REVIEW

Progress on Platinum-Based Catalyst Layer Materials for H$_2$-PEMFC

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ABSTRACT

The constant increase in energy demand and related environmental issues have made fuel cells an attractive technology as an alternative to conventional energy technologies. Like any technology, fuel cells face drawbacks that scientific society has been focused on to improve and optimize the overall technology. Thus, the cost is the main inhibitor for this technology due to the significantly high cost of the materials used in catalyst layers. The current discussion mainly focuses on the fundamental electrochemical half-cell reaction of hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) that are taking place in the catalyst layers consisting of Platinum-based and Platinum-non noble metals. For this purpose, studies from the literature are presented and analyzed by highlighting and comparing the variations on the catalytic activity within the experimental catalyst layers and the conventional ones. Furthermore, an economic analysis of the main platinum group metals (PGMs) such as Platinum, Palladium and Ruthenium is introduced by presenting the economic trends for the last decade.

Abbreviations

AFC	Alkaline Fuel Cell
AOR	Alcohol Oxidation Reaction
CA	Chrono Amperommetry
CV	Cyclic Voltammetry
DRIFT	Diffuse Reflectance Infrared Fourier Transform
ECSA	Electrochemical Surface Area
EIS	Electrical Impendence Spectroscopy
EDX	Energy Dispersive X-Ray
FCEV	Fuel Cell Electric Vehicle
HOR	Hydrogen Oxidation Reaction
LSV	Linear Sweep Voltammetry
MCFC	Molten Carbonate Fuel Cell
MOR	Methanol Oxidation Reaction
ORR	Oxygen Reduction Reaction

PAFC   Phosphoric Acid Fuel Cell
PEMFC   Proton Exchange Membrane Fuel Cell
PGM   Platinum Group Metal
RDE   Rotating Disk Electrode
SOFC   Solid Oxide Fuel Cell
SEM   Scanning Electron Microscopy
TEM   Transmission Electron Microscopy
XRD   X-Ray Diffraction
XPS   X-Ray Photoelectron Spectroscop

1 Introduction

The need for clean power in modern societies is constantly increasing as energy requirements increase. Many countries seek new policies, strategies, and technologies to compensate for the constantly growing emissions rate. To this extent, the emissions adversely affect both nature (climate change, thermal pollution, and water pollution) and human health, issues that have been discussed over the last two decades. In addition to environmental and human problems, the depletion of fossil fuels has led researchers, scientists, and policymakers to discover alternative ways to utilize energy sources such as renewables, nuclear, and hydrogen.

Fuel cells are a promising technology that converts the chemical energy of hydrogen into electricity without emitting any greenhouse gases. The low emissions, zero noise, and pollution have made them one of the cleanest power sources. Fuel cells can be categorized according to the type of electrolyte and fuel used. Thus, various types of fuel cells have been developed throughout the years, such as Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), Solid Oxide Fuel Cells (SOFC), and Proton Exchange Membrane Fuel Cells (PEMFC), with the latter being one of the most reliable and ready to deploy fuel cell types from small to large applications. The main advantages of PEMFCs are the high-power densities, significantly low operating temperatures, fast start-up times, and easy stacking, allowing them to be a proper solution for mobile and stationary applications. In Table 1, the various types of fuel cells, their main components, and operating conditions are listed [1].

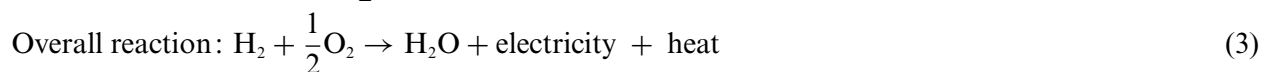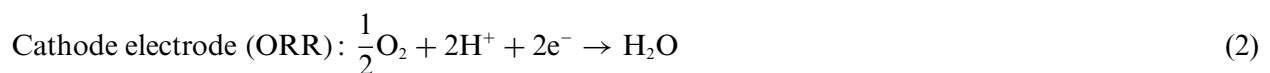**Table 1:** Fuel cell types and their characteristics [2,3]

Fuel cell type	Electrolyte	Operating temperature	Typical stack size	Electrical efficiency	Example of applications
Alkaline (AFC)	Liquid KOH	90–100°C	10–100 kW	60%	• Backup power • Transportation
Phosphoric acid (PAFC)	Phosphoric acid soaked in a matrix	150–200°C	400 kW	40%	• Distributed generation
Molten carbonate (MCFC)	Molten carbonate	600–700°C	300 kW–3 MW	45–50%	• Electric utility • Distributed generation

Table 1 (continued)

Fuel cell type	Electrolyte	Operating temperature	Typical stack size	Electrical efficiency	Example of applications
Solid oxide (SOFC)	Yttria stabilized zirconia	500–1000°C	1 kW–2 MW	60%	• Auxiliary power
					• Electric utility
					• Distributed generation
Polymer electrolyte membrane (PEMFC)	Porfluoro sulfonic acid	<100°C	<1 kW–100 kW	60%	• Backup power
					• Portable power
					• Transportation

In terms of PEMFC's operation, the anode side (fuel electrode) is supplied with hydrogen while simultaneously the cathode side is fed with pure air or oxygen. Hydrogen in the anode is oxidized through an electrochemical half-cell reaction to protons (H^+) and deliberates electrons–Hydrogen Oxidation Reaction (HOR). The electrons flow through an external electric circuit to the cathode side. At the same time, protons are conducted by the polymer electrolyte and transferred to the cathode side, where they recombine with oxygen, protons, and electrons, forming H_2O–Oxygen Reduction Reaction (ORR) as is depicted in Fig. 1. Eqs. (1)–(3) describe the electrochemical reactions that are taking place [4]:

$$\text{Anode electrode (HOR)}: H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$\text{Cathode electrode (ORR)}: \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

$$\text{Overall reaction}: H_2 + \frac{1}{2}O_2 \rightarrow H_2O + \text{electricity} + \text{heat} \tag{3}$$

The aforementioned electrochemical procedures and the corresponding transport phenomena of the reactants are taking place in the main components from which the PEMFC is structured. The components of a PEMFC are the ion exchange membrane with a solid structure, the porous gas diffusion layers (GDL) in both anode and cathode sides, which are electrically conductive. The catalyst layers (CL) are located at the interface between the gas diffusion layer and the membrane in which the electrochemical half-cell reactions of HOR and ORR occur. The cell interconnects the flow plates that feed the fuel (H_2) and the oxidant to the reactive sites through flow channels. More specifically, the GDL, CL, and the electrolyte are constructed together, forming the so-called Membrane Electrode Assembly (MEA), which can be characterized as the heart of the PEMFC. In general terms, PEMFCs are prepared as single cells to cover small power requirements or stacks where many cells are connected in series for achieving the voltage and power output according to the application.
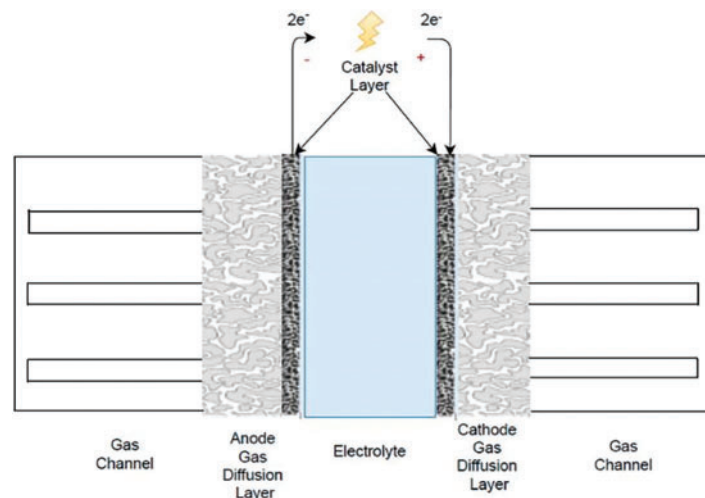
Figure 1: Schematic representation of PEMFC [5]

However, PEMFCs still face some essential issues in terms of cost, durability, and performance. In this respect, researchers have conducted significant work to examine these issues to provide solutions and turn the PEMFCs into a more reliable and efficient technology. In this context, the main interest of research has been focused on challenges regarding (1) the anode and cathode catalyst layer poisoning with impurities which can lead to the decrease of PEMFC's performance, (2) the geometry of gas flow channel for achieving the optimum conditions of mass and heat transfer phenomena on both sides, (3) minimization of platinum loading on catalyst layers and (4) the electrolyte crossover. At this point, relative studies regarding the issues mentioned above will be discussed to provide a general view of the work done in each field.

Shabani et al. [6] studied the durability and performance degradation of PEMFCs considering the most critical associated with the current technology. The air contaminants, fuel impurities cleansers, and some materials, from which PEMFC is composed, have been proved to impact PEMFC's performance negatively. Their work highlighted the solutions for increasing the tolerance of PEMFC catalyst layers to deal with poisonous impurities. Yang et al. [7] studied the performance of PEMFC using a new type of gas channel, the so-called waved flow channel. The main parameters investigated were velocity, concentration, and electrical performance. The results showed that the waved channel has better benefits regarding the transport phenomena in porous layers. That relies on the fact that the waved channel improves the forced convection and causes a higher amount of reactant gases to flow through the GDL. Francia et al. [8] highlighted that hydrogen crossover could cause undesired diffusion of the gas from the anode to the cathode through the membrane, which usually can lead to deterioration of perfluorinated ionomer membranes causing gradual degradation on PEMFC's performance. Thus, in their research developed a mathematical model to directly determine hydrogen crossover permeation rate. The results showed that hydrogen crossover current densities increased from 0.12 to 0.32 mA/cm^2 by decreasing the membrane's thickness and the operating temperature.

As discussed previously, catalyst layers are the main part of PEMFCs where half-cell reactions of HOR and ORR are initiated. In PEMFCs, platinum is commonly used because it is the most active noble metal. In general, platinum-based catalysts are preferred for PEMFC with comparatively clean reactants. Nonetheless, the major challenge of the platinum-based catalysts arises when the supplied fuel contains residual carbon monoxide (CO), which can gradually degrade PEMFC's performance. The catalytic activity on the cathode side (ORR) by applying other metal surfaces such as Au, Ir, Rh has been investigated. On the other hand, the electro-catalytic activity of the anode side (HOR) has also been examined using various platinum-group metals, including Pt, Ru, Pd, Ir, Os, and Rh. The overall improvement of PEMFCs' performance by applying different noble metals will be extensively discussed in the following chapters. The current work will be focused on bimetallic CLs consisting of Pt alloyed with noble metals and Pt combined with non-noble metals for HOR and ORR in PEMFCs. Worth mentioning that significant efforts have been conducted regarding the investigation of CLs in Alcohol oxidation reaction (AOR) on both noble and non-non noble metals [9–11] as well as in the trimetallic CLs for Methanol oxidation reaction (MOR) [12]. However, the scope of the current work relies on the materials applied in the CLs of PEMFCs for HOR and ORR.

2 Existing Solutions on Applied CL Materials

As mentioned in the previous section, electrocatalysts are the heart of PEMFCs in which electrochemical reactions are taking place and consequently affect the fuel cell's overall performance and life. In this respect, tremendous efforts have been reported further to optimize the existing solutions applied on CLs in terms of (1) optimizing the platinum loading, (2) applying additional noble or non-noble metals for enhancing the performance of the electrochemical reaction, and minimizing the construction cost of CLs. Usually, platinum (Pt) nanoparticles are loaded in carbon support (Pt/C), making the most widely used and reported case of CL. The main benefits of Pt/C CLs rely on their high catalytic activity and better stability than other noble metals. However, the application of Pt/C is impeded with various challenges, mainly due to the significantly increased cost of Pt and the fact that it can easily be dissolved and aggregated when the operating conditions are significantly poor. In addition, the standard carbon supports materials for Pt and Pt-alloy CLs experience corrosion due to electrochemical oxidation on the surface, leading to the dissolution of the Pt nanoparticles [13].

On the other hand, considerable efforts were made on developing non-noble metal-based CLs. The Platinum group metal-free (PGM-free) CLs can be described as metal-nitrogen-carbon (M-N-C) structure in which M is an earth-abundant transitional metal (M = Co, Fe, Ni, Mn, etc.). These metals have gained attention due to the high catalytic activity presented on ORR, simultaneously with the utilization of abundant and inexpensive materials [14]. Considering the anode and cathode PEMFCs, Pt/C electrocatalyst cannot be characterized as a state-of-the-art material. At the same time, they cannot provide significantly high catalytic performance at feasible platinum loading accounting due to the high cost. One of the main disadvantages of applying Pt as a single catalytic unit is the CO tolerance of the CL when the supplied reactant gas is not 100% pure. This can lead to the occupation of the active catalytic sites and cause a reduction in the efficiency of the CL. Alloying Pt with a second element has been ascertained, enhancing the primary element's electric activity [15]. However, even with reduced Pt loading, the catalytic performance has not met the requirements for broad commercialization in fuel cells. Thus, the production of cheap CLs is one of the main challenges. In this context, the binary alloyed CLs can be separated into the Pt/noble metals and Pt/non-noble metals CLs.

3 ORR and HOR on Platinum Groups Metal

This section describes the ORR on both Pt alloys and other noble metals. Initially, the catalytic activity of Pt is strongly dependent on its O_2 absorption energy, the dissociation energy of O-O bond, and the corresponding binding energy of OH on the Pt surface. Moreover, theoretical calculations on O_2 binding energy on various metals have been conducted and have shown that Pt has the highest catalytic activity. In more detail, the catalytic activity among other noble metals follows this order: Pt > Pd > Ir > Rh. When Pt is alloyed with other metals, enhanced catalytic activity is presented. This is explained by the change in the electronic structure and the corresponding geometric effect in terms of Pt-Pt interatomic distance. More precisely, Pt alloying presents changes in lattice contraction, which leads to those as mentioned above favourable Pt-Pt distance, causing better O_2 adsorption.

As discussed previously, ORR in other noble metals such as Au, Ir, Rh, etc., has also been investigated. These metals show lower catalytic activity than Pt, while they are not electrochemically stable. Fig. 2 shows the trend in ORR activity for various noble metals, indicating that Pt has the highest activity compared to other materials.
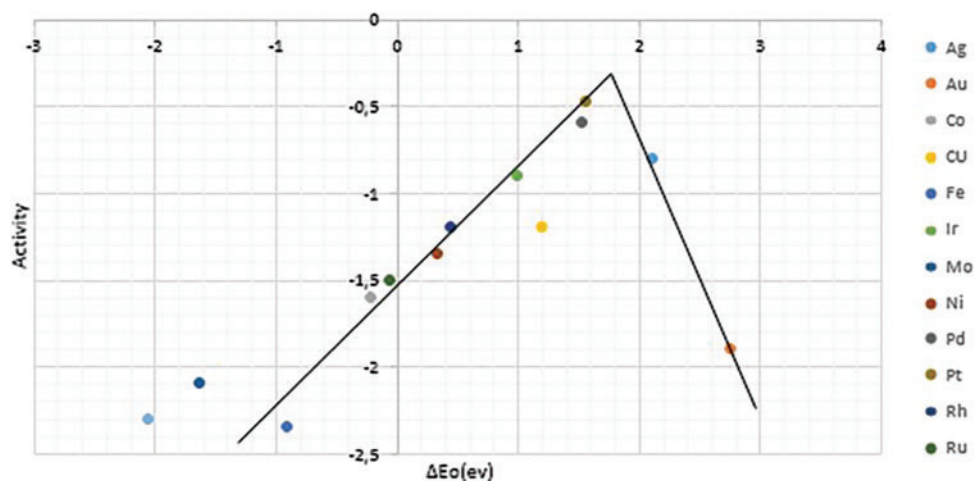

Figure 2: Trends in oxygen reduction activity plotted as a function of the oxygen binding energy [16]

On the other hand, HOR is one of the most important areas of fuel cells where the interaction with the catalyst surface activates the reactants. Since the catalyzed electrochemical reaction occurs at the catalyzed electrode/electrolyte interface, the electrochemical reaction strongly depends on the potential difference between the catalyst, the electrolyte, and the catalyst's surface morphology. Indicatively, the exchange current density can vary from 10^{-3} A·cm^{-2} at a Pt electrode to 10^{-12} at a Mercury (Hg) electrode for the HOR, and from 10^{-10} A·cm^{-2} at a Pt electrode to 10^{-8} A·cm^{-2} at a Copper (Cu) electrode for ORR. Worth mentioning that HOR on Pt is approximately 5 to 7 magnitudes more rapid than the ORR.

Thus, the adsorption and desorption of reactants on the catalyst surface can directly affect the catalytic ability. In this respect, the exchange current density of the HOR in relation to the enthalpy of H adsorption is correlated. If the enthalpy is too small, a slow adsorption kinetic will occur. If the enthalpy is too high, the desorption of H becomes difficult. Hence, an intermediate value in the enthalpy of H adsorption is required for the CL to be active [15].

Although HOR has fast kinetics on pure Pt catalyst surfaces, poisoning should be addressed when the supplied hydrogen contains impurities such as carbon monoxide. As a result, CO is absorbed from the active areas, affecting the reactivity of the electrode surface by blocking H_2 adsorption. Another disadvantage relies on the significantly high cost of Pt. Therefore, research has been conducted in the last decades focusing on the development of catalysts by alloying Pt with other metals that are CO tolerant for reducing the use of Pt. Nonetheless, alloying Pt with a second element has been proved to enhance the first material's electrocatalytic performance, achieved by (1) bifunctional effects whereby the second component provides one of the necessary reactants, (2) electronic effect in which the second component alters the electronic properties of the catalytically active metal, and (3) morphological effects, in which the dilution of the active component (Pt) with catalytically inert metal changes the distribution of the active sites which can lead to opening new pathways of reaction [15].

4 Pt-Noble Metals in CLs

4.1 Pt-Based CLs

Noble metal based catalyst layers (NMBCs) have been a hotspot with significant interest for tackling several issues presented in PEMFCs due to the high utilization of noble metals, cost efficiency, and the promoted catalytic properties. Materials alloyed with Pt include Ruthenium (Ru), Palladium (Pd), and Gold (Au). For this purpose, major studies are reported regarding the materials that have been applied with Pt for examining the performance of CL. Additional studies will be presented regarding the investigation of various compositions on common Pt/C CLs and the effects on PEMFC's performance. The studies reported in the following sub-chapters concern the overall operation and performance of PEMFCs considering both anode and cathode electrochemical reactions.

4.1.1 Pt-Ru CLs

Ruthenium (Ru) is a noble metal usually applied on ORR electrocatalysts because of its improved tolerance on CO [15]. Albers et al. [17] examined a series of Pt-Ru/C fuel cell catalysts combining several techniques such as transmission electron microscopy (TEM), scanning transmission electron microscopy (SEM), energy dispersive X-ray microanalysis, X-ray diffraction (XRD), and inelastic incoherent neutron scattering. The local composition of the precious metal particles with different sizes and compositions indicated a proportional increase between particles and the Pt/Ru ratio. At the same time, Ruthenium is shown to prevent the agglomeration of the platinum particles from retaining smaller particle sizes. Saeed et al. [18] evaluated the performance of a PEMFC considering various parameters such as the flow pattern, flow rate, and the degradation of Pt-Ru/C CL. In their study, scanning electron microscopy (SEM) images for the topography of the electrode were used and showed degradation in the elements of CL due to the corrosion phenomenon as a direct result of the electrochemical reaction among Pt-Ru. The authors concluded that the metals alloyed presented an increased current at less negative values while others showed a decrease in the current to less positive values. Brkovic et al. [19] issued the durability in terms of poisoning of CLs and cost for the commercialization of PEMFCs. The authors developed a tungsten-carbide-oxide as a new noncarbon based catalyst support for Pt-Ru (Pt-Ru/$W_xC_yO_z$) based anode PEMFC CL. The performance of the developed CL was investigated via cyclic voltammetry, linear can voltammetry, and rotating disk electrode voltammetry. The developed CL was tested as an anode CL in a PEMFC. A synthetic reformate was used as a fuel in PEMFC, which presented a significant power drop of 35.3% for a commercial Pt-Ru/C CL, while for the developed CL anode catalyst, this drop was around 16%. Henry et al. [20] studied carbon supported Pt-Ru/C CLs used in the anode side of the PEMFC. In this respect, the evolution of MEA after 1000 h of operation for ageing was investigated. Their analyses showed

the dissolution of Ru from the PtRu/C within the micro-porous layer and the membrane. Overall, the results indicated that within the membrane, the Ru reduction is catalyzed by Pt and hydrogen. In addition, the localization of the precipitation band near the cathode showed that Pt came from the dissolution of cathodic Pt/C and that both Pt and Ru ions were reduced by the hydrogen crossover. Chen et al. [21] studied the performance of a PEMFC with an active area of 112.85 cm^2 and with anode CL consisting of Pt-Ru. The PEMFC stack was examined under various reformate gases of different concentrations of CO. The results showed that the increase of CO concentrations or decrease of H$_2$ concentration of the CO-contained reformate gas has a negative impact on the performance of the PEMFC. The study showed that the PEMFC stack consisting of a Pt-Ru anode CL could tolerate a CO concentration above 50 ppm under non-diluted H$_2$, whereas in the case of diluted H$_2$, the CL could tolerate a CO concentration of 10 ppm.

4.1.2 Pt-Pd CLs

Another possible candidate for alloying Pt is the palladium (Pd), which presents identical facets and lattice constants and similar outer electronic configuration as Pt [22]. Zhou et al. [23] compared two types of CLs, Pt-Pd/C, and Pt/C, evaluated as ORR CLs. For both types of CLs, physical and electrochemical techniques were applied to investigate the structure, performance, and durability. Overall, the electrochemically active surface area, particle size distribution, polarization behaviour, and electrochemistry impedance spectroscopy suggested that Pt-Pd/C has better durability than Pt/C. Cho et al. [24] presented a study proposing a new structure of bimetallic electrocatalysts to investigate ORR performance relative to a CL based on monometallic Pt nanoparticles. The examined CL was platinum on non-spherical Pd-Pt bimetallic supported on functionalized graphene (Pt-on-PdPt/fG). This CL presented enhanced ORR activity and durability in comparison to commercial Pt/C. More specifically, a specific activity of 1.89 mA/cm^2 at 0.9 V was achieved from the Pt-on-PdPt/fG. At the same time, the commercial CL presented a specific activity around 0.23 mA/cm^2 at 0.9 V. Carlos Calderón et al. [25] studied catalysts consisting of Pt-Pd (35 wt% and atomic ratio around 1:2) supported on carbon black, carbon nanofibers and carbon xerogels for evaluating their activity towards the ORR. Both XRD and TEM analyses showed low particle and crystallite sizes with good dispersion on carbon supports. Regarding the ORR, the Pt-Pd nanoparticles supported on black appeared to have the best performances in terms of high current densities, high specific and mass activities, and the number of moles participating in ORR and water formation. Thus, the improved performance of the examined CL was explained due to the modification of Pt-Pt interatomic distance by Pd and the holding of the hydrogen peroxide formed during the ORR process. Brouzgou et al. [26] investigated Pt-Pd on carbon supports in terms of CO tolerance and durability as both anode and cathode CLs on PEMFCs. The durability and electrocatalytic activity were investigated via electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA), and rotating disk electrode (RDE). The authors found that Pt-Pd$_3$/C presented exhibit performance compared to Pt/C in terms of CO tolerance. Moreover, Pt-Pd/C and Pt-Pd$_3$/C presented the highest mass activities, estimated at 339.4 and 410 mA/mg$_{Pt}$ at 0.9 V, which was 4 and 5 times higher ascertained in commercial Pt/C (82.75 mA/mg$_{Pt}$). Zhang et al. [27] investigated the synthesis of Pd-Pt-based core-shell nanoparticles. Pd-Pt/C CL was compared with Pd-PtNi/C, and the latter presented enhanced ORR mass activity, estimated at 1.29 A/mg$_{Pt}$. Worth mentioning that by incorporating a third metal into the shell layer, the optimized mass activity of Pd@PtNiFe/C and Pd@PtNiCu/C CL was 1.1 and 1.4 times higher than Pd@PtNi/C. Bharti et al. [28] examined a CL consisting of Pt-Pd/CNT (Carbon NanoTubes) and prepared via microwave assisted, polyol route in the presence of sodium dodecyl sulfate (SDS) Pt-Pd/CNT-S or cetyltrimethylammonium bromide

(CTAB) Pt-Pd/CNT-C, and their performance was compared with Pt-Pd/CNT, which was prepared identically without using any surfactant. The *in-situ* electrochemical characterization improved the catalytic activity Pt-Pd/CNT-S compared to Pt-Pd/CNT-C and Pt-Pd/CNT. Moreover, high fuel cell performance achieved by Pt-Pd/CNT-S having less Pt loading around (−12 wt%) than commercial pure Pt or Pt/C (20 wt%) CLs.

4.1.3 Pt-Au CLs

Another noble metal studied is gold (Au). The incorporation with Pt can restrain the dissolution and migration of CO poisoning, resulting in improved performance of the electrochemical reaction of ORR [29]. Deng et al. [30] studied the performance of Pt-Au/TiO$_2$ CL for the ORR by examining various Pt/Au/Ti ratios. The scope of the study was to enhance the electrocatalytic activity of platinum-based CLs for ORR in PEMFCs. The results presented an improved performance above 4.19 times in mass activity compared to commercial Pt/C CLs with a ratio of 20% Pt/C. Jiang et al. [31] examined the performance of bimetallic Pt-Au nanoalloys. The *in-situ* diffuse reflectance infrared fourier transform (DRIFT) and X-ray photoelectron spectroscopy (XPS) proved that the electronic synergy effect between Au and Pt reduced the agglomeration of the noble metal and thus reduced CO poisoning. Furthermore, due to the synergy effect, the catalytic activity of the alloy increased by 20% compared to the single metal Pt catalysts. Lin et al. [32] investigated carbon supported Au-Pt core shell nano structured CLs. The developed CL was tested in terms of ORR activity via LSV and RDE. According to the authors, Au-Pt with atomic ratio 2:4 had the best catalytic performance towards ORR. Additionally, the stability of Au-Pt/C was examined via CV for 500 cycles. The performance of the MEA prepared by Au-Pt/C as cathode CL produced a maximum power density of 479 mW/cm^2 with the operating conditions being at 0.431 V using H$_2$ and O$_2$ at 80°C. Jeong et al. [33] examined Pt-Au on carbon catalysts at various Pt/Au ratios for ORR in PEMFC. The maximum power was increased with Au loading reaching a maximum value at 370.3 mW/cm^2 with Pt/Au ratio at 90/10. On the other hand, when more than 10% gold was added, the maximum power was decreased, while the CL with 20% Au loading presented lower maximum power compared to the Pt/C. The authors concluded that the CL with 10% Au loading had the highest performance by exhibiting a 30% higher power density than Pt/C (370.3 mW/cm^2 compared to 293.3 mW/cm^2). Beltran-Gastelum et al. [34] examined CL consisting of Pt-Au supported on reduced graphene oxide (Pt-Au/rGO). The nanomaterials were characterized by Raman, XRD, thermogravimetric analysis, and TEM. The developed CL was evaluated as an electrocatalyst for ORR. Furthermore, Pt-Au/rGO was compared to Pt/rGO to study the performance of the PEMFC. Thus, it concluded that the maximum power density was 20 mW/cm^2 and 70 mW/cm^2 for Pt/rGO and Pt-Au/rGO, respectively. Finally, Dorjgotov et al. [35] designed an Au-Pt core-shell nanocatalyst with high activity and stability. Using density functional theory, the authors validated their experimental results. In this sense, a power density above 2 W/cm^2 was achieved at low Pt loading (around 0.1 mg/cm^2) using a bilayer Au-Pt core-shell CL, which was highly durable.

4.2 Pt/C CLs

PEMFCs usually incorporate Pt catalysts since they provide a large surface area and large accessible pores for hydrogen and oxygen to reach the CLs. In this respect, numerous efforts have been conducted for optimizing and extracting the maximum performance from these types of CLs. Chen et al. [36] examined the utilization of Pt for reducing mass transfer losses and improving the performance of PEMFC under low humidity and high current densities. Polarization curves, CV, and EIS were employed to characterize and compare the effects of Pt/C ratio and Nafion content

gradient on the performance of PEMFCs under different humidification conditions. Their results indicated that the performance of the MEA could be significantly improved by allocating more Nafion and Pt/C in the sublayer near the membrane in the cathode catalyst layer. The MEA with optimal gradient cathode catalyst layer resulted in improved catalysts utilization, compared to MEA with a single cathode catalyst layer (0.403 g_{Pt} kW^{-1}_{rated} and 0.711 g_{Pt} kW^{-1}_{rated} under 80 RH% and 20 RH%, respectively). van Dao et al. [37] introduced a study to fabricate an efficient structural catalyst electrode of Pt/C consisting of double catalyst layers. The prepared Pt/C double catalyst layer electrode with Pt-dispersed and Pt-concentrated catalyst layers demonstrated better electrochemical properties than the individual Pt/C single catalyst layer electrode. The improved electrochemical performance of double catalyst layer electrodes was due to the increase of the Pt catalytic active area to the electrolyte when separating Pt catalysts into two layers, compared to single catalyst layer electrodes. Fan et al. [38] studied the degradation characteristics of PEMFCs with Pt black and Pt/C catalyst after 100 h of operation. The CL was investigated via electrochemical techniques and morphological characterization methods. Their experiments found that the degradation of Pt black CL was more severe than that of Pt/C CL. According to SEM, TEM, and XPS results, the decay of Pt black catalyst was mainly caused by Pt agglomeration and oxidation, causing a higher ohmic resistance, higher mass transfer resistance, and severer degradation of performance. The degradation of Pt/C catalyst was mainly due to reducing electrochemical surface area and carbon corrosion. The larger carbon corrosion made micropores and thicker supporting structures, resulting in performance degradation. Ostraverkh et al. [39] investigated the case of thin-film Pt with ultra-low metal loading ranging within 1 to 200 $\mu g/cm^2$. The role of platinum loading and membrane thickness was investigated considering ionomer free carbon substrates. The results were compared with the commercial electrodes applied in PEMFCs and showed that thin-film Pt electrodes could provide platinum utilization 2 orders of magnitude higher than the standard Pt/C catalysts by achieving simultaneously similar power efficiency and long-term stability. Samad et al. [40] emphasized on different cases of supported CLs and separated them into two main categories (1) carbon-based and (2) non-carbon-based. The study compared the various CL supports in terms of morphology, electro-catalytic activity and structural characteristics. To this extent, all the discussed catalyst supports, presented high potentials as possible catalyst support candidates.

5 Pt and Non-Noble Metals in CLs

As already mentioned, the cost reduction of CL is one of the main challenges. The combination of Pt with other metals can increase the catalytic efficiency with simultaneous reduction of the Pt loading. Some of the non-nobles that have been already investigated are Sc, Ti, V, Cr, Mn, Fe, Co, Ni, etc. [41]. The Pt-Ni, Pt-Cu, Pt-Co, and Pt-Fe are some of the cases that have been examined as solutions for lowering the cost and enhancing catalytic activity compared to other monometallic materials [13]. In recent studies, Nickel (Ni) has been used to form Pt-Ni, due to the improved electronic characteristics it provides to Pt by shifting the electron transfer from the first material to the second via the synergistic effect presented when Pt and Ni are combined. To this extent, Beermann et al. [42] studied the properties of Pt-Ni alloy nanoparticles and reported remarkable high activities for ORR, providing exceptional potential on the fuel cell's cathode. More specifically, ~25 times higher ORR was observed (2.7 A mg^{-1}_{Pt} at 0.9 V) compared to commercially available Pt/C CLs. Nigel et al. [43] investigated Pt-Ni CLs by controlling the ratio between Pt and Ni. The analysis showed ~6 times higher mass activity for ORR about Pt/C. The high catalytic activity was attributed to the enhanced Ni loading near the surface. Hennining et al. [44] investigated unsupported PtNi alloy aerogel CL in PEMFC. The results showed that the optimized CL had 2.5 larger surface specific ORR activity

than Pt/C and maintained 90% of the initial electrocatalytic activity. Kim et al. [45] introduced a Pt-Cu alloy thin film CL, which could be prepared by electrodeposition. The test was conducted using a single cell. The experiment revealed that a porous thin Pt-Cu alloy catalyst layer was successfully formed on the micro-porous layer/carbon paper. The synthesized Pt-Cu alloy catalyst was more durable than a conventional Pt/C in single cell tests. Ohyagi et al. [46] examined the durability of Pt-based Co alloy catalyst supported on carbon. In their study, the catalyst layer was studied via cyclic voltammetry to evaluate the electrochemical surface area (ECSA) and they investigated the polarization properties for assessing the activity of Pt-Co/C CL. Their results showed that the ECSA for Pt-Co/C was slowly decreased compared to the Pt/C CL during testing, with an initial ECSA at 62% and 37% for Pt-Co/C and Pt/C, respectively.

6 Economic Trends of the Materials Used in CLs

Platinum is a widely used material in the electronics sector, forecasted to be increased by over 40% in 2021, also considering the fuel cells' demand. Worth mentioning that the transport sector is expected to be the largest contributor to fuel cell demand growth. Toyota alone announced to produce around 30,000 fuel cell electric vehicles (FCEVs). It should also be considered that heavy duty vehicles will start to incorporate fuel cells, leading to additional growth of fuel cells [47]. From a technical perspective, batteries in heavy duty vehicles are less suitable for long distances considering the significantly high weight of tracks comparing to fuel cells [47]. The total share of platinum used in fuel cells different sectors is presented in Fig. 3 for the 2016–2021 period. Road vehicles and stationary power applications are the sectors that fuel cells are widely used. Furthermore, in the transportation sector (including road and other vehicles), fuel cell applications are constantly increased, indicating the transition into greener solutions. The evolution of Pt price is presented in Fig. 4. The price has a downward trend ranging between 1500–1800 $ in 2011 and reaching 950 $ in 2021. However, on a short term, Pt price presents many fluctuations, which affect the fuel cells' construction cost.
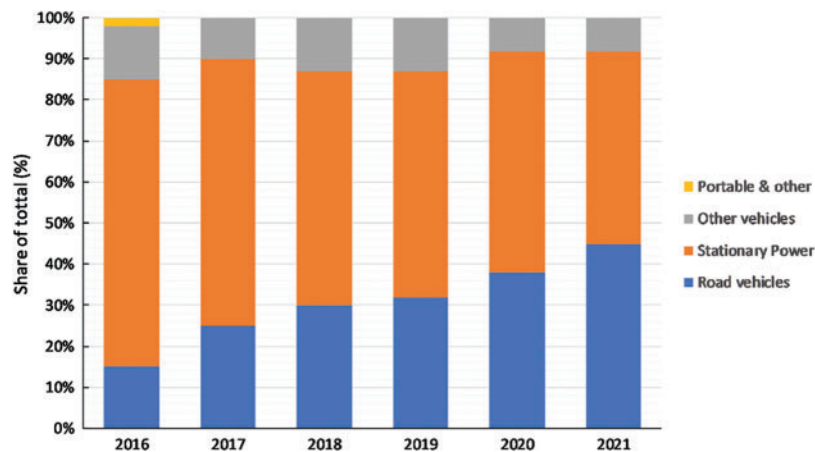

Figure 3: Platinum share in fuel cells demand [47]

On the other hand, Palladium (Pd) is used in fuel cell catalysts to reduce platinum loading. Pd has been tested in fuel cells as Pt co-catalyst [48]. However, the Palladium market still remains on deficit on 2021 with industrial and autocatalyst demand exceeding the needs on primary and secondary supplies [47]. High Palladium prices have fueled active thrifting programs at virtually all global auto markets, starting to rise. Moreover, there is still some scope for near-term growth in PGM loadings in several major markets.

Figure 4: Platinum range price per ounce [49]

Palladium's share of the PGM mix is expected to fall as platinum-containing formulations find wider acceptance. In this respect, the palladium market remained in deficit in 2021, with industrial and autocatalyst demand greatly exceeding combined primary and secondary supplies. In Fig. 5, Palladium's price is depicted, showing that the overall price of Pd is lower in comparison to Pt at the beginning of the previous decade. Worth mentioning that a constant increase is presented in the Pd's price in the last decade, reaching prices higher than Platinum. However, a price drop is highlighted during the second semester of 2021. Considering Fig. 6, some of the industrial applications present significant gains this year, while others have shown a long downward trend. To this extent, electronics sector have decreased the use of Palladium replacing it with Nickel, while the application on chemicals' sector, the utilization of Pd has been increased.

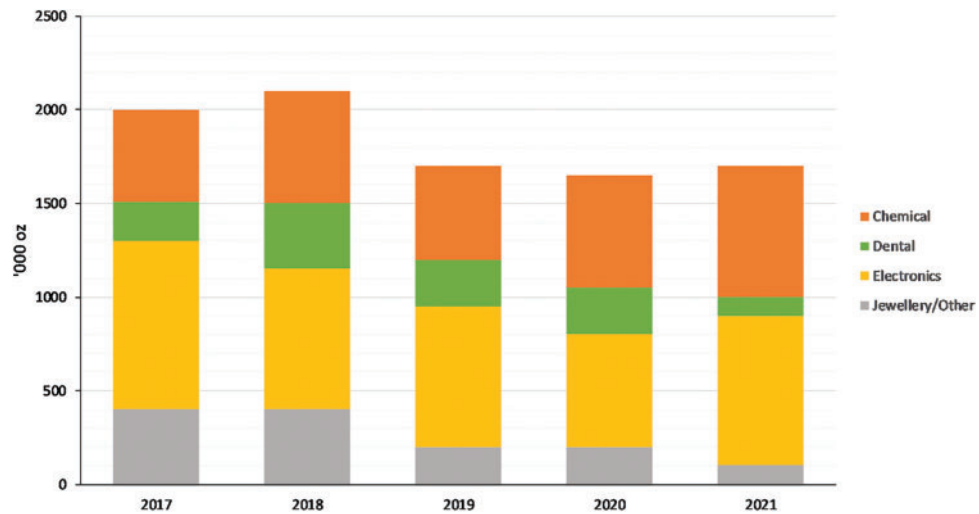**Figure 5:** Palladium range price per ounce [49]

Figure 6: Palladium share in industrial applications [47]

Ruthenium is also one of the most promising materials for reducing the Pt loading on PEMFCs and being a co-catalyst. From a supply point of view, Ru price is at significant low levels considering the high levels of other PGMs such as rhodium (Rh) and iridium (Ir) which may it leads to a future demand for Ru as a suitable replacement for PGMs. In this context in Fig. 7, the Ru price is depicted for the last ~10 years, indicating significantly lower prices compared to Pt and Pd. More specifically, a considerable increase in the Ru price has been highlighted in the last three years but still at a lower levels comparing to Pt and Pd. In Fig. 8, the share of Ru in various industrial applications is depicted, concluding that the overall share of Ru has remain constant the last five years while individual sectors are presenting similar share through the years.
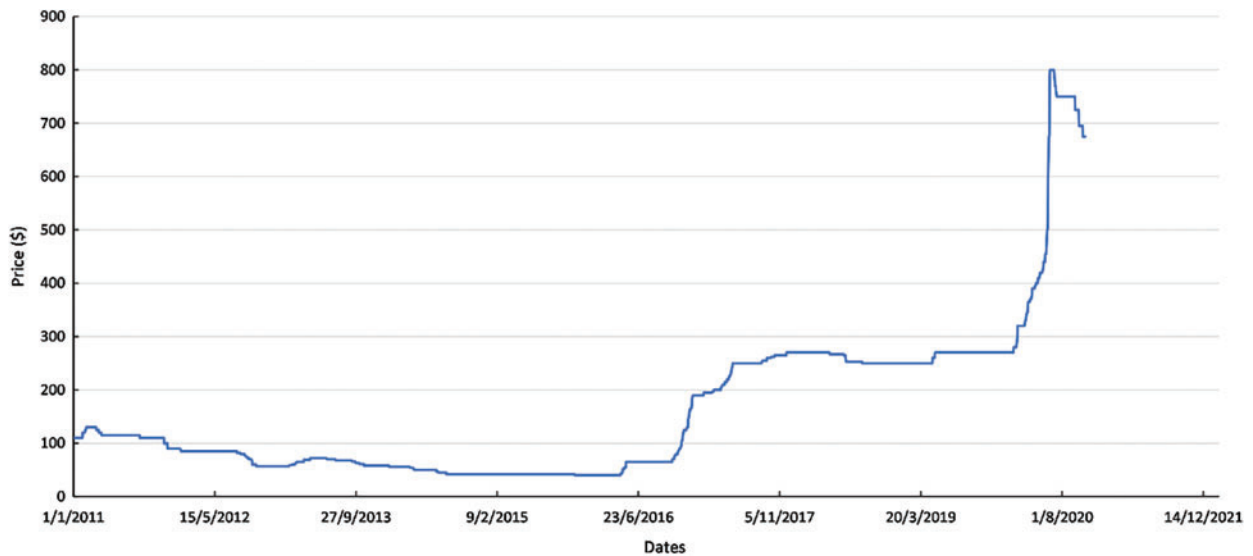

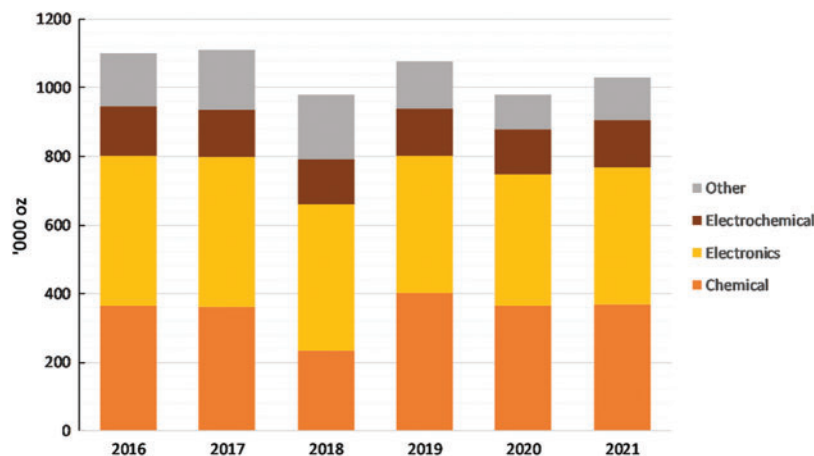**Figure 7:** Ruthenium range price per ounce [49]

Figure 8: Ruthenium share in industrial applications [47]

7 Discussion

In the current work, various studies have been examined to present a clear view of the work done in the specific field towards minimizing the Pt loading and establishing CO tolerant catalyst layers. Thus, the studies are separated into two main categories. The first category concerns those examining the properties of CLs consisting of Pt and Pt alloyed with a noble metal and the second on CLs consisting of Pt alloyed with non-noble metals. The first category is subdivided into the CLs alloyed with Ru, Pd, and Au. For each category, tables with information such as the scope and the conclusion of each study is introduced. The same structure is following for the cases of Pt alloyed with non-noble metals for a comprehensive summary which helps the reader to compare the differences between each case and identify the promising solutions.

In Table 2, the studies concerning PEMFCs with CLs consisting of Pt-Ru are presented. Worth mentioning that a significant effort has been made in the last years to comprehend the benefits of Ru. In all examined cases, Pt-Ru CLs were investigated to evaluate the performance of PEMFC using a different type of CL to minimize the cost and enhance the durability (CO tolerance). Ru can be determined as a poor catalyst being several orders of magnitude less active ($\sim$0.002 A/cm^2 while pure Pt has $\geq$ 0.3 A/cm^2). Due to the significant high catalytic activity of Pt, CLs alloyed with Pt can sustain HOR at a decent level in terms of current density reaching $\sim$500 mA/cm^2 [50]. Overall, Pt-Ru CLs are shown to improve the operation of PEMFCs and can be considered as a viable and promising solution.

Table 2: Studies with Pt-Ru as catalyst layers

Ref.	Authors	Scope	Concluding remarks
[17]	Albers et al.	Examination of a series of PtRu/C catalyst layers via scanning transmission electron microscopy EDX, XRD, and inelastic incoherent neutron scattering.	The study showed that noble metals with different sizes can increase the Pt-Ru ratio and Ru showed to prevent the agglomeration of the platinum particles from retaining smaller particle size.

(Continued)

Table 2 (continued)

Ref.	Authors	Scope	Concluding remarks
[18]	Saeed et al.	Evaluation of PEMFC performance considering the degradation of Pt-Ru/C catalyst layer.	The results showed that the electrochemical reaction that occurs in the Pt-Ru/C catalyst layer presented an obvious degradation. The metals in combination present an increase in the current to less negative values, and others might show a decrease in the current to less positive values.
[19]	Brkovic et al.	Examination of the durability regarding the degradation and poisoning of Pt-Ru/$W_xC_yO_z$ catalysts layer to obtain better performance regarding CO tolerance in relation to other commercial catalyst layers PtRu/C.	The experiments concluded that the best performances were obtained by Pt-Ru/$W_xC_yO_z$ and tested as an anode catalyst in PEM fuel cells. A significant power drop was obtained about 35.3% for commercial Pt-Ru/C and 16% for Pt-Ru/$W_xC_yO_z$.
[20]	Henry et al.	Investigation of the operation of a PEMFC consisting of a catalyst layer from Pt-Ru/C in terms of carbon monoxide tolerance.	Results suggested that within the membrane, the Ru reduction is catalysed by Pt. Moreover, the localization of the precipitation band near the cathode seemed to indicate that the Pt in the precipitates came from the dissolution of cathodic Pt/C and that both Pt and Ru ions were reduced by the hydrogen crossover.
[21]	Chen et al.	Developing, a PEMFC stack consisting of an MEA with Pt-Ru in the anode catalyst layer in order to be examined regarding the CO tolerance.	The results showed that by increasing the CO concentration or by decreasing the H_2 concentration of the CO-contained reformate gas, negatively affects the performance of the PEMFC stack. Moreover, the PEMFC stack with the Pt-Ru anodic catalyst could tolerate a CO concentration of up to 50 ppm under non-diluted H_2.

In Table 3 studies in which Pt-Pd was applied as the main CL in PEMFCs are presented. In all examined cases, the proposed CLs were investigated in terms of durability in CO tolerance and electric activity to verify if the specific type of CL can be a promising solution. Pt-Pd was examined as both anode and cathode CLs for HOR and ORR. The results presented an optimized electrochemical surface area compared to the conventional Pt/C. The electric activity was also enhanced in all examined

cases, confirming that Pt-Pd can provide significant benefits. In general, Pd could partially replace Pt in CLs.

Table 3: Studies with Pt-Pd as catalyst layers

Ref.	Authors	Scope	Concluding remarks
[23]	Zhou et al.	Evaluation of Pt-Pd/C and Pt/C catalysts for ORR under dynamic loading.	The electrochemical active surface area (ECSA) loss, particle size distribution, polarization behavior, and EIS suggested that the Pt-Pd/C showed better durability than Pt/C.
[24]	Cho et al.	Proposal of a new structure of bimetallic electrocatalysts to realize the synergistic effects on the ORR performance through effective integration of the fine-sized Pt NPs, PdPt bimetallic nanocrystals, and non-covalently functionalized graphene with ionic polymers.	This Pt-on-PdPt/fG with synergistic effects based on the enlarged active surface area, ligand, and interfacial linking effects, exhibited substantially enhanced ORR activity (specific activity: 1.89 mA/cm^2 at 0.9 V) compared to the commercial Pt/C (specific activity: 0.23 mA/cm^2 at 0.9 V).
[25]	Carlos Calderón et al.	Investigation of catalyst layers consisting of Pt-Pd supported on carbon black, carbon nanofibers, and carbon xerogels for evaluating their activity towards the ORR.	The Pt-Pd catalyst supported on carbon black showed better activity features toward the ORR in terms of high diffusional current densities, specific and mass activities, number of electrons involved in the reaction, and corrosion resistance.
[26]	Brouzgo et al.	Investigation of Pt-Pd on carbon supports in terms of CO tolerance and durability as both anode and cathode CLs on PEMFCs.	Pt-Pd/C and Pt-Pd$_3$/C presented the highest mass activities, (339.4 and 410 mA/mg$_{Pt}$ at 0.9 V), which were 4 and 5 times higher ascertained in commercial Pt/C (82.75 mA/mg$_{Pt}$).
[27]	Zhang et al.	Investigation of the synthesis of PdPt-based core-shell nanoparticles.	Pd-Pt/C CL compared to Pd-PtNi/C and presented enhanced mass activity, estimated at 1.29 A/mg$_{Pt}$.

(Continued)

Table 3 (continued)

Ref.	Authors	Scope	Concluding remarks
[28]	Bharti et al.	Examination of a CL consisting of Pt-Pd/CNT and prepared via microwave assisted, polyol route in the presence of SDS (Pt-Pd/CNT-S) or CTAB (Pt-Pd/CNT-C). Performance was compared with Pt-Pd/CNT, which was prepared identically without using any surfactant.	The study showed improvement in the catalytic activity Pt-Pd/CNT-S compared to Pt-Pd/CNT-C and Pt-Pd/CNT.

In Table 4 research work done on CLs consisting of Pt-Au is included. As in the previous cases, PtAu were investigated in terms of CO tolerance and the overall enhancement of PEMFCs performance for both anode and cathode CLs. The characterization of the CL was obtained via XPS and TEM techniques. The data provided by the experimental studies were compared with commercially available Pt/C CLs and showed significant improvement on PEMFC's performance. Generally, by taking into consideration the results from the reviewed studies on Tables 2–4, it is obtained that bimetallic CLs are a promising solution solving many issues that are presented in the technology of PEMFCs. Nonetheless, further investigation should be made on a larger scale to identify the performance of PEMFC stacks to achieve a more detailed view of the operation when bimetallic CLs are applied and the drawbacks that could be arise.

Table 4: Studies with Pt-Au as catalyst layers

Ref.	Authors	Scope	Concluding remarks
[30]	Deng et al.	Enhancement of the activity and durability of Pt or Pt based catalysts for ORR in PEMFCs. A series of Pt-Au/TiO_2 NWs catalysts with different Pt/Au/Ti ratios were synthesized.	The optimized $Pt_1Au_1/(TiO_2)_1$ NWs exhibited 4.19 times in mass activity and 2.82 times in SA when compared with commercial Pt on carbon catalyst (20% Pt/C). The stability test showed that the ECSA of $Pt_1Au_1/(TiO_2)_1$ NWs presented an almost 20% decrease, while the 20% Pt/C dropped more than 40% under the same condition.

(Continued)

Table 4 (continued)

Ref.	Authors	Scope	Concluding remarks
[31]	Jiang et al.	Bimetallic Pt-Au nanoalloys were loaded *in-situ* on titanium dioxide in one step by flame spray pyrolysis (FSP).	The *in-situ* DRIFTs and XPS revealed that the electronic synergy effect between Au and Pt weakened the agglomeration of the noble metal and reduced the CO poisoning. This synergy effect made the alloy catalyst's low-temperature catalytic activity to be increased by 20% compared to the single-metal Pt catalyst.
[32]	Lin et al.	Synthesize Carbon-supported Au-Pt core shell nanostructured catalysts and characterization via vis spectroscopy, XPS, and TEM techniques.	The performance of MEA prepared by Au-Pt (2:4)/C as the cathode catalyst in a single PEMFC generated a maximum power density of 479 mWcm^{-2} at 0.431 V using H$_2$ and O$_2$ at 80°C.
[33]	Jeong et al.	Examination of Pt and Au supported on carbon catalysts with various Pt/Au ratios prepared using a reduction method as the cathode in a PEMFC.	The electrocatalytic activity for oxygen reduction was evaluated using a rotating disk electrode system. The results showed that activity and stability dependents on the electrode composition Pt/Au ratio.
[34]	Beltran-Gastelum et al.	Synthesis and evaluation of Pt and Pt-Au nanoparticles supported on reduced graphene oxide (rGO) via reverse micro-emulsion method with metal loading of 20 wt%.	Maximum power density achieved at 20 mW/cm^2 and 70 mW/cm^2 for Pt/rGO and Pt-Au/rGO, respectively, those values increased up to 365 mW/cm^2 when Pt-Au nanoparticles supported on multiwall carbon nanotubes (CNT) was used as a spacer.
[35]	Dorjgotov et al.	Design of small-sized Au-Pt core-shell nanocatalysts with high activity and stability (is a crucial area for a wide range of electronic and chemical devices).	Top-quality power density above 2 W/cm^2 at low Pt loading (0.1 mg/cm^2) was achieved by a bilayer small-size Au-Pt core-shell catalyst with excellent durability over 10,000 cycles by ADT, which is, indeed, beyond the recent DOE targets for a proton exchange membrane fuel cell system.

Table 5: Studies with Pt/C as catalyst layers

Ref.	Authors	Scope	Concluding remarks
[36]	Chen et al.	Examination of Pt mass transfer loss and reducing the performance of PEMFC under low humidity and high current densities.	The results indicated that the performance of MEA can be significantly improved via allocating more Nafion and Pt/C in the sublayer near the membrane in the cathode CL.
[37]	van Dao et al.	Study of structural catalyst electrode of Pt/C consisting of double catalyst layers.	Improved electrochemical performances of double catalyst layer electrodes was observed due to the advantages of separating Pt catalysts into two layers, which provides more Pt catalytic active sites to the electrolyte than those in single catalyst layer electrodes.
[38]	Fan et al.	Studying of the degradation characteristics of PEMFCs with Pt black and Pt/C catalyst after 100 h of operation by electrochemical techniques and morphological characterization methods.	According to SEM, TEM, and XPS results, the decay of Pt black catalyst was mainly caused by Pt agglomeration and oxidation, causing a higher ohmic resistance, higher mass transfer resistance, and severer degradation of performance.
[39]	Ostraverkh et al.	Studying thin-film Pt catalysts with ultra-low metal loadings (ranging from 1 to 200 $\mu g/cm^2$) prepared by magnetron sputtering onto various carbon-based substrates. Performance of these catalysts acting as an anode, cathode, or both electrodes in PEMFC was investigated in H_2/O_2 and H_2/air mode.	The results were compared with a series of benchmark electrodes made from commercially available state-of-the-art Pt/C catalysts. It was demonstrated that the platinum utilization in PEMFC with magnetron sputtered thin-film Pt electrodes could be up to 2 orders of magnitude higher than with the standard Pt/C.
[40]	Samad et al.	Studying carbon and other platinum-supporting materials as electrode catalyst components of low temperature fuel cells.	All the examined catalyst support materials reviewed were considered to be promising, high potential candidates that may find commercial value as catalyst support materials for fuel cells.

Tables 2–5 present studies investigating CLs composed with Pt and additional noble metals such as Ru, Au, Pd, considering also the conventional cases of Pt/C CLs. For each case, the catalyst composition and the corresponding results regarding the experimentally measured performance are presented commercially available electrodes, with typical composition of Pt/C. Concluding remarks are briefly described in each case and also summarized below. Study [21] showed that increasing the CO

concentration or decreasing the H_2 concentration of the CO-contained reformate gas can negatively affect the PEMFC stack's performance. Moreover, the PEMFC stack with the Pt-Ru anodic catalyst can tolerate a CO concentration of up to 50 ppm under non-diluted. Furthermore, study [24] examined the case of Pt-Pd and compared it with Pt/C electrodes. Auspicious results were presented, indicating a catalytic enhancement activity around 8.2 times to Pt/C catalysts. The new electrode composition delivered 1.89 mA cm_{Pt}^{-2} while the conventional electrode produced 0.23 mA cm_{Pt}^{-2}, measured at 0.9 V. In addition, study [30] examined the use of Au compared to a conventional catalyst having a composition of 20% Pt/C. Significant good results were presented, indicating an enhancement in mass activity around 4.19 times and 2.82 times regarding the specific activity. However, should also be considered, except for the significantly improved catalytic properties, is the high cost of Au. Study [39] examined Pt/C catalysts with ultra-low loading to settle the optimum point in terms of loading in both anode and cathode catalyst layer sides. Their results showed that loading range between 2–8 μg Pt per cm^2 on the anode catalyst and 30–50 μg Pt per cm^2 on the cathode catalyst proved to enhance the overall performance of the PEMFC.

The application of non-noble metal as CLs in PEMFCs could help the sustainable commercialization of the technology. Regardless of the various challenges, such as the catalytic activity and the poor stability, non-noble metals are an attractive and promising solution with a lot of interest being focused on the last years. Non-noble metals are in abundance and significantly low cost. To this extent, in Table 6 the case of Pt alloyed with non-noble metals is presented, describing the scope of each study and the corresponding results.

Table 6: Pt-non noble metal CLs

Ref.	Authors	Scope	Concluding remarks
[42]	Beermann et al.	Study of the properties of Pt-Ni alloy nanoparticles.	The catalytic activity was estimated ∼25 times higher than commercial Pt/C (2.7 A mg_{Pt}^{-1} measured at 0.9 V).
[43]	Nigel et al.	Investigation of Pt-Ni CLs by controlling the ratio between Pt and Ni.	The study showed ∼10 times higher and ∼6 times higher mass activity for ORR compared to commercial Pt/C. Mass activity: 0.98 A/ mg_{Pt}; Specific activity: 1.5 mA/cm^2.
[44]	Hennining et al.	Investigation of unsupported Pt-Ni alloy aerogel CL in PEMFC.	The results showed that the optimized CL had 2.5 larger surface specific ORR activity than Pt/C.
[45]	Kim et al.	Introduction of a Pt-Cu alloy thin film CL.	Pt-Cu/MPL presented 2 times higher current density than commercial Pt/C (24 A cm^{-2}_{Pt}).

(Continued)

Table 6 (continued)

Ref.	Authors	Scope	Concluding remarks
[46]	Ohyagi et al.	Examination of the durability of a carbon supported Pt-based Co alloy catalyst (Pt–Co/C) during voltage cycling tests under supersaturated humidity conditions to simulate events such as flooding.	The results showed that the ECSA for PtCo/C decreased more slowly than Pt/C CL during the test, with an initial ECSA at 62% and 37% for Pt-Co/C and Pt/C, respectively.

Studies [42–44] investigated Pt-Ni catalysts. In all three cases, Pt-Ni catalysts showed significantly enhanced results compared to conventional Pt/C catalysts. Moreover, these catalysts can be more efficient for ORR, as presented in Table 6, showing significantly improved mass and specific electrochemical activity. In more detail, study [42] concluded that Pt-Ni catalysts could provide an enhanced catalytic activity around 25 times in relation to common Pt/C electrodes. Study [43] focused on ORR's performance in Pt-Ni catalysts. The results showed that specific activity was ~10 times higher and ~6 times higher mass activity for ORR compared to commercial Pt/C. Additionally, study [44] investigated Pt-Ni aerogel CL in PEMFC. The results showed an increased specific surface by 2.5 for ORR compared to conventional Pt/C. Study [45] investigated Pt-Cu catalysts which presents 2 times better catalytic activity in relation to Pt/C electrodes. The under-examination electrode produced a current density of 59 A cm^{-2} at 0.6 V, while the Pt/C electrode produced 24 A cm^{-2}. Study [46] examined Pt-Co/C catalysts in terms of durability. The results showed that the electrochemical surface area was decreasing at a lower rate than the Pt/C catalysts.

Last but not least, it should be mentioned that additional research should be conducted in all the aforementioned CL cases to examine the performance of PEMFCs as an integrated system and not only the performance of specific catalyst layer compositions. This could lead to additional challenges that should be resolved while, at the same time, more conclusions on the behaviour of PEMFC in terms of both electrochemical and transport phenomena will be drawn. Nonetheless, the cost of producing state-of-the art CLs was presented. In Chapter 6 the economic trends of the most studied noble metals is showed by presenting the price fluctuations during the last decade. Pt remains at a higher prices compared to Ru and Pd. Thus, the need to turn into more economically viable materials is a priority for the technology of fuel cells. Worth mentioning that in the studies above, the cost of construction of CLs hasn't been considered. To this extent, the cost of constructing new electrode compositions should be further examined to enable commercial feasibility.

8 Conclusion

To sum up, an increased interest has been raised for PEMFCs in the last few years, leading to novel approaches and significant breakthroughs in material properties. The CL compositions examined in the present work seem to be ambitious. Numerous studies have investigated Pt with noble metals and Pt-free CLs. Most of them consider carbon support, with fewer studies on non-carbon materials. Furthermore, the significantly high cost of Pt has been a major limitation for years. The reduction

of Pt loading on cathode loading without decreasing the durability and the overall performance of PEMFC remaining a demanding task. Another major problem in PEMFCs is the activation losses presented on ORR. Several studies have been focused on optimizing the ORR catalytic activity by alloying Pt with other noble metals, presenting encouraging results. In this respect, they reduce the Pt loading using transition metals such as Ni, Co, Ru, Au, etc. Moreover, the reduction of Pt loading can lower the overall performance of fuel cells, but the presence of modified carbon support can create stronger metal support and thus could maintain the durability and the corresponding catalytic activity of PEMFC, even under reduced Pt loading. Future work that should be done can be separated into four levels: (1) minimizing the cost of synthesis of state-of-the-art CLs which can help to accelerate fuel cell commercialization, (2) develop an efficient synthesis that can lead to a high electrochemical surface area, emphasizing on parameters such as metal weight ratio and temperature should be highlighted, (3) research on molecular modelling provides an insight view of the phenomena and the interactions between the metal catalyst and its support and investigates the morphology of the CL, the active sites, and the corresponding electronic structure and conduction, (4) enhance the research on macroscopic modelling of PEMFC including all the information from the molecular modelling to examine PEMFCs as an integrated system and identify how the changes in CL affect the overall operation.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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