subsequent mass production, the applications such as hydrogen fuel cells or metal-air batteries would be viable options for the shift to sustainable and environmentally friendly renewable energy technologies.

Author Contributions: Conceptualization, M.T.; investigation, F.G., Z.G.; writing—original draft preparation, M.T.; writing—review and editing, M.T., F.G., Z.G., J.S. All authors have read and agreed to the published version of the manuscript.

Funding: The result was developed within the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088, cofunded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI programme and, in the follow-up sustainability stage, supported through CENTEM PLUS (LO1402) by financial means from the Ministry of Education, Youth and Sports under the National Sustainability Programme I.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in a publicly accessible repository.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

PEMFC	Proton exchange membrane fuel cells
PGM	Platinum group metals
ORR	Oxygen reduction reaction
HOR	Hydrogen oxidation reaction
GDL	Gas diffusion layer
NHE	Normal Hydrogen Electrode
ICE	Internal combustion engines
MEA	Membrane electrode assembly
BoL	Beginning of Life
NPMC	Non-precious metal catalyst
DoE	Department of Energy (USA)
RHE	Reversible Hydrogen Electrode
CNT	Carbon nanotubes
NC	Nanocluster

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