

Nanostructured Pt-based catalysts for Oxygen Reduction Reaction in alkaline media

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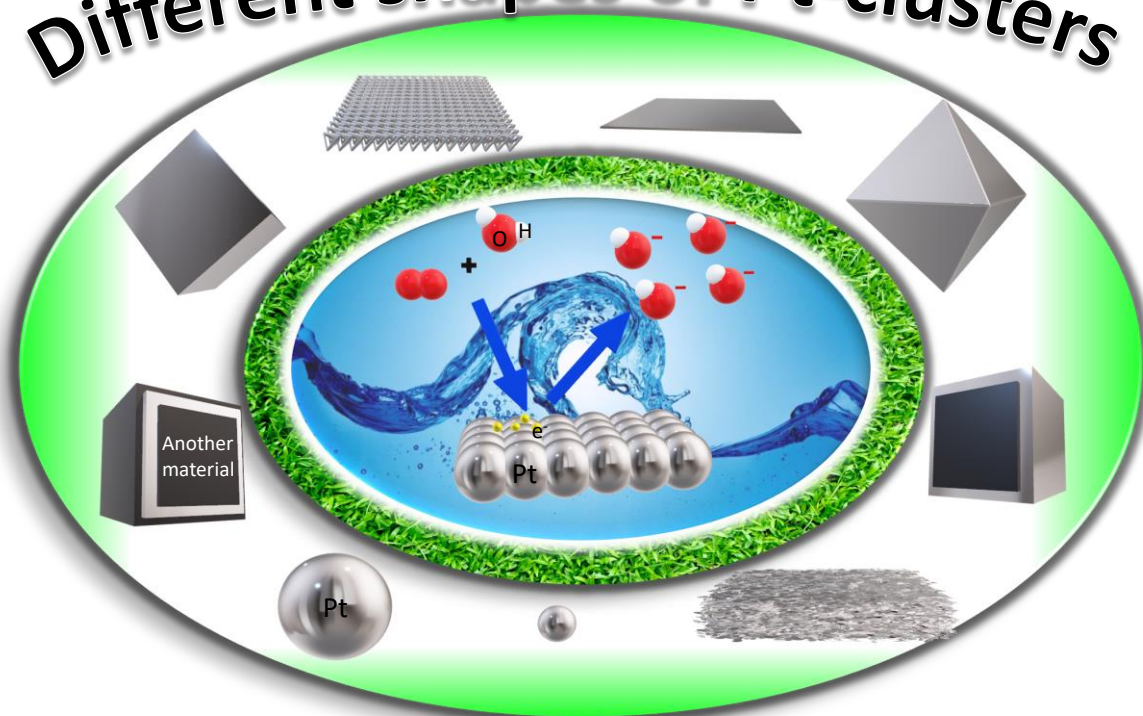
nanostructured Pt, nanoparticles; Pt clusters, Oxygen Reduction Reaction, decorated Pt alloys

Highlights:

- Nanostructured Pt with active behaviour for Oxygen Reduction Reaction
- Pt-based nanoparticles for ORR with low amount of precious metal
- ORR in alkaline environment on Pt-based cluster electrodes

Graphical Abstract

Different shapes of Pt-clusters



Abstract

The concern about global warming bound to CO₂ emissions has shifted the attention of the scientific, industrial, and social communities from the mere use of cheap and abundant energy sources to the exploitation of renewable energies and the expansion of the relevant transmission network.

Within this frame, H₂ is progressively assuming the role of preferred energy vector thanks to i) its abundance, it is possible to obtain from water (photo-)electrolysis; ii) its “combustion products”, water, without any other by-product when used in Fuel Cells. In this review, the attention is focused on Pt-based electrocatalysts, in term of chemical composition, morphology and size with the aim of reducing the content of the precious metal, used to prepare electrodes for the Oxygen Reduction Reaction in alkaline media.

1. Introduction

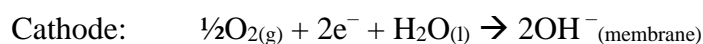
H₂ become fundamental for an efficient exploitation of renewable sources of energy, like wind and solar, that are variable in time and not-well distributed on the planet. To fully take advantage of the renewable energies, it is necessary to convert them into H₂ by means of (photo-) electrolysis of abundant reactant as water. In this frame “hydrogen economy” [1–8] is considered as an effective method to reduce or completely avoid the necessity of fossil fuel [8]. But this “new paradigm” asks for a versatile, powerful, and low-cost device to convert H₂ in electric energy. Fuel Cells (FC) can accomplish very well this task, but, still now, some component must be optimized for a long lasting and stable performance [6,9–11]. Main issues are still connected with the sluggish Oxygen Reduction Reaction, ORR, also when alkaline media has been used, especially when non-Pt Group Metal (PGM) catalysts have been used. On this topic two mainstream can be individuated: researchers devoted to study Pt-free catalysts for ORR in alkaline medium [12], thus decreasing the cost of the materials but, very often, renouncing to increase the performance of the device; researchers still working with PGM [13,14], but with the aim to reduce the total amount of the precious metal, increasing its activity by acting on morphology and surface decoration, e.g. synthesizing nanostructure with high surface area. Finally, it must be highlighted the possibility of Reversible Fuel Cells, devices that can operate in dual mode: when sun or wind is present the device can act as electrolyser, thus producing H₂; when renewable sources are absent, device can be used as fuel cell, thus generating electricity burning the stored H₂. For this purpose, electrodes where oxygen can be produced or consumed must be formed by materials which possess high performance for both the electrochemical reactions: ORR and OER. In this context, PGM are actually the best electrocatalytic materials, but the amount of precious metal must be reduced for economy issues.

1.1 Fuel Cell (FC)

Fuel cells are primary cells in which hydrogen and oxygen (as pure oxygen or air) are continuously fed to the anodic and cathodic compartments, respectively, to convert the chemical energy into electrical energy [15–20]. This device implies a triple contact between the electrode, the gas, and the electrolyte. When the two reactant gasses reach the catalysts on the electrodes, the exchanged electrons must be transferred from the catalysts to the current collectors that are connected to the external circuit and at the same time the electrolytic species, produced by the reaction, must be exchanged through the membrane located between the electrodes. Diverse types of fuel cells are already available or still under study:

- a. The *Proton Exchange Membrane Fuel Cell (PEMFC)*
- b. The *Phosphoric Acid Fuel Cell (PAFC)*
- c. The *Molten Carbonates Fuel Cell (MCFC)*
- d. The *Solid Oxide Fuel Cell (SOFC)*
- e. The *Alkaline Fuel Cell (AFC)*
- f. The *Anionic Exchange Membrane Fuel Cell (AEMFC)*

This review focuses the attention on the very new electrocatalytic materials to be employed as cathodes in the AEMFCs, whose the two electrode semi-reactions can be written as follows:



This type of cell offers several potential advantages over the mature PEMFC [9,11], even if they still suffer for some drawbacks: the poor stability of the anionic membranes and the cost and stability of the cathode electrocatalytic materials, but the promising advantages have made the AEMFC an attractive energy converter [11].

1.2 Oxygen reduction reaction (ORR) mechanism in alkaline environment

This cathodic reaction in both alkaline and acidic media leads to the formation of many different intermediate, physical or chemical adsorbed also, oxide products such as O, OH, O₂⁻, HO₂⁻ and H₂O₂, thus rendering difficult the determination of the true reaction mechanism that is still under debate. In any case, at least two types of mechanism can be individuated [21–23]:



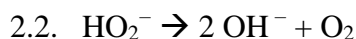
it is a four-electron reaction in which oxygen undergo a complete reduction to hydroxyl ions.



followed by:



or by a disproportionation reaction of HO_2^-



The second scheme is formed by two-electrons reactions in which oxygen undergo a partial reduction forming the HO_2^- as intermediate of the reaction that are successively reduced. Both schemes are characterized by a low reaction rate even if they are carried out in alkaline medium, thus asking for a precious metal, as Pt, to increase the kinetics. For this reason, all over the world researchers have been involved in a run to reduce or completely avoid the use of Pt [6,21,22,24,25].

1.3 Platinum as Catalyst for ORR

Pt and Pt-based catalysts are the most commercially electrocatalyst materials used to prepare ORR electrodes for the cathode of FCs, due to its highest catalytic activity and stability [26]. But the use of Pt and Pt-based catalyst has some problems that are not only correlated to the high price and low abundance of the selected material. These problems are:

- 1- Pt is sensitive to NO_x , SO_x and especially to CO and CO_2 . The atmospheric oxygen as fuel in FC is mandatory for the automotive applications, for example because this allows for the reduction of weight and volume of the energy converter. But the poisoning decrease activity and durability of catalyst loaded on the electrodes [27].
- 2- On Pt occur not only 4-electron reaction but also the 2-electron reactions that produce oxidant intermediate which cause the corrosion of the electrode, leading to the detachment of Pt from the conductive support or the corrosion of the support and other important part of the FC [28].
- 3- The kinetic of ORR is slower than that of HOR and cause a higher overpotential on anode respect to the cathode [10].

Hence, in the years, the object of the research correlated to the use of Pt-based catalyst is devoted to increase both the mass activity (MA) of the catalyst, in term of $\text{A} \cdot \text{g}_{\text{Pt}}^{-1}$, to reduce the amount of Pt on the FC positive electrode and the stability of Pt electrocatalysts by finding new method to disperse and anchor precious metal, with the scope of increasing durability by decrease the corrosion [6,29]. Also, the use of nonprecious metal has been investigated in recent years [9,12,16,30,31], but Pt remains the best electrocatalytic metal to facilitate the ORR, as can be underline by the volcano plot in Figure 1 [26] and the relevant discussion.

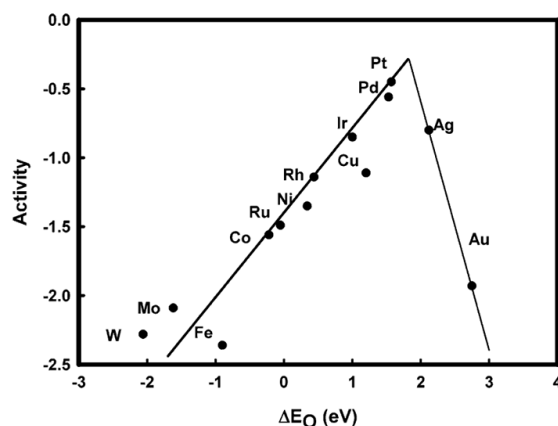


Figure 1. Trends in oxygen reduction activity plotted as a function of the oxygen binding energy [26].

This review intends to present and discuss some very recent papers on the possibility of both to reduce, increasing the activity, Pt micro- or nano-powder as catalytic materials for ORR electrodes in alkaline FC and to disperse or anchor the Pt particles, by modifying the synthesis procedure, on the carbonaceous support for new ORR electrodes.

2. Nanoscale structure design of Pt

In the ORR process, the exposure of Pt active sites plays a vital role. For example, a Pt cube of 20 nm has only 6% atoms on its surface, while if the cube side length is reduced to 3 nm, the atoms located on the cube surface are 6 times higher than that of 20 nm cube [32]. Nanostructured metal particles present very often, due to the large number of unsaturated exposed surface atoms, both a high electrochemically active surface area (ECSA) and a high MA. Moreover, to reduce the usage of Pt, controlling the morphology and exposing more Pt atoms is a promising method [24]. Fan et al. synthesized 2D Pt nanosheets with high porosity via a facile NaCl templated methods. As a result, porous Pt nanosheets possessed a specific activity of $5.09 \text{ mA}\cdot\text{cm}^{-2}$ at 0.9 V, which is 1.8 times larger than that of commercial Pt black in alkaline medium [33]. In any case, 1D Pt based nanostructures have the preferential exposure of the reaction crystal surface, and high electron transfer rate, which can improve the performance of fuel cells. Zhang et al. reported Pt cubic and octahedral nanocages enclosed by {100} and {111} facets, respectively. The ECSAs of the cubic and octahedral nanocages only dropped by 13 and 6% after 5000 cycles and by 32 and 23% after 10,000 cycles, respectively [34]. Besides, the Pt octahedral nanocages showed the best performance with the ORR mass activity, which is in accordance with the previous reported observation that the dynamics of ORR on different Pt(hkl) surfaces follows the rule: Pt (100) < Pt (110) < Pt (111) in alkaline medium [34–37]. As a result, optimizing the Pt structure led to a more Pt atoms exposed and reduced the usage of Pt and improved electrocatalytic activity.

3. Pt cluster-based catalyst

By controlling the synthetic approaches, it is possible to finely tune the size of Pt nanoparticles from a few to hundreds of nanometers. The smaller particles have larger surface areas and higher MA than larger ones. However, the ORR activity decreases when the Pt size is less than 2 nm. These very small particles present a larger number of edges and vertices that interact very strongly with O/OH species, leading to a kind of surface poisoning [38]. Thence, synthesizing subnanometer Pt clusters can avoid the poisoning of the metal and allow for a better control of the particles size. In our previous work, we prepared Pt molecular metal clusters based on CO-ligated Pt compounds with different sizes and structures, then the carbonyl ligands were removed by thermal treatment. The obtained Pt cluster size was about 0.5 – 2 nm and it showed the highest MA of 0.225 A·mg_{Pt}⁻¹ at 0.9 V vs RHE since the very low particle size and their high strain and defect density enhanced electrocatalytic properties [39]. The sized of Pt cluster not only influences the electrocatalytic activity of the obtained electrode incorporating the clusters, but it turned out also to be an important physical parameter for the powder stability and, thus electrodes durability, as evidenced also in acidic media. Imaoka et al. [40] constructed a series of Pt cluster (from 12 to 60 atoms of Pt) and electrochemically characterized these clusters for the ORR in acidic media. The results, presented in Figure 2 highlighted that Pt₁₇ and Pt₁₉ exhibited higher electrocatalytic performance than the other series, because Pt₁₇ and Pt₁₉ clusters possessed highly active sites, which were mainly located on the two sides of each sharp edge of the specific clusters. In conclusion, the modification of the atom number affected the atomicity-specific structures of platinum clusters and the ORR performance changed dramatically. Figure 2 refers to the characterization carried out in acidic environment, but we believe that a similar behavior can be expectable in alkaline medium, as evidenced from the very recent results obtained by Fracchia et al. [39].

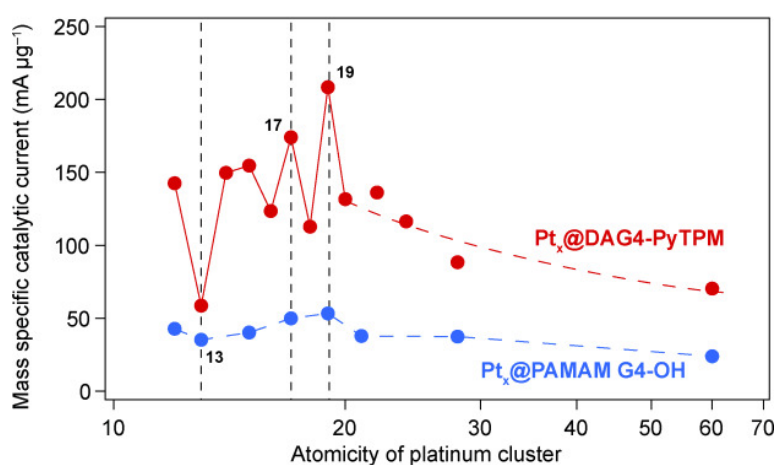


Figure 2. Variations of the mass-specific catalytic current versus the atomicity of the platinum clusters. Measurements were conducted under oxygen saturation in an acidic aqueous electrolyte (0.1 M HClO₄) [40].

4. Compositing Pt with metal

To face the problem of both cost and scarcity of Pt, mixing it with another 3d transition metals to form Pt-M composite electrodes, where M denotes transition metals with high oxygen affinity, *e.g.*, Mn, Co, Ni, Cu, Pd and Fe *etc.*, has been also carried out. These composite materials: alloys, intermetallic compounds, core shell particles, promise unprecedented electrochemical properties, also generated by possible synergistic effects between the noble and 3d transition metals.

4.1 Alloy

It has been already highlighted [41] that Pt-M alloys are able to address the production of the ORR radicals toward low energy pathways, thus leading both to a time reduction of the chemical intermediates adsorbed on the surface of the electrocatalyst and to an increasing of the reaction rate. Finally, the dilution of Pt with these low-cost metals allowed for a total reduction of the material costs to prepare an active cathode [41]. In addition, DFT analysis highlighted that Pt-M alloy present a lattice contraction, witnessed by a shift of the Pt *d*-band center downward, thus speeding up the ORR due to the weakening of the bond between the alloy surface and the adsorbed oxygenated intermediates [42].

4.2 Intermetallic compounds

Already in 2007, Markovic et al. reported that Pt₃Ni(111) was 10 and 90 times more active for ORR than the Pt(111) and Pt/C catalyst, respectively [43], due to the energetic position of the *d*-band and the Pt surface enrichment of the intermetallic compound. On the contrary, how to improve the performance of PtNi, in term of high activity, durability, and stability thus reducing the usage of Pt, is still under investigation.

4.3 Core shell nanoparticles

Zysler et al. prepared ultralow platinum Pt@Ni@Pt core–bshell nanorods (less than 1 wt % of Pt) via a solvothermal reaction, with a very good control of the thickness of the octahedral Ni shell on the Pt cores (Pt@Ni) or nanorods (Pt@Ni@Pt). The structure is presented in Figure 3.

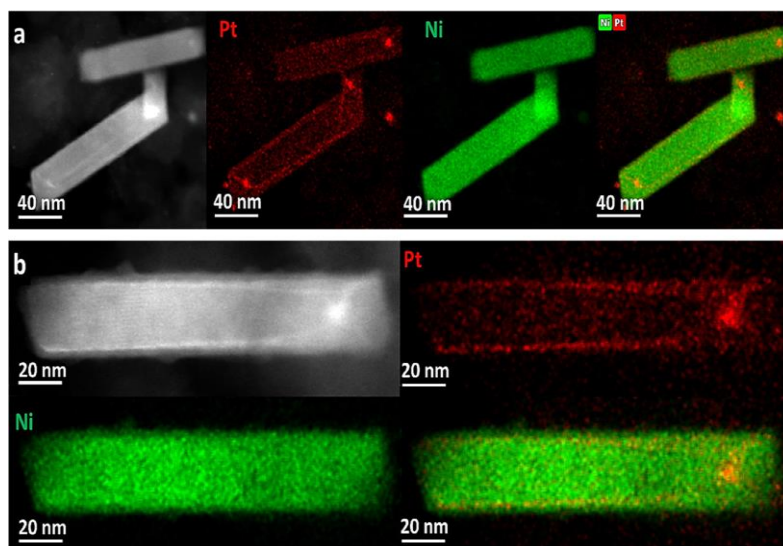


Figure 3. HAADF-STEM and elemental mapping for selected $\text{Pt}_P@Ni_{XL}$ particles (platinum = red, nickel = green). (a) low-magnification and (b) high-magnification selected particle [44].

As a result, Pt@Ni@Pt maintained a very high MA value of $0.32 \text{ A}\cdot\text{mg}_{\text{Pt}}^{-1}$ at 0.85 V for the ORR [44]. Soto-Pérez et al. also constructed PtNi-Nanowire by a solvothermal reaction and loaded it on Vulcan (PtNi-NWs/V), and PtNi-NWs/V provided the highest specific activity with logarithmic values of 0.707 and $1.01 \text{ (mA}\cdot\text{cm}_{\text{Pt}}^{-2})$ at 0.90 and 0.85 V vs RHE, respectively. Meanwhile, the durability test showed that the performance loss of PtNi-NW/V was like that of a commercial Pt/V after 10,000 cycles [45]. The Pt based multi-metallic nanoparticles can also be synthesized through Under Potential Deposition (UPD) replacement, electrochemical de-alloying, reaction-driven process [46] and hydrothermal methods [47], which allow for a fine control of the nanoparticles structure and size, thus leading to form cathodes with very different performance. Some nanostructured Pt-based catalyst are listed in Table 1, with the relative features.

Moreover, many other researchers created ternary metallic composite materials to improve the performance of Pt based catalysts for ORR. Chen et al. synthesized a ternary metallic CuPdPt nanocatalyst (NC) via a wet chemical reduction method. They used Cu@Pd as the core of the above atomic Pt clusters, that formed a shell. The obtained Cu@Pd/Pt has been tested for almost 40,000 cycles and the synthesized powder still maintained a very high electrocatalytic activity, evidenced by a residual current of 92.6%, 5.2 times higher than that of commercial Pt catalysts, at 0.85 V vs. RHE. Authors explained this extraordinary activity due to both the electron localization on Pt clusters together with the lattice compression in the near-surface region of the Pd, and the substantial electron injection from Pd to Pt atoms [48]. Furthermore, other Pt-based ternary metallic composites were synthesized to reduce the usage of Pt and improve the performance in ORR, such as $\text{PtNi}_{0.55}\text{Co}_{0.1}/\text{C}$ [49], $\text{Pt}_{37}\text{Cu}_{56}\text{Au}_7$ porous film [50], $\text{Pt}_{\text{ML}}/\text{Pd}_9\text{Au}_1/\text{C}$ [51], PtPdIr [52], which can modulate the oxygen

binding energy, weakening it in comparison with to the Pt (111) surface, of the Pt-based catalysts [53].

Table 1. ORR performance for different nanostructured Pt-based catalyst in alkaline conditions

Samples	Structures	Mass activity $A \cdot mg_{Pt}^{-1}$	Current density $mA \cdot cm^{-2}$	Reference
Pt ₃₇ Cu ₅₆ Au ₇	Porous film	0.871	–	[50]
Pd ₃ Pb@Pt ₃ Pb	Nanocubes	4.69	6.69	[54]
CuPt-NC	Nanocage	0.32	0.47	[47]
PtNi/C	Octahedral	0.70	–	[55]
Pt ₃ Cu	Particles	0.12	–	[56]
Pt/C (HiSpec 4000, 40 wt % Pt)	NanoParticles	0.15	0.097	[57]
Pt/CaMnO ₃	NanoParticles	0.38	1.06	[57]
Ag-Pt-Ag	core-shell-shell nanocubes	0.00108	–	[58]
Ag-Pt	core-shell nanocubes	0.0033	–	[58]
Pt-coated Pd	core-shell nanocubes	–	0.708	[59]
Pt	Nanoparticles	–	0.272	[59]
Pt/ITO	NanoParticles	0.825	5.2	[60]
Commercial Pt/Vulcan 37.5% wt	\	0.376	6.5	[60]
Pt ₂₉ Pd ₅₉ Ni ₁₂	NanoSheet	0.25	–	[61]
Pt ₃₂ Pd ₄₈ Ni ₂₀	NanoSheet	0.54	–	[61]
Pt ₂₈ Pd ₃₇ Ni ₃₅	NanoSheet	0.28	–	[61]
Commercial Pt/C	\	0.11	–	[61]
Pt ₃₂ Pd ₆₈	NanoSheet	0.33	–	[61]
Pt ₃₀ Pd ₅₀ Fe ₂₀	NanoSheet	0.27	–	[61]
Pt ₃₄ Pd ₄₄ Co ₂₂	NanoSheet	0.4	–	[61]
Pt(Mn, Al) ₃ O ₄	NanoSheet	0.46	–	[62]
Pt/C 40% w (Johnson Metthey)	\	0.04	–	[62]
Pt ₃ Ni/C	Nanoparticles	0.352	–	[63]
Pt/Ti ₃ C ₂ T _x	Nanoparticles	–	1.32	[64]
Commercial Pt black	\	–	2.83	[33]
Commercial Pt nanochains	Nanochain	–	2.2	[33]
Thick Pt nanosheet	Nanosheet	–	3.9	[33]
Porous Pt nanosheet	Nanosheet	–	5.09	[33]
Pt _{3.5%} NiPF	Porous film	0.268	–	[37]
Pt/C carbon nanotube	cluster	0.067	–	[41]
CuPP-03 (PP= PtPd)	Decorated cluster	0.408	–	[41]
CuPP-02 (PP= PtPd)	Decorated cluster	0.498	–	[41]
CuPP-01 (PP= PtPd)	Decorated cluster	0.639	–	[41]
Pt/C reference	Nanoparticles	0.054	0.555	[44]

PtS@NiS	Core shell nanoparticles	0.002	0.012	[44]
PtM@NiM	Core shell nanoparticles	0.019	0.172	[44]
PtL@NiL	Core shell nanoparticles	0.001	0.003	[44]
Pt@NiXL	Core shell nanoparticles	0.029	0.023	[44]
PtNi-NWs	Nanowires	0.133	0.023	[45]
PtNi-NWs/V (V= Vulcan)	Nanowires	0.446	0.071	[45]
PtNi-NWs/V-NH ₃ (V= Vulcan)	Nanowires	0.337	0.001	[45]
Commercial Pt/V (V= Vulcan)	Nanoparticles	0.696	0.090	[45]

5. Conclusion and perspectives

In past years, a huge number of research groups has made great progresses in preparing composite cathodes for ORR, finely tuning size, shape, and morphology in order to reduce more and more the amount of the very effective and active but costly Pt, especially when cathodes are used in acidic environment. It seems that less interest has been addressed to the preparation and characterization of similar composite materials for ORR in alkaline media. The present review has been focalized on this niche aspect: the synthesis of composite Pt-based cathodes, tuning shape, and morphology to reduce Pt amount and, at the same time, increasing the cathode electrochemical activity for ORR in alkali. In this framework, also the possibility of increasing electrocatalytic activity, by alloying Pt with other metals, has been faced by discussing some very recent papers. In any case, for this review only a part of the many methods used to reduce the amount of Pt have been presented and discussed. In summary, we found that the main goal many Authors can claim is the possibility, tuning the synthesis by means of different methods, to nanostructure Pt surface with high electroactive crystal phase or planes, thus leading to a real reduction of the amount of precious metal loaded in the electrode, still maintaining the electrochemical performances. Some Authors have reached similar results mixing the Pt with less noble and costly metals, evidencing, in some cases, synergistic effects between Pt and the alloying metals.

The perspectives for the worldwide research groups working in this field are clearly defined by the comments and discussions present in the papers herewith cited. Moreover, with the aim of promoting a real hydrogen economy, we believe that the real goal is the investigation of new devices able to convert the energy in a dual mode: as electrolyzer when renewable sources are exploitable as generator when wind and/or sun are not available. In this context, the electrode composite materials for ORR and OER in alkaline media must contain, at least up to now, Pt. Hence, the issue is to reduce the Pt amount in the electrode using methods described in the literature herewith cited. We believe in the possibility of decorating Pt surface, thus increasing its activity while reducing its quantity, and of mixing Pt with less costly metals. Fe, eco-friendly and abundant

metal on earth, can be a good candidate to dilute Pt in the electrode but its low stability in alkali leads to problems of durability of the devices and this phenomenon must be still better investigated. In principle, it could be possible that mixed clusters of Pt and Fe lead to long stability and high activity of electrodes for ORR and OER in alkali. Research group should take this path to rapidly verify these possibilities. Furthermore, Pt diluting metals already successfully tested in acidic environment for ORR and OER should be also investigated in alkaline media to verify the possibility of their usage. Moreover, nanostructured mixed Pt must be better stabilized onto the support surface, to avoid its dissolution and degradation. One solution can be the use of pre-treated or pre-shaped carbonaceous support as: activated carbon, graphene carbon, carbon nanotubes, etc. Finally, the possibility to regenerate or to reuse the Pt inserted in a cathode for ORR in alkaline media should be deeply scouted. This will allow to compensate for the scarcity and the cost of this noble metal.

Conflict of interest

None.

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* Paper of special interest

** Paper of outstanding interest

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This review presents a critical vision of the current state of the arts of hydrogen production to use as an energy vector, comprising its storage technologies, de-mand market, and economics aspect.

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This review reports the recent advances in metal-based catalysts for ORR that are fundamental for some Fuel Cell technologies. It reports also structural properties, synthesis methods, performance characterizations, and mechanisms.

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This review presents the fundamentals of electrocatalysis in alkaline media and applications in alkaline-based energy technologies from different aspects in detail, including structure of catalyst, the mechanisms in ORR and so on.

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In this work, the authors introduce the use of molecular metal clusters as precursors for the in-situ formation of nanoparticles with a high activity and surprising stability as electrocatalysts in energy conversion. And this article explains well about the relationship between the structure of Pt cluster with the performance.

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This paper provides new view to understand the relationships between the composition of a material and its structure and properties, which is a fundamental objective and a key challenge in nanoscience research.