

Controlling the mixed potential of polyelectrolyte-coated platinum electrodes for the potentiometric detection of Hydrogen Peroxide

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Abstract

The use of a Pt electrode coated with a layer of Nafion has been described in previous works as an attractive way to perform the potentiometric detection of hydrogen peroxide. Despite of the attractive features of this approach, the nature of the non-Nernstian response of this system was not properly addressed. In this work, using a mixed potential model, the open circuit potential of the Pt electrode is shown to be under kinetic control of the oxygen reduction reaction (ORR). It is proposed that hydrogen peroxide acts as an oxygenated species that blocks free sites on the Pt surface, interfering with the ORR. Therefore, the effect of the polyelectrolyte coating can be understood in terms of the modulation of the factors that affects the kinetics of the ORR, such as an increase of the H^+ concentration, minimization of the effect of the spectator species, etc. Because of the complexity and the lack of models that accurately describe systems with practical applications, this work is not intended to provide a mechanistic but rather a phenomenological view on the problem. A general framework to understand the factors that affect the potentiometric response is provided. Experimental evidence showing that the use of polyelectrolyte

coatings are a powerful way to control the mixed potential open new ways for the development of robust and simple potentiometric sensors.

Introduction

Potentiometry is a well-established analytical technique that shows an unrivalled combination of robust performance and overwhelming simplicity. During the last few years, potentiometric methods have also regained interest for the development of distributed analytical platforms –such as wearable¹⁻³ and low cost paper-based sensors⁴⁻⁷- where the large-scale deployment of sensors is required. Unfortunately, despite of the many attempts, the great success of potentiometric methods for monitoring ions in solution has not been matched for sensing biomolecules. Some examples of these efforts to develop potentiometric biosensors are the sensors for heparin or creatinine as well as enzyme-based potentiometric sensors using ZnO nanostructures and 3D carbon-based materials recently reported.⁸⁻¹³ This reflects the continuous and renewed interest in the development potentiometric biosensing platforms that can provide robust, simple and affordable detection approaches.

A plethora of biosensing platforms are based on the generation of hydrogen peroxide, which is then determined using optical or electrochemical (most commonly amperometric) methods. In the majority of situations, a redox mediator is required in the detection step. Our group has recently described a simplified alternative approach for the direct (mediator-free) potentiometric sensing of hydrogen peroxide.¹⁴⁻¹⁶ It has been shown that when a Pt electrode is coated with a layer of Nafion, the typically erratic, low-sensitivity and unspecific response of the bare electrodes becomes highly stable and more selective towards hydrogen peroxide. Even more, these Nafion-coated electrodes show sensitivities that can reach up to 120 mV/decade of H₂O₂, which is significantly higher than the roughly 20 mV/decade of their bare counterparts. This approach has been successfully applied to the development of a paper-based device for the determination of glucose in blood¹⁶, showing promise to become a potentiometric biosensing platform. However, there are several aspects of the nature of the potentiometric response and the factors that affect it –such as the role of the matrix on the enhancement of sensitivity¹⁵- that cannot

be explained by conventional redox approaches using Nernst equation. A better understanding of these fundamentals characteristics may help to enhance and expand the analytical usefulness of this system.

The open circuit potential (OCP) of a metal electrode –such as Pt- exposed to a solution lacking of a well-defined redox couple is generally explained by a mixed potential (MP) mechanism.¹⁷ Unlike equilibrium, where the electrode potential is the result of the exchange currents generated by the same forward and backwards reaction, MP are originated by exchange currents produced by different reactions involving the electrode material, the solvent and other solution components. The theory of MP, first proposed by Wagner and Traud¹⁸, is widely used to study corrosion phenomena and is also extensively applied in other fields, such as heterogeneous catalysis. In chemical analysis, MP are typically used for the development of gas sensors. Fewer and sporadic applications for sensing in solutions have been proposed. Voigt et al used the MP to explain the high sensitivity of the OCP of some sodium tungsten bronzes to dissolved oxygen, which reach values of 120 mV/decade.¹⁹ Meruva and Meyerhoff, who pioneered the development of mixed potential sensors in solution, studied the MP of several metal electrodes, such as Cu, Pt and Co and their potentiometric response to dissolved oxygen.²⁰ They reported that Cu electrodes show sensitivities to O₂ of up to 120 mV/decade. Also, they demonstrated that the formation of a porous oxide layer on the surface of a Co electrode allows the generation of a mixed potential, where the oxygen reduction reaction (ORR) is the main cathodic process. Interestingly, they showed that the OCP of this system has a response that may reach up to 112 mV/decade of dissolved O₂. Applications of the MP for developing sensors for dissolved oxygen using Zn electrodes have been also proposed.²¹ Additionally, a phosphate sensor based on the interfering effect of this anion on the cathodic exchange current of the Co electrode has been proposed and revisited through the years.²² Very recently, Bard et al. proposed a very innovative use of MP to detect Pt nanoparticles in solution using a Au electrode.²³ They stressed the high sensitivity that can be obtained when monitoring the MP of a Pt microelectrode and showed that the manipulation of the kinetic parameters by the modification of the electrode geometry or surface can be

used to tune the response of the system. In essence, MP offers a rich ground to explore novel sensing approaches. Nevertheless, due to its kinetic nature, the MP strongly depends on the solution composition and the transport phenomena.²² Thus, its application in chemical analysis is severely restricted by problems of instability and lack of reproducibility. Any attempt to develop an analytical tool must address these issues simultaneously.

In a previous work, where we have shown that a Pt electrode coated with Nafion can work as a potentiometric sensor for hydrogen peroxide, we had focused mostly on the application, and had ascribed the response to the combination of redox and Donnan potential of the system.¹⁴⁻¹⁶ This work is devoted to provide a general framework to understand the response of this system using the MP models and its application to the detection of hydrogen peroxide. Unfortunately, mechanistic aspects of these systems are still a matter of intensive research.^{24,25} Thus, the efforts will be focused on a qualitative discussion – instead of a quantitative, mechanistic approach- that stresses the analytical value of this solution. By understanding the predominant role of the oxygen reduction reaction (ORR) in the electrode response, it is shown that the polyelectrolyte coating is fundamental for modulating the kinetic factors that control the analytical response. The results presented show that this combination of polyelectrolyte coating with a mix potential mechanism may open the way to explore new and powerful applications of OCP measurements in different fields, such as decentralized biosensing devices.

Figure 1.

Experimental Section:

Reagents. Nafion® 117 solution (5% in a mixture of lower aliphatic alcohols and water); Aquivion® D98-25BS consisting in a liquid dispersion, 25% in water, PFSA eq. wt. 980 g/mole SO₃H with CF₃ polymer and chain ends as stabilizer, Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PSS), sulfonated solution 5wt. % in 1-propanol and dichloroethane, hydrogen peroxide (30 wt. % in water) were purchased from Sigma-Aldrich. Phosphate buffer saline (PBS) pH=7.4 (0.1 M NaCl, 0.003 M KCl, 0.1 M Na₂HPO₄, 0.02M K₂HPO₄) prepared using 18.2 MΩ cm⁻¹ double deionized water (Milli-Q water systems, Merck Millipore) and analytical grade salts purchased from Sigma-Aldrich. Nitrogen gas (N₂) (99.9992%, H₂O 2 ppm in molar, O₂ 3 ppm in molar), Air gas (Air) (99.995%, H₂O 3 ppm in molar, O₂ 20.9% (±1%)).

Paper sensor construction.

In a previous work we have introduced the use of paper-based Pt electrodes, which showed similar response to the conventional electrodes. However, being disposable and freshly made from sputtering of Pt, the paper-based electrodes showed a more reproducible response. Details of the construction have been provided elsewhere. In short, Whatman® Grade 5 qualitative filter paper circles were coated with a 100 nm Pt layer using a radiofrequency sputtering process (ATC Orion 8-HV, AJA International) operated at 3 mTorr, for 65 s at 200 W. Two plastic masks (AR Care 8259, Adhesives Research, Inc., PA, USA) are glued together making a “sandwich” with a Pt-sputtered paper strip inside. The upper plastic mask has a 3 mm circle orifice or “electrochemically active window” that delimits the area in which the electrode is in contact with the solution. In this window a drop of Nafion® 5% (or corresponding polymer such as Aquivion and PSS) membrane is drop cast.²⁶ This electrode is used for potentiometric measurements as a working electrode (WE). Further details of the electrode preparation have been described elsewhere (Figure S1, Supplementary Information).¹⁴⁻¹⁶

Electrochemical Measurements.

Electromotive force (EMF) was measured with a high input impedance (10 Ω EMF16 multichannel data acquisition device (Lawson Laboratories, Inc. Malvern, USA) at room temperature (22 °C) in a stirred solution (distilled water, PBS). A double junction Ag/AgCl/KCl 3 M reference electrode (type 6.0726.100, Methrom AG) containing a 1 M LiAcO electrode bridge and the paper electrode (WE) coupled to a small metallic clamp were connected to the measuring instrument and immersed in the solutions.

For controlling the gases in the solutions all measurements were performed using the setup showed in the Figures S2 and S3 (Supplementary Information).

The Dissolved Oxygen content (% dissolved O₂) was measured with a InLab[®] OptiOx optical dissolved oxygen sensor (Measuring range: 0 – 500 %; ©Mettler-Toledo) in combination with a Seven2Go pro meter (©Mettler-Toledo) at room temperature (22 °C) in a well-stirred solution (distilled water, PBS). This sensor was calibrated with two points, 100 % O₂ with distilled water and 0 % O₂ with deoxygenated distilled water (deoxygenation by Zero Oxygen tablets, ©Mettler-Toledo AG, Analytical).

For low oxygen content measurement, Pt bare and Nafion covered Pt electrodes are immersed in a 500 rpm stirred distilled solution, when a stable OCP in the electrodes was obtained, a constant N₂ flow is added in the chamber gas inlet (Figure S2a) for getting a stable N₂ atmosphere. After 15 min the deoxygenation starts by adding a constant N₂ flow in the solution gas inlet (Figure S2b), when a 0 %O₂ in the solvent is obtained the N₂ inflow in the solution is stopped.

Calibration curves were obtained by the successive additions of H₂O₂ with a syringe (Figure S2j) thorough a Teflon tube (Figure S2c). All solutions were prepared in the suitable solution and in the case of the low oxygen measurements the H₂O₂ solutions were previously deoxygenated with a N₂ flow for at least 5 min.

To assess the influence of convection, Pt bare and Nafion covered Pt electrodes are immersed in a 500 rpm stirred distilled water, then a constant airflow is added in the chamber gas inlet (Figure S2a) to reach a stable air atmosphere. When a stable OCP in the electrodes is obtained an airflow is added in the solution

to produce a bubbling: the bubbling intensity is controlled by setting the air pressure in the solution gas inlet (Figure S2b).

Results and discussion

a) *The resting potential of a Pt electrode*

When a metal electrode –such as Pt- is immersed in a solution in the absence of a well-defined redox couple, different Faradaic reactions may occur on the surface, leading to anodic (j_a , oxidation, electron donor) and cathodic (j_c , reduction, electron scavenger) exchange currents. To avoid charge accumulation, this Faradaic production of species must be balanced, so in the steady state:

$$j_a + j_c = 0 \quad (1)$$

Each one of these currents can be described by the Butler-Volmer approximation, which relates the electrode potential to the corresponding exchange current:

$$j_k = j_k^0 \left(e^{-\frac{\alpha_k n_k F \eta_k}{RT}} - e^{\frac{(1-\alpha_k) n_k F \eta_k}{RT}} \right) \quad (2)$$

where j_k is the current density for “ k ” (i.e., either anodic or cathodic) reaction, j_k^0 is the exchange current density, α_k is the symmetry factor, n_k is the number of electrons exchanged in the rate-limiting step. The overpotential η_k is the difference between the resting potential of the electrode (E) and the equilibrium potential (E_k^0) of the reaction ($\eta_k = E - E_k^0$) under study, and F , R and T are the Faraday’s constant, universal gas constant and the absolute temperature, respectively. The MP of the system can be calculated by solving equation (1) when the anodic and cathodic exchange currents are expressed in terms of equation (2). This calculation yields the value of the electrode potential (E) required to generate anodic and cathodic overpotentials that make the absolute value of both exchange currents similar. This is the most fundamental difference between redox equilibrium -where the overpotential is zero- and the MP, a steady state in which the need to balance the Faradaic production of species of different reactions results

in a net, non-zero overpotential (η). This overpotential acts as a driving force for the continuous generation and consumption of chemical species. Therefore, since the resting potential is the result of the balance of different kinetically controlled reactions occurring on the surface of the electrode, MP do not show a Nernstian behavior. To simplify the study, the Tafel approximation (i.e, to consider that for a given reaction the forward -or backward- rate is negligible compared to the corresponding backward -or forward- rate) is normally used:

$$j_k = j_k^0 \left(e^{-\frac{\alpha_k n_k F \eta_k}{RT}} \right) \quad (3)$$

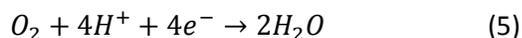
Which shows that for a given reaction there is a linear relationship between the electrode resting potential (E) and the logarithm of the exchange current:

$$E - E_k^0 = \eta_k = \frac{RT}{\alpha_k n_k F} \ln j_k^0 - \frac{RT}{\alpha_k n_k F} \ln j_k = \frac{\beta_k}{n_k} \ln j_k^0 - \frac{\beta_k}{n_k} \ln j_k \quad (4)$$

Under standard conditions ($\alpha = 0.5$, $T = 298\text{K}$), the value of $\beta_k = \frac{2.303RT}{\alpha_k F}$ is 120 mV/decade. Evidently, the

Tafel slope ($\frac{-\partial E}{\partial \log j} = \frac{\beta_k}{n_k}$) for a reaction that involves one electron in the rate limiting step ($n_k = 1$) is 120 mV/decade. For example, for one of the most common contributors to cathodic processes of MP -the oxygen reduction reaction (ORR)- Tafel slopes of 120 or 60 mV/decade, depending on how the conditions affect the reaction mechanism. As it was mentioned above, to evaluate the MP, j_a and j_c can be expressed according to (3), and solving the system according to equation (1), as illustrated in Figure 1. Meruva et al have performed this approach when evaluating the MP for a Co electrode used as a phosphate sensor.²²

Because of these kinetic (Tafel) relationships, it is evident that the reaction that has a rate-limiting step has a major influence on the overall behavior of MP. For metallic surfaces in aqueous electrolytes, for example, metal oxidation is often the anodic process, while the ORR is one of the most common cathodic processes. In acidic media, the ORR can be expressed as:



In many of these systems, the ORR acts as a rate-controlling process. For that reason, the OCP of many metal electrodes follows the Tafel dependence of this cathodic reaction (suggesting that the anodic process has a negligible influence in the overall kinetics).^{19,20} This is the reason why some potentiometric sensors for dissolved oxygen that have been reported in the literature show sensitivities of 120 mV/decade.²⁰ The exchange current changes linearly with the O₂ concentration, and the electrode potential will accommodate accordingly following the Tafel relationship, as shown in equation (4)

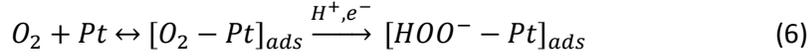
In general terms, these considerations are also valid for Pt, although this system shows a significantly higher level of complexity. The anodic reactions in Pt are usually ascribed to the metal surface oxidation, oxidation of impurities or even Pt dissolution.²⁴ From a kinetic point of view, these anodic reactions show low activation energy, so they do not play a central role. The most important cathodic reaction in the Pt surface is the ORR (equation 5). Figure 3a shows the OCP of a Pt electrode in an electrolyte solution whose dissolved oxygen is being removed by N₂ bubbling. It is found that when the dissolved oxygen has been reduced by one order of magnitude, the electrode potential has dropped by approximately 14 mV (Figure S4 Supplementary Information). This influence of O₂ on the electrode potential is a clear evidence of the MP nature of the Pt OCP and the role played by the ORR. Qualitatively, it is clear that a reduction of the concentration of dissolved oxygen produces a decrease of the electrode potential. As a cathodic reaction, the ORR is an electron-scavenging process, any decrease on the ORR activity should lead to a lower rate of electron removal, leading to a steady state at a more negative electrode potential.¹⁷ No quantitative conclusions can be derived, since the type of experiments required to perform kinetic measurements (described elsewhere) fall beyond the scope of this work. As a matter of fact, due to the several factors that affect the kinetics of the ORR in bare Pt, the ideal Tafel dependence can be hardly found in systems with practical applications (high ionic content, etc.) Controlling these factors is fundamental for the use of the Pt MP with analytical purposes.

The actual mechanism of the ORR in Pt is still a matter of research, and there is no general consensus on the reaction pathways, intermediaries, etc. Eikerling *et al.* et al have recently proposed a general framework to study this system, where three main factors affecting the Pt surface have to be considered: a) the chemical reactions (exchange currents), b) the electrostatic effects and the surface charge, and c) the composition and morphology of the surface.²⁷ Figure 2 re-elaborates this framework in terms of the MP. It is the tight interdependence between these factors what adds to the complexity and makes the system very hard to study. In aqueous solutions, the Pt surface gets partially covered by a thin surface oxide layer. The degree of oxide coverage plays a crucial role in the electrode behavior, since the presence of oxide in the surface blocks the free Pt sites, affecting the ORR. At the same time, the absorption of different species –especially anions- affects the surface charge, modifying the electrode potential (which, in turn, modifies the potential-dependent kinetic constants). In short, the ORR is part of a complex process affected by several factors related to the solution composition and the Pt surface state.

Figure 2.

Chemical reactions

The main cathodic reaction taking place in the MP of a Pt electrode is the ORR (equation 5). Interestingly, despite of being one of the most studied electrochemical reactions, the mechanism of the ORR in Pt is still elusive. Even though Pt is one of the best catalysts for the ORR, the reaction is sluggish, does not proceed in a reversible way and the mechanism includes a number of elementary steps with different intermediaries and pathways that strongly depend on the reaction conditions.^{28,29} It is generally accepted that the rate-limiting step includes a first step of adsorption of O₂ onto free Pt sites, followed by a one-electron transfer:



Under very careful conditions, the experimental evidence (and theoretical models) show Tafel slopes of 120 mV/decade²⁸-supporting this mechanism-, which also shows a first order dependence on the concentration of O₂ and H⁺. According to this, Damjanovic et al. have proposed a modified Tafel equation³⁰:

$$j_{ORR} = K_{ORR}^o [H^+] [O_2] \left(e^{-\frac{\alpha_k n_k F \eta_k}{RT}} \right) \quad (7)$$

(where K_{ORR}^o accounts also for several constant and coverage dependent activation energy). According to this, the OCP could show a dependence of 120 mV/decade of O₂, as has been also reported by some authors.²⁰ However, because of the many factors that affect the ORR (Figure 2), experimental values ranging from 20 to 80 mV/decade of O₂ are usually found, depending on the reaction conditions. This is one of the reasons why in the plot in Figure 3a the OCP of the Pt electrode does not show a more pronounced change.

Figure 3.

Surface chemistry

As the rate-limiting step of the ORR is the adsorption of O₂ on free Pt sites (equation 6), is evident that the surface condition, in particular the availability of free sites, plays a major role on the ORR. As a matter of fact, the *Pt* in equation 6 is often represented as *Pt*^{*}, in order to stress the need to have free, pristine Pt sites. For this reason, site-blocking (due to either competitive adsorption or surface oxide coverage) has a major influence on the reaction kinetics. Among the spectator species with high affinity for Pt, the adsorption of anions is highly relevant because it produces 3 major simultaneous effects: competitive adsorption, surface charge modification, and water structure alteration.^{29,30} The plot in Figure 3c shows

that different anions affect the OCP depending (in part) on the different chemisorption energies on Pt. The addition of a 10 mM solution of sodium salts of the three selected anions (ClO_4^- , orange; Cl^- , red; H_2PO_4^- , blue) produce a positive increment of the OCP from 40 up to 80 mV. It is hard to predict the effect of these adsorbed electrolytes, since from one side they block the free sites for the ORR, but at the same time affect the water activity –i.e. the structure of water- and the non-covalent interactions on the surface of the electrode.³¹ Also, some anions –such as phosphate- with acid-base behavior may also alter the local pH, thus producing additional changes on the ORR. From an analytical standpoint, the most serious issue is the variable effect of the different anions, which adds uncertainty due to unspecific matrix effects.

One of the key factors affecting the ORR is the degree of surface oxide coverage, since it acts as a powerful blocker of the free platinum sites and promotes the adsorption of species –particularly protons- creating a pH-dependent electrode surface charge. Figure 3d shows that the OCP of the bare Pt electrode has a marked dependence with the pH, which reaches values close to 45 mV/unit of pH. This dependence, of course, is connected to the direct effect of the proton concentration on the ORR (equation 5), and the surface-charge effect on the electrode potential. In any case, the adsorption of substances –in particular oxygenated species- modulates the ORR. A corrected Tafel equation accounting for this surface effect has been proposed³²:

$$j_{ORR-effective} = j_{ORR-Tafel}(1 - \theta)^x \quad (8)$$

Where x is usually unity and θ is a factor that accounts for the total surface coverage by adsorbing spectator species, such as anions, oxygenated species, etc. ($\theta = \theta_{anions} + \theta_{oxide} + \dots$). Thus, the electrode mixed potential becomes a function of the surface coverage by species that modulate the ORR kinetics. This is a central concept that will be used when discussing the response to hydrogen peroxide: the electrode potential will have a direct relationship with the chemisorbed oxygen species on the Pt surface.

Surface charge

As in any electrochemical process, the metal surface charge density plays a fundamental role in the electrode processes. Dipole orientation, migration of charged species –in particular protons-, and direct effect on the electrode potential -which in turn affects the kinetic constants- are some of the aspects where the surface charge has a direct effect. Eikerling *et al.*²⁷ have shown that the effect of a positive surface charge is a decrease of the interfacial proton concentration and thus the ORR activity. This effect can be modulated through the ionic strength. In general, they point out that increasing the ionic strength diminishes the effect of the surface charge.

In summary, the OCP of Pt in an electrolyte solution without a well-defined redox couple responds to the concentration of dissolved oxygen through a mixed potential mechanism. Unfortunately, the complexity of the interfacial chemistry of Pt makes this system hard to control with analytical purposes. The interdependence of the several factors involved introduces a level of variability that is hard to predict, since some elements may produce opposite effects. Anions, for example, may be blocking free sites due to absorption, from one side, but facilitating the ORR due to surface charge effects, from the other. Which is the prevalent factor strongly depends on the working conditions. Significant efforts have been made to develop models that can explain and predict the behavior of this system, but this has not been yet possible.

Adding to the long list of issues of bare Pt electrodes, Figure 3b shows the significant increase in the noise levels of the OCP of a bare Pt electrode when the solution is stirred by bubbling air. This is another evidence of the weakness of MP as analytical tool. The continuous generation and consumption of chemical species at the electrode surface generates complex concentration gradients that make the system highly sensitive to mass transport. Overall, this bare Pt surface is a highly unstable electrochemical interface, which is a severe barrier from an analytical standpoint.

The detection of H₂O₂

As it has been mentioned above, there is abundant evidence showing that the degree of coverage by oxygenated species, θ , produces a powerful site-blocking and negative energetic effect, becoming one of the most relevant contributions to the modulation of the ORR.²⁵ Since these oxygenated species (such as OH) -originated either from the solution or from ORR intermediates- have adsorption energies similar to O₂, they have a powerful inhibitory effect on the ORR.

Figure 4.

Interestingly, one of these species is H₂O₂, which is considered an intermediary of the ORR,²⁴ as shown in Figure 4. The electrochemical behavior of this molecule is still a matter of debate. It has been proposed that peroxide spontaneously decompose into OH radicals on the Pt surfaces. Recent evidence has shown that peroxide is absorbed on the surface of Pt competing with oxygen for free Pt sites.^{32,33} It is evident that, whether it is intact or dissociated, the addition of peroxide interferes with the ORR reaction pathway. When this happens, the cathodic exchange current changes according to equation (7), and this will affect the electrode OCP following a Tafel-like dependence. The fate of peroxide is strongly linked to the working conditions, since it is well known that the stability of surface oxygenated species is heavily influenced, for example, by the surface atom orientation and the type of anions from the supporting electrolyte.³⁰ A Pt oxygen-peroxide mixed potential in alkaline solutions has been reported.³⁴ In this case, if a MP through the hydrogen peroxide reduction reaction (also with a Tafel slope of 120 mV/decade) is considered, as a cathodic process this reaction should be seen as an increment on the electrode potential. The response observed for peroxide on Pt is the opposite, i.e., a decrease in the OCP, which corresponds either to an anodic reaction or to a decrease of a cathodic process. In fact, it has been shown before that a decrease of the O₂ concentration leads to a decrease of the electrode OCP due to a drop of the ORR. The addition of peroxide produces an effect that is similar to reducing the O₂ concentration. Experimental results

shown in Figure 5 indicate that the OCP of a bare Pt electrode has negative response to hydrogen peroxide, with values that are highly dependent on the working conditions. The values of the slope ($\partial E / \partial \log[H_2O_2]$) reach -48 mV/decade (Table 1) within a very narrow concentration range for neutral pH, and become very low at extreme pHs (2 and 10). Figure 5a shows the results for an acidic pH and with an anion with very little affinity for Pt. With reduced competitive adsorption and high proton concentration, these conditions are ideal for the ORR (as revealed by the high electrode potential). On the other extreme, Figure 5d shows the response at pH 10, where high competitive adsorption from OH species is expected. In this case, with low electrode potential and high surface oxide coverage, the conditions do not favor the ORR. The two regions at intermediate pH, figures 5b and 5c, show that an optimum response for peroxide is found at neutral pH. It is hard at this point to go beyond the phenomenological description, since the microkinetic analysis of these systems is still uncertain. In any case, this bell-shaped response in the bare electrodes is heavily modulated by the matrix composition through competitive adsorption on the Pt surface (Figure 5 and Table 1),²⁸ which makes this system unattractive from an analytical standpoint.

Figure 5.

Table 1

Modulating the MP through polyelectrolyte coatings

For decades, polyelectrolyte coatings –such as Nafion- have been successfully applied in amperometric sensors with two main purposes: first, preventing interferences from redox-active anions and second, minimizing bio-fouling. Nafion is a negatively charged sulfonated tetra-fluoroethylene-based polymer. The structure and transport mechanisms within the Nafion membranes is still a matter of study, but the

evidence suggests that Nafion forms membranes with the negatively charged hydrophilic sulphonate domains segregated from the organic phase, forming nanochannels that allow the transport of polar substances. These channels act as effective permselective barrier blocking larger anions, such as ascorbate. Beyond permselectivity, Nafion has several properties that affect the chemical environment in the vicinity of the electrode. First, the highly acidic nature of the sulphonate moieties modifies the local pH and give ion-exchange capacity to the membrane. Second, the strong electrostatic effect of the sulphonate groups means that the water in the nanochannels is strongly bound to the hydration sphere of ions. In other words, Nafion membranes incorporate a good amount of water, but most of it enters as the hydration sphere of ions. This means that the water activity within the membrane is relatively low. Third, the solubility of oxygen in Nafion is almost 20 times higher than in water, which means that the membrane acts as a reservoir for this substance.²⁶ The distribution of O₂ between hydrophobic and hydrophilic domains, however, makes that not all the O₂ in the membrane is electrochemically active. It is evident that, if the study of the MP of Pt in electrolytes is complex, the addition of Nafion –a biphasic, nanostructured, highly charged and acidic polymer- makes the problem even more difficult at the microkinetic level.

Due to all these properties, Nafion has a marked effect on the MP. One of the first experimental evidences is that Nafion-coated electrodes show a resting potential significantly higher than their bare counterparts (Table 1). This is shown in all the plots in Figure 3. Figure 3a, for example, shows that the decrease on the OCP as a function of the dissolved oxygen shows the higher value of the Nafion-coated electrodes. It should be stressed that the actual concentration of O₂ in the electrode surface is significantly different than in the bulk solution when Nafion is used, and that is hard completely eliminate the O₂ in these systems. Clearly, the properties of Nafion have a direct effect each one of the critical factors that influence the ORR, as illustrated in Figure 2. First, due to a permselectivity effect, Nafion reduces the anion loading on the Pt surface, minimizing the site-blocking by competitive adsorption with O₂. Additionally, there is a

direct effect on the kinetics of the ORR by increasing the local O_2 and H^+ concentration (see equation 7). Although not all the oxygen is electrochemically available, the membrane acts as a reservoir, as it has been already shown by Wang et al.²⁶ Also, the high acidity of the sulfonate groups provides protons that are quickly consumed during the ORR. It has been shown that in mildly acidic conditions a gradient of protons is created that may slow down the reaction or even force a change of mechanism.³⁵ The dependence of the OCP with pH (Figure 3d) shows that Nafion significantly dampens the effect of increasing the pH. A change from pH 2 to 7.4 produces a change of more than 200 mV in a bare Pt electrode, while it is less than half this change (approximately 70 mV) for the Nafion-coated system.

Several other factors play a role in the OCP. The permselectivity of Nafion not only frees Pt sites but it also minimizes the anions surface-charge effects. These aspects of charge and surface chemistry of the Nafion-Pt interface are still a matter of intensive study because of its central role in fuel cell technology. The density of negatively charged sulfonate groups determines the ion-exchange capacity, which leads to the generation of a Donnan potential in the system.³⁶ Ion exchange is one of the main mechanism of water uptake, incorporated mostly as part of the hydration shell of the ions. Water acts as a membrane plasticizer, affecting the mechanical and transport properties. In summary, upon ion-exchange with the solution, electrostatic, chemical and rheological changes of the membrane have a direct effect on the ORR (and thus, the OCP). As it has been previously shown, the resting potential of a Nafion-coated electrode follows a Nernstian dependence with the total electrolyte concentration¹⁴. As shown in Figure 3c, the higher the ionic strength, the higher the resting potential of the electrode. Interestingly, Nafion introduces a more marked dependence with the ionic strength, which might be considered deleterious from an analytical standpoint. However, for a wide range of substances, this relationship is well characterized and independent of the type of ion involved, which makes it easier to control or account for. Last, but not least, the interaction of the polymer with the metal surface, which is produced through the fluoride groups of the polymer backbone,³⁷ has also influence on the surface chemistry of Pt, and thus the ORR.

An additional factor where Nafion plays an important role is the stabilization of the transport properties at the electrode interface. As shown in Figure 3b, the Pt interface is unstable, particularly upon convection, due to the generation of the different chemical gradients on the surface of the electrode. The Nafion coating minimizes the fluctuations, while it is also found to improve the electrode-to-electrode reproducibility.

In a previous work, we have shown that one of the most attractive features of this Nafion-Pt system is the possibility of detecting hydrogen peroxide.¹⁴⁻¹⁶ As it was already mentioned, adsorbed on Pt surfaces peroxide is a powerful site-blocker of the ORR. In bare Pt, however, this effect is heavily masked by interferences. The use of Nafion coatings create conditions that enhance the ORR and minimize the interference by other species, allowing a significant improvement of the detection of peroxide.^{14,15} Figure 5 (and Table 1) show that the pattern of response with Nafion emulates the bare Pt, but with an enhanced response. Thus, the bell-shaped pH sensitivity also reaches a maximum at pH 7, but in the case of Nafion coated electrodes the sensitivity is 129 mV/decade, i.e., close to a Tafel slope. In a previous work we have shown that the ion concentration also affects, so the higher the ionic strength, the higher the sensitivity.¹⁴ Figure 6a shows a decrease in sensitivity that is produced when the pH remains constant, but the total buffer concentration is reduced 2 orders of magnitude. Because of this, we had initially considered the effect of the Donnan potential as a major factor influencing the sensitivity. Nevertheless, as it has been already mentioned, the ion-exchange produces marked changes on the membrane properties that affect the ORR. The stability of surface oxygenated species is strongly dependent on the surface atom orientation as well to the presence of anions from the supporting electrolyte.³⁸ The surface coverage of $\text{OH}_{\text{ad}}/\text{O}_{\text{ad}}$ and the kinetics for their adsorption/desorption, which are very sensitive to the change in electrode potential and solution pH,³¹ and the local properties, such as the interfacial charge and the water structure at the interface, are also factors that play an important role³⁹ and can heavily influenced by the Nafion membrane properties.

While the mechanisms controlling the changes on the OCP in the Pt-Nafion-H₂O₂ system are not yet fully elucidated, it is possible to modulate the response by controlling the solution and the Nafion membrane composition. The calibration plot for peroxide in a solution where the oxygen concentration has been significantly reduced (Figure 6b, [O₂] < 0.1 ppm), shows that the sensitivity remains constant, but the linear range is shifted almost half an order of magnitude towards lower concentrations. It should be remembered that even when the oxygen is removed from the solution, the membrane acts as a reservoir,²⁶ which is interesting from an analytical standpoint when dealing with O₂-consuming system, such as in many enzymatic sensors.

The contact of Nafion with an ionic solution produces a moderate ion-exchange. A more drastic change can be induced by conditioning the membrane for a prolonged time with an electrolyte solution. Figure 6c compares the calibration curve for peroxide after the electrode had been left soaking overnight in a sodium chloride solution. In this case, a more thorough replacement of H⁺ by Na⁺ occurs, and the sensitivity is significantly reduced, reaching values in the order of 60 mV/decade. This change could be explained, at least in part, by the removal of protons from the membrane, which would lead to an increase of the local pH that would directly affect the ORR.

Figure 6.

These results show that the Nafion coating produces a modulation of the MP, which under ideal conditions leads to an increased sensitivity for peroxide. However, a major limitation from an analytical standpoint is that the limited range of concentration where this occurs. In fact, we have illustrated the analytical advantages of this approach through a paper-based potentiometric cell for monitoring glucose in blood. A major shortcoming of this system, however, was the need of dilution of blood, which seriously limits the applicability in real settings, i.e. the required linear range should be extended to 10 mM. In distributed

sensors, the linear ranges of the sensors must match the range of interest in order to avoid any sort of sample manipulation.

One additional way to modify the MP is through the use of membranes with slightly different characteristics. Polymeric materials sharing some similarities with Nafion, but with different charge density have been tested to evaluate the effect on the MP. Platinum electrodes coated with Aquivion (a polymeric material from the same family than Nafion but with a higher density of sulfonate groups) and polystyrene sulphonate (PSS) (a polymer with a lower density of sulfonate groups, see Figure S5 Supplementary Information) were evaluated. The results for the calibration of hydrogen peroxide using shows a very interesting feature: the sensitivity remains constant, and the linear range remains limited, but it shifts to lower or higher concentrations depending on the density of sulfonate groups, as shown in Figure 6d. The higher the density of sulfonate, the linear range shifts to higher concentration (up to one more order of magnitude). This is a very attractive feature when designing biosensors for different types of applications.

Conclusions

The attractive features of MP systems have been stressed for many decades. Nevertheless, from practical standpoint, these systems showed significant barriers that prevent their application in chemical analysis. This work has shown that through the use of a polyelectrolyte coating –such as Nafion- it is possible to control the MP and use it with analytical purposes. These membranes show a significant improvement on the system stability and selectivity, while at the same time create conditions to modulate the reactions involved in the MP. This allows the tuning of the analytical parameters. The example of the modulation of the parameters for the determination of hydrogen peroxide opens an attractive way to generate enzymatic biosensors. For instance, the detection in undiluted biological fluids is likely to be the next step in this field. These advantages, however, should not be limited to Pt and peroxide, as it has been

demonstrated for many other systems. Additionally, as it was recently pointed out,⁴⁰ these systems show a high degree of versatility, which leads to manipulations of the analytical response through the electrode geometry, composition, etc. This work aimed to stress once again the attractive features of MP systems and practical ways to control them, which could lead novel applications in potentiometry, and may also help to rationalize other approaches that have been presented in the past.

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Conflict of interest

The authors have no conflict of interest.

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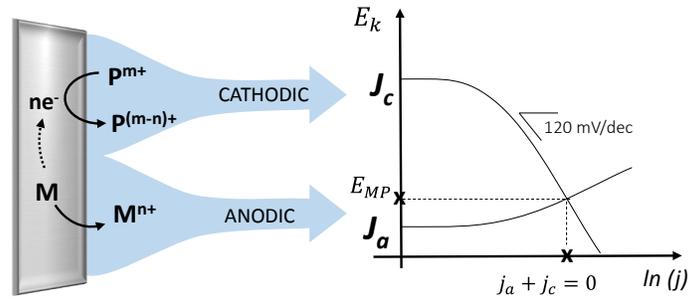


Figure 1. Representation of the processes in the electrode (left) and the corresponding Tafel plots (right) that can be used to calculate the electrode mixed potential (E_{MP})

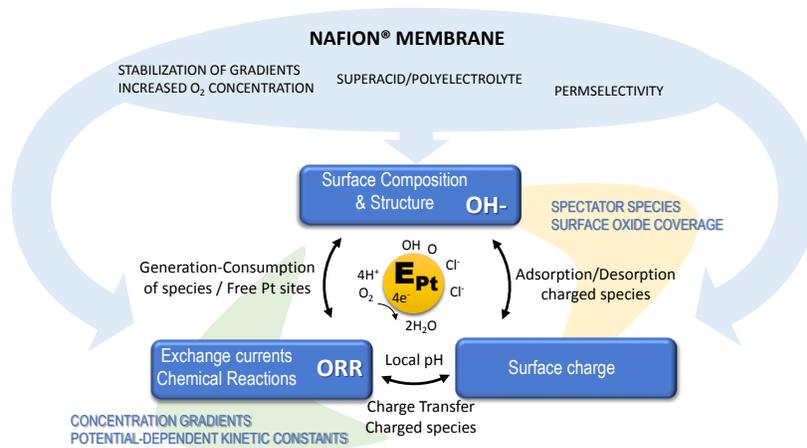


Figure 2. Schematic view of the parameters affecting the OCP of the Pt electrode (according to Ref 27) and the effect of the Nafion membrane

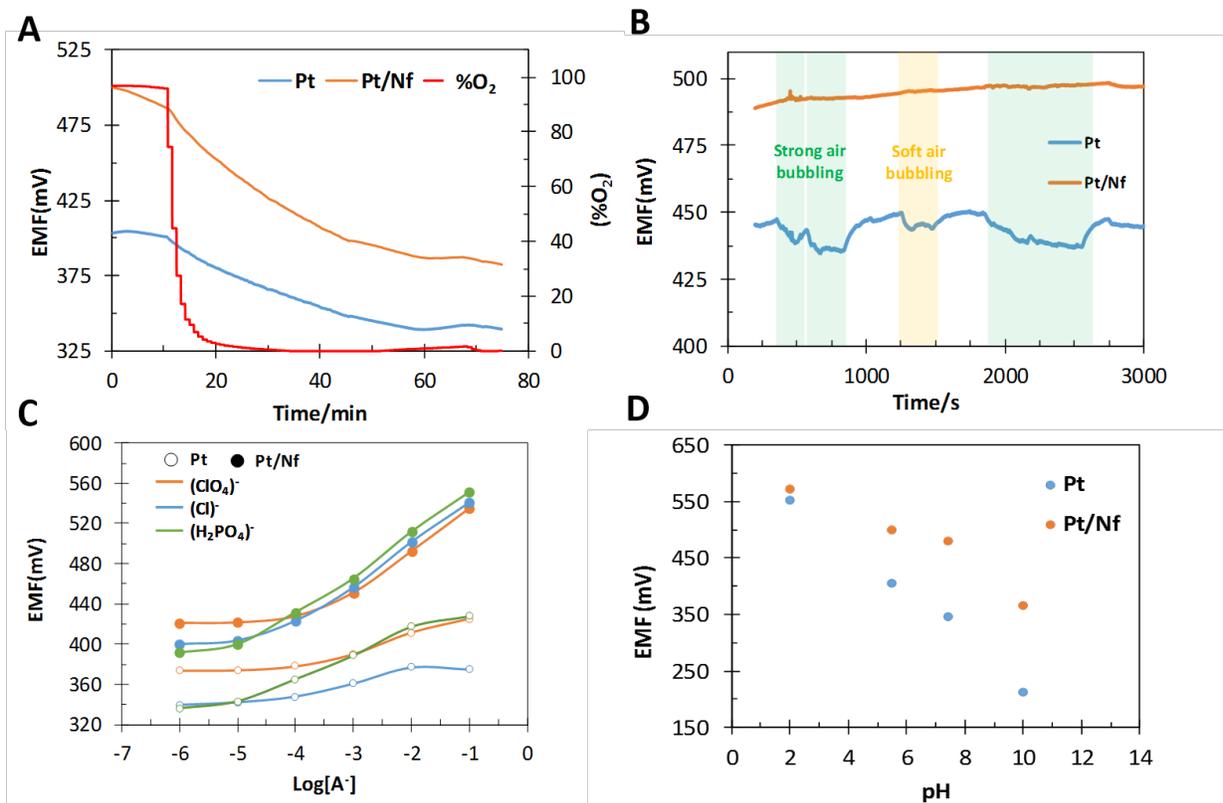


Figure 3. (A) OCP plot of a platinum paper-based electrode (Pt, blue) and a platinum paper-based electrode coated with a Nafion layer (Pt/Nf, orange) as a function of [O₂] (red) in PBS 0.1 M pH 7.4. **(B)** Response of a Pt and Pt/Nf paper-based electrode as a function of convection (with strong and soft air bubbling). **(C)** Response of Pt and Pt/Nf paper-based electrode as a function of the sodium salt concentration (ClO₄⁻, orange; Cl⁻, red; H₂PO₄⁻, blue); For better visualization, an Offset of +50mV was applied in the EMF values for H₂PO₄⁻ response of Pt paper-based electrode. **(D)** OCP plot of Pt and Pt/Nf paper-based electrode as a function of pH (pH 2 in HClO₄; pH 5.5 in H₂O; pH 7.4 in 0.1 PBS and pH 10 in NaOH).

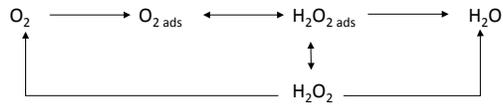


Figure 4. Typical reaction mechanism proposed for the ORR²⁴

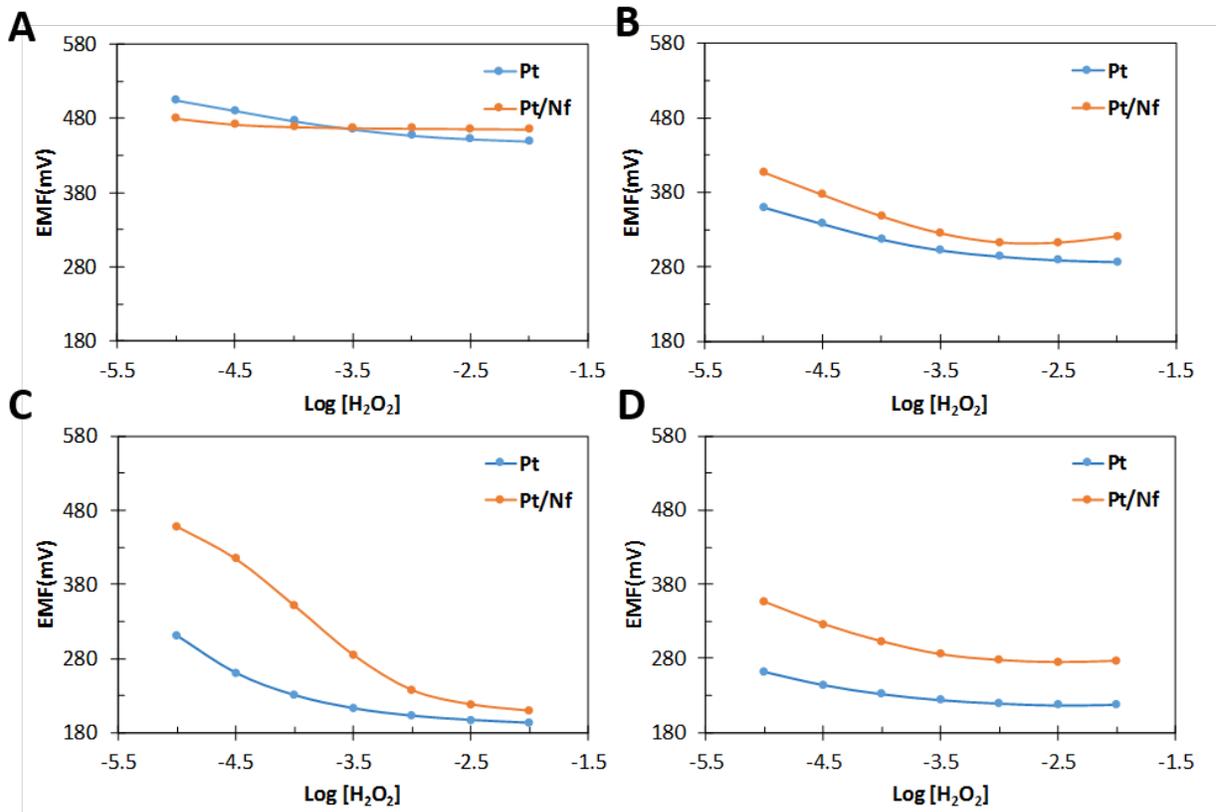


Figure 5. Calibration curve of a platinum paper-based electrode and platinum paper-based electrode coated with Nafion in different media: (A) HClO₄, 0.01 M pH=2, (B) H₂O pH=5.5, (C) PBS, (0.1 M) pH=7.4; (D) NaOH (0.01 M) pH= 10.

Table 1 Analytical parameters (RP for resting potential) of Pt and Pt/Nf paper-based electrodes in (A) HClO₄, 0.01 M pH=2, (B) H₂O pH=5.5, (C) PBS, (0.1 M) pH=7.4; (D) NaOH (0.01 M) pH= 10.

Media	Pt			Pt/Nf		
	RP (mV)	Sensitivity mV/dec [H ₂ O ₂]	Linear range	RP (mV)	Sensitivity mV/dec [H ₂ O ₂]	Linear range
H₂O pH=5.5	404	-42.85 ± 2.00	(-3.5 / -4.5)	499	-59.83 ± 7.60	(-3.5 / - 4.5)
PBS (0.1 M) pH=7.4	345	-48.02 ± 0.92	(-3.5 / -4.5)	480	-129.23 ± 5.10	(-3.5 / - 4.5)
NaOH (0.01 M) pH=10	305	-29.27 ± 2.60	(-4 / -5)	420	-56.81 ± 2.00	(-4 / - 5)
HClO₄ (0.01 M) pH=2	551	-24.62 ± 0.32	(-3.5 / -4.5)	572	-28.14 ± 0.94	(-3.5 / - 4.5)

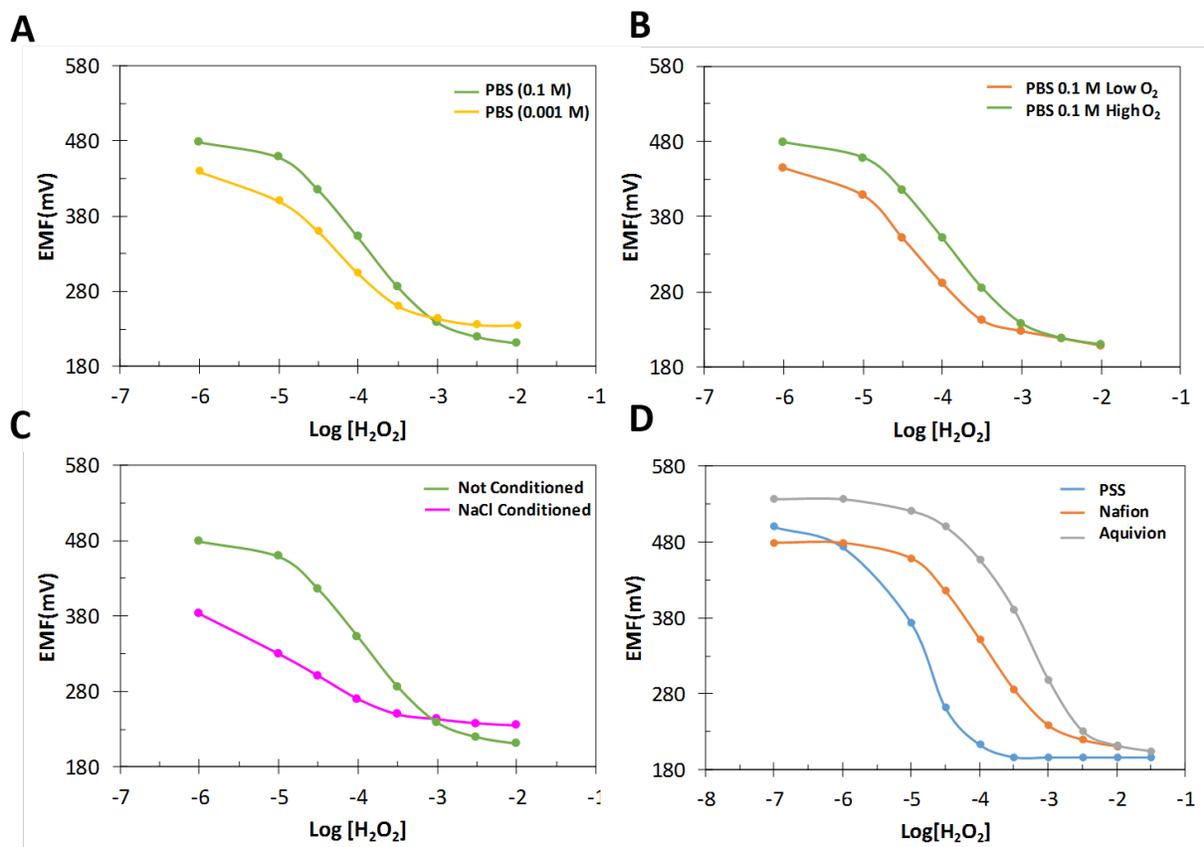


Figure 6. (A) Calibration curve of a Pt/Nf paper-based electrode in PBS 0.1 M and 0.001M; (B) in PBS 0.1 M with high (100 %) and low O_2 content (inferior to 1% (0.09 mg/L)); (C) in PBS 0.1 M with overnight conditioning in NaCl 0.01 M; (D) Influence of the polymer coating on the analytical performance (PSS coating, Nafion coating and Aquivion coating).