

Enhanced Potentiometric Detection of Hydrogen Peroxide Using a Platinum Electrode Coated with Nafion

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Abstract

The potentiometric response to hydrogen peroxide of a platinum electrode coated with a layer of Nafion is presented. The results show that the Nafion membrane acts as an effective permselective barrier, thus significantly reducing the response to some redox active species, such as ascorbate. Even more interesting, these coated electrodes show a significantly enhanced sensitivity to hydrogen peroxide (H₂O₂) when the measurements are performed in solutions of high ionic strength. The influence of pH, ionic strength and supporting electrolyte on this enhancement are presented. Under optimized conditions these coated electrodes show a linear dependence with the logarithm of the concentration of H₂O₂, with sensitivities of -125.1±5.9 mV decade⁻¹ (several times higher than the bare electrodes) and a linear range that spans from 10⁻⁵ M to 10⁻³ M of H₂O₂. Preliminary studies suggest that the coupling between the redox potential on the Pt electrode and the Donnan potential of the membrane play a role on this enhancement. Considering this improved sensitivity, selectivity, stability and linear ranges, this system shows promise as a future platform to build enzyme-based potentiometric biosensors.

Keywords: hydrogen peroxide, potentiometric sensors, Nafion ion-exchange membrane, Donnan potential

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1 Introduction

The working principle of a large number of chemical and biochemical sensors is based on the use of an enzymatic reaction that generates hydrogen peroxide (H₂O₂), a substance that is then detected using a suitable analytical technique [1–5]. Therefore, finding alternative methods for the sensitive and selective detection of H₂O₂ may have significant impact in all those fields -such as clinical diagnostics [6], food [7] and environmental analysis [8], etc. -where these biosensors play a central role.

Among the many different alternatives, the detection of H₂O₂ using electrochemical techniques is particularly attractive since it allows the integration of the enzyme-electrode system into a simple and compact arrangement. Voltammetric techniques have been traditionally preferred because they provide high sensitivity and low limits of detection. As a result, bioanalytical platforms [9,10] using enzyme-based amperometric sensors have become almost the norm, and because of this success the development of alternative solutions has been somehow hindered [11,12]. Nevertheless, with the growing interest on devices for point of care and decentralized measurements, new platforms that can offer additional advantages -such as simplicity of operation and cost- are increasingly required [13,14]. For this reason, potentiometric detection is regaining momentum. Potentiometry shows unrivalled simplicity of operation and instrumentation, low power

consumption, easy of miniaturization and -with the recent trends, such as paper-based devices [15] -ability to produce ultra-low-cost sensors [16]. Therefore, in many applications where extremely low limits of detection might not be a main issue-, potentiometric tools may offer a simple and affordable alternative [17].

A major limitation for the electrochemical detection of H₂O₂ is the interference produced by other redox-active species, such as ascorbic acid [18,19], often present in biological media. To deal with this problem, the use of polyelectrolytes as permselective membranes has been successfully applied [20]. Nafion® -for example- a negatively charged sulfonated tetra-fluoroethylene-based polymer, has been used as an effective barrier against electrode fouling and the interference produced by large negative ions [21–23]. Amperometric electrodes that are coated with this polymer have shown an improved stability and selectivity towards negatively charged redox species, such as ascorbate [24,25]. In the case of potentiometric methods, the direct detection of H₂O₂ can be easily performed using a platinum electrode. However, it is evident that this approach is also heavily interfered by the presence of redox active species [26]. Interestingly, to the best of our knowledge, the use of permselective membranes (such as Nafion) to coat platinum (Pt) electrodes for the potentiometric detection of H₂O₂ has not been yet reported.

It is worth noticing that the nature of the potentiometric response between H_2O_2 and bare Pt electrodes is not yet fully understood and has been the subject of many recent studies [27–29]. It has been shown that the H_2O_2 -Pt system presents a non-Nernstian response, with the slopes that vary depending on the crystalline structure of the Pt, the surface of the electrode and its interaction with the solution pH and composition, as well as the several the reactions involved in the decomposition of H_2O_2 . Additionally, the use of polyelectrolytes for coating the electrodes adds complexity to the system. The electrochemical response of electrodes coated with polymer films -and in particular with Nafion- has been reported several decades ago [30,31]. As a polyelectrolyte with ion-exchanging capabilities, Nafion membranes generate a Donnan potential at the solution interface. Naegeli *et al.* have demonstrated that magnitude of this potential is coupled to the different equilibriums (acid-base, redox) and the electrolyte composition of the solution [32]. All in all, the potentiometric response of a Nafion-coated Pt electrode to the addition of H_2O_2 is complex and cannot be easily predicted.

In this work, the potentiometric response to the addition of H_2O_2 of Pt electrodes coated with Nafion is studied. The results show that the Nafion not only prevents the interfering effect of negatively charged redox anions -such as ascorbate-, but that it also produce a significant enhancement of the potentiometric response that depends on the ionic strength of the solution. The data suggest that this enhancement is connected to an additional effect resulting from the Donnan potential generated by the polyelectrolyte coating of the electrode. It is shown that this enhanced sensitivity and selectivity show promise for the development of enzyme-based potentiometric biosensors.

2 Experimental

2.1 Reagents and Solutions.

A Nafion 117 solution (ca. 5% in a mixture of lower aliphatic alcohols and water) used as received, sodium ascorbate, hydrogen peroxide (H_2O_2) (30 % wt in water), glucose oxidase (GOx) from *Aspergillus niger* type X-S, lyophilize powder, 100,000-250,000 units/g solid, D-glucose, boric acid and analytical grade sodium salts of acetate, phosphate, sulphate, nitrate, potassium hydrogen phosphate, potassium hexacyanoferrate salts and chloride salts of potassium, sodium and calcium were also purchased from Sigma-Aldrich. Initial measurements were performed in a 0.1

M phosphate buffer solution (PBS) at pH 7. Acetate, phosphate and borate buffer 0.1 M were used for the experiments involving the change of pH. All solutions were prepared using Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$). Fresh solution of hydrogen peroxide (H_2O_2) was prepared daily. All measurements carried out with PBS contained 0.135 M of NaCl.

2.2 Materials.

A 99.95 % purity Platinum wire of 1mm \varnothing diameter, (Goodfellow Cambridge Limited, England) was inserted into a Teflon® (polytetrafluoroethylene, PTFE) body to make a flat-disc electrode. The electrodes were polished with 1 μm and 0.3 μm alumina and then thoroughly rinsed with double-distilled water. After that, three steps of 10 minutes bath sonication with acetone, then ethanol and finally with double-distilled water were performed. Thereafter, an electrochemical cleaning step was performed. The electrodes were immersed for 2 min in 0.5 M H_2SO_4 solution at a potential of +1.96 V vs. a single junction Ag/AgCl in 3M KCl reference electrode (type 6.0733.100, Metrohm AG). This process should eliminate organic residues and also anodically dissolves trace metals [33]. Finally, electrodes were rinsed with double-distilled water and dried at room temperature. The coating with Nafion was performed by drop casting 10 μL of Nafion solution on top of the platinum electrode. This electrode was left drying overnight at room temperature. For the enzyme-based potentiometric electrode, a similar construction was applied. After the first Nafion layer, a 10 μL drop (100 mg mL^{-1} GOx) was cast onto the Pt electrode and let it dry at 4°C 24h. Subsequently, a second 10 μL Nafion layer was again drop cast. The enzymatic electrode was left drying overnight at 4°C and keep it at 4°C when not in use.

2.3 Electrochemical Measurements.

Electromotive force measurements (EMF) were performed at room temperature (25 °C) in well stirred solutions using a high input impedance ($10^{15} \Omega$) EMF16 multichannel data acquisition device (Lawson Laboratories, Inc. Malvern). A double-junction Ag/AgCl in 3M KCl with 1 M LiAcO bridge reference electrode (type 6.0726.100, Metrohm AG) containing a 1 M LiAcO electrolyte bridge was used. The experiments were performed in a 20 mL beaker. The EMF values were corrected using the Henderson equation for the liquid-junction potential.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed by using an electrochemical analyzer/workstation (model 600 Series, CH Instruments). A single-compartment three-electrode cell arrangement with a double-junction Ag/AgCl in 3M KCl with 1 M LiAcO bridge reference electrode (type 6.0726.100, Metrohm AG), a glassy carbon rod as counter electrode and the electrode under study as a working electrode was used. The impedance spectra were recorded in the frequency range 100 kHz-10 mHz by using a sinusoidal excitation signal that was superimposed on a constant direct current potential, (E_{dc}) 0.2 V. The electrodes were studied using excitation amplitude of ± 10 mV. The measurements were taken in a solution of 0.1 M KCl at room temperature (25°C). For cyclic voltammetry (CV) experiments, a potassium hexacyanoferrate (III) and potassium hexacyanoferrate (II) ($\text{Fe}(\text{CN})_6^{3-/4-}$) solution (5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and 100 mM NaCl as a supporting electrolyte) was used as redox couple. The working electrode was cycled from 0.4 V to -0.2 V at 50 mV s^{-1} . Both experiments were performed at room temperature (25°C).

3 Results and Discussion

3.1 Potentiometric detection enhancement.

Figure 1A shows the typical potentiometric response obtained for a bare and for a Nafion-coated Pt electrode upon the addition of H_2O_2 in 0.1 M PBS at pH 7. For the bare electrodes a decrease of the potential as the concentration of H_2O_2 increases is observed. In general, this is in agreement with results already reported [34, 35]. However, a positive potentiometric signal for H_2O_2 is also described [36]. This type of response might be ascribed to the MnO_2 microparticles that are oxidized upon the addition and thus reduction of H_2O_2 .

In this work, the Pt electrode is sensing the changes on the redox potential of the solution produced by the addition of peroxide. The redox half-reaction of H_2O_2 on the Pt surface can be expressed as:



and the half-cell potential (E) can be calculated according to the Nernst equation for this reaction (at 298 K):

$$E = E^0 - \frac{0.059}{2} \log \frac{[\text{H}_2\text{O}_2]}{p\text{O}_2[\text{H}^+]^2} \quad [2]$$

where the brackets represent the activities of the species, $p\text{O}_2$ is the partial pressure of oxygen, and E^0

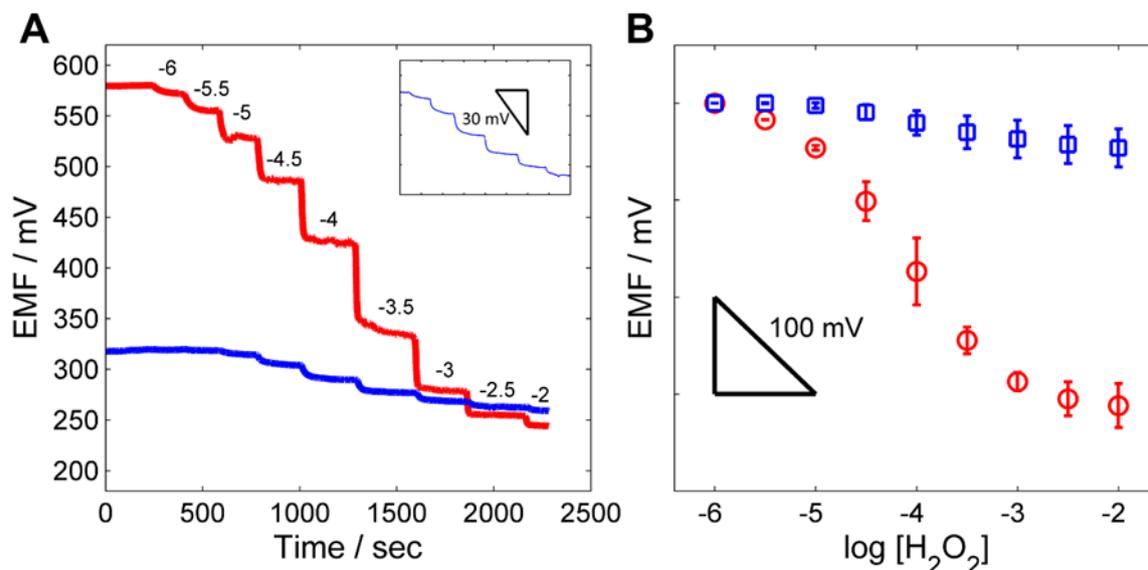


Fig. 1. Potentiometric response curves. (A) Time-trace for bare (blue line) and Nafion-coated (red line) platinum electrode in PBS pH 7 at 25°C (mean \pm S.D., $N=2$). Inset shows a magnification of the calibration curve for bare platinum electrode. (B) Corresponding calibration plots for bare (blue, \square) and coated (red, \circ) electrodes. Initial potentials have been subtracted to better illustrate the differences between the two systems. Error bars correspond to the standard deviation ($N=2$).

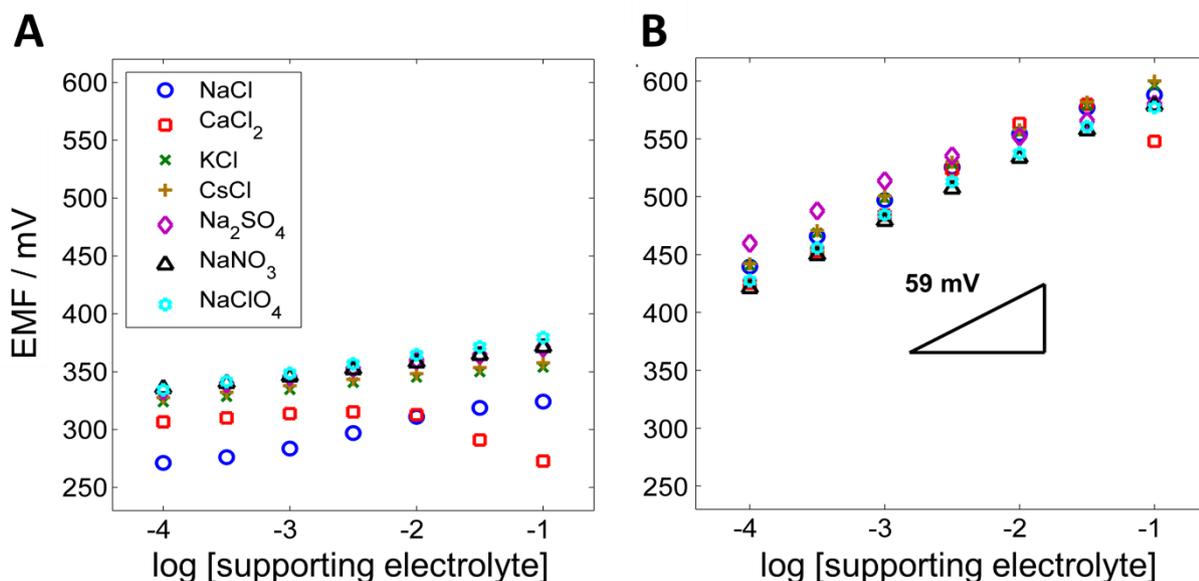


Fig. 2. Comparison of the initial potential as a function of the total electrolyte concentration for (A) bare and (B) Nafion-coated platinum electrodes upon increasing concentration of different supporting electrolytes at 25°C.

(O_2/H_2O_2) is the standard potential for this reaction (0.695V). This equation predicts a linear decrease of the potential with the increase of the logarithm of the activity of peroxide (at a constant pH), as it is observed in Figure 1. The expected slope should be around 0.028V/decade. However, because of the many factors affecting the electrochemical behaviour of peroxide on Pt surfaces, [27,28] this equation is of limited use in quantitative terms. In fact, different values for this slope have been reported depending on the surface of Pt, crystalline structure, etc.

The first experimental evidence that shows the difference between bare and Nafion-coated electrodes is the initial potential (i.e., the potential before the addition of peroxide). Electrodes coated with Nafion show a significantly higher initial potential when compared to the bare Pt electrodes. These differences could be attributed to the accumulation of charges at the Nafion-solution interface. Nafion has significant ion-exchange capabilities [37,38] due to the negatively charged sulfonate groups. Thus, a Donnan potential can be generated by the incorporation of cations from the solution [32].

Interestingly, these electrodes coated with Nafion show also a decrease on the potential with the addition of H_2O_2 , but the magnitude of the change observed is much more pronounced. First, it has been shown that Nafion forms bi-continuous nanostructures [39] that allows the transport of small and neutral molecules. Previous studies have shown the permeability of this material to H_2O_2 [40]. Therefore, it is not surprising that

peroxide reaches the surface of the Pt electrode and produces a redox response. What is more interesting, however, is that this response is somehow modulated by the presence of Nafion. Figure 1B compares the response as a function of the logarithm of the concentration of H_2O_2 for both electrodes, and regression parameters from these plots are presented in Table 1.

Table 1: Comparison of analytical figures of merit for the determination of H_2O_2 with the two types of electrodes in 0.1 M PBS buffer (pH=7).

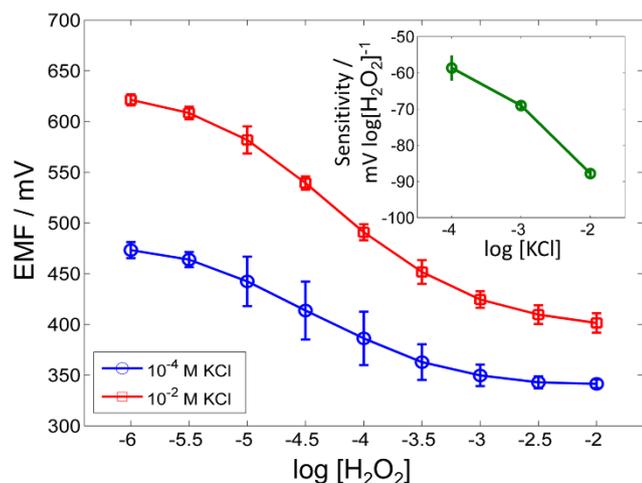
Parameters	Bare Pt	Nafion-coated Pt
Sensitivity (mV decade ⁻¹)	-18.5 ± 7.9	-125.1 ± 5.9
Linear Range (M)	$10^{-4.5}$ to 10^{-3}	10^{-5} to 10^{-3}
LOD (M)	$10^{-5.1}$	$10^{-5.4}$

Since both, coated and uncoated electrodes reach a similar potential at higher concentration of peroxide, the improvement in sensitivity observed can be ascribed to the higher initial potential displayed by the Nafion-coated electrodes, which -as it has been suggested- it is in direct relationship with the Donnan potential originated at the Nafion-solution interface.

To further explore this point, the dependence of this initial potential on the total concentration of the supporting electrolyte for bare (Figure 2A) and coated electrodes (Figure 2B) was evaluated. The results show a limited response for the bare Pt electrodes, while a marked linear increase with an almost Nernstian dependence is observed when the electrodes are coated

with Nafion. This type of response has been already reported for analogous systems and strongly supports the idea of the Donnan contribution in the initial potential of the coated electrodes [38].

Fig. 3. Comparison of the H_2O_2 calibration curves using coated electrodes at different concentrations of supporting electrolyte (KCl): 10^{-2} M (\square) and 10^{-4} M (\circ) (mean \pm S.D., $N = 2$). Inset displays H_2O_2 sensitivity versus supporting electrolyte (KCl) concentration.



For this reason, calibration plots for peroxide at different electrolyte concentrations were also performed and the results are displayed in Figure 3. As the electrolyte concentration in the solution decreases, the slope also decreases and approaches that of bare Pt electrodes. In essence, the sensitivity to peroxide of the electrodes coated with Nafion is dependent on the total concentration of electrolyte. It is also worth noticing

that the increase of the concentration of electrolyte improves the reproducibility of the response between electrodes.

The influence of pH on this phenomenon has been also evaluated. Figure 4 also shows the response of bare (Figure 4A) and coated electrodes (Figure 4B) to the addition of H_2O_2 in a range of pH from 4 to 9. It is worth mentioning that the sensitivity for H_2O_2 on bare electrodes increases considerably as the pH increases. It has been suggested that this is in part due to a decrease on the stability of H_2O_2 at neutral and basic pH [41]. At the higher concentrations, the bare Pt electrodes yield an almost Nernstian dependence with the pH, as predicted by Equation 1. The coated electrodes, on the other hand, show also a range with a linear dependence with pH (for a given H_2O_2 concentration) but with slopes that are higher than the expected Nernstian value. These results, however, are hard to interpret. First, the changes in pH also imply a change in the total ionic concentration, which modulates the response of the electrode. Second, the changes in the pH of the bulk solution do not imply similar changes on the pH at the interface or at the bulk of the membrane. In other words, the modulation of the pH at the interface induced by the Donnan potential may have a significant effect on the redox response of the electrode. From the plots of Figure 4B it is evident that Nafion-coated electrodes display an enhanced sensitivity at all pH values. Nevertheless, the relative enhancement is more pronounced as the pH increases. As the sensitivity increases, the linear range is shifted towards lower

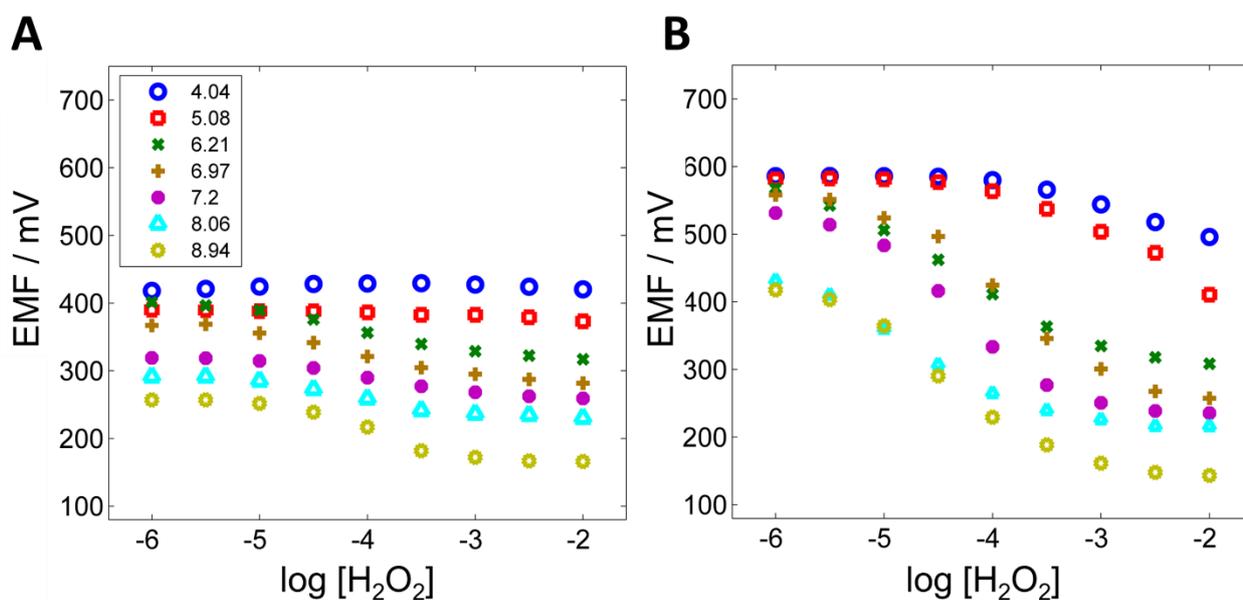


Fig. 4. Calibration plots at several pH for (A) bare and (B) Nafion-coated electrodes in 0.1 M buffers of different pH at 25°C.

concentrations, which results in an improvement of the limits of detection for H_2O_2 at higher pH.

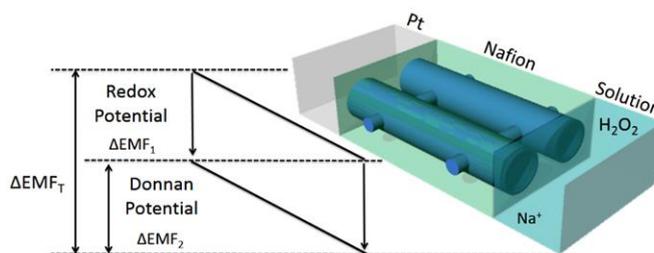
As it was mentioned before, there are many factors that make difficult to elaborate an accurate description of the mechanism involved in the phenomena observed. First, the reactivity of H_2O_2 on Pt is complex and highly dependent on the experimental conditions. Second, many of the properties of Nafion are still under study [37,42,43]. Third, the combination of both systems (i.e., redox-sensitive electrodes coated with polyelectrolytes) adds another level of complexity, since it has been reported that in these types of systems the chemical equilibria in solution (redox, acid-base) are strongly coupled with the ion-exchange properties of the membrane. Last, but not least, reactions between Nafion and H_2O_2 could also occur and they might -up to a certain degree- play a role on these results. This last point, however, is less likely, since the electrodes can be washed and re-used, obtaining reproducible results. All in all, a detailed study of the mechanism of generation of the potential in this system falls well beyond the scope of this work, and only some general observations can be elaborated.

Regarding the role of the Nafion membrane, it is important to remark that the coated electrodes are stabilized in a solution with high ionic strength (in general 0.1 M NaCl, unless stated otherwise) in neutral to slightly basic pH. Under these conditions, the membrane incorporates Na^+ from the solution (releasing H^+). This ion-exchange capacity of Nafion with singly charged electrolytes is well known [32]. The detection of H_2O_2 is performed after this stabilization has taken place. Beyond the permselective behaviour, the response obtained with the coated electrodes seems to be an enhanced form of the response obtained with the bare electrodes. Thus, it could be assumed that the same underlying mechanism operates in both cases, (i.e., the reaction between Pt and H_2O_2), but that some amplification factor operates when Nafion membranes are present. From the previous evidence (see Figure 2B), this amplification is related to the Donnan potential as a result of the ionic concentration of the solution.

The Nafion membrane is stabilized between two different interfaces: the Pt-membrane interface, from one side, where the membrane strongly interacts with the metal through the hydrophobic Nafion domains [44]; and the membrane-solution interface, from the other, where the ion-exchange process generates the Donnan potential. The gradient of electrochemical potential of the system Pt||membrane||solution is altered when H_2O_2 reaches the surface of the Pt. First, the metal-membrane interface registers a drop of the redox

potential. As a result of this change, a rearrangement of the ionic species in the membrane and at the interface under the new equilibrium conditions may occur, which results in the amplification of the electrode response. If some oxidation of the H_2O_2 takes place inside Nafion membrane, the increase of the H^+ concentration might be leading to a leach of cations at the solution interface and a change on the internal pH of the membrane. Thus, the amplification of the signal might be in two directions: first, a rearrangement of the membrane-interface ionic distribution that is able to change the Donnan potential of the system; second the acid-base behaviour of the adjacent charged groups of Nafion might be different from the pH of the buffer, then an amplification of the signal is generated. Clearly, this is at this point speculation, and more work needs to be conducted to understand the conditions inside the membrane and the mechanisms involved. Figure 5 is an attempt to illustrate the suggested mechanism. Interestingly, there are many works devoted to the study of the interactions between platinum and H_2O_2 , but there is not complete agreement on the mechanisms involved. Similarly, the recent works on the structure and properties of Nafion membranes reveal the lack of models to fully understand the behaviour of this material.

Fig. 5. Schematic representation of the Nafion-coated electrodes mechanism studied in this work. The exchange capacity and the redox reaction performed the suggested mechanism.



3.2 Nafion as a permselective membrane.

In order to evaluate the electrochemical properties of the interface, an electrochemical impedance experiment was carried out. The comparison of the impedance spectra between bare and Nafion-coated Pt electrodes (Figure S1 of the Supporting Information) exhibits a typical capacitive mechanism for the coated electrode, with a single high-frequency semicircle related to the

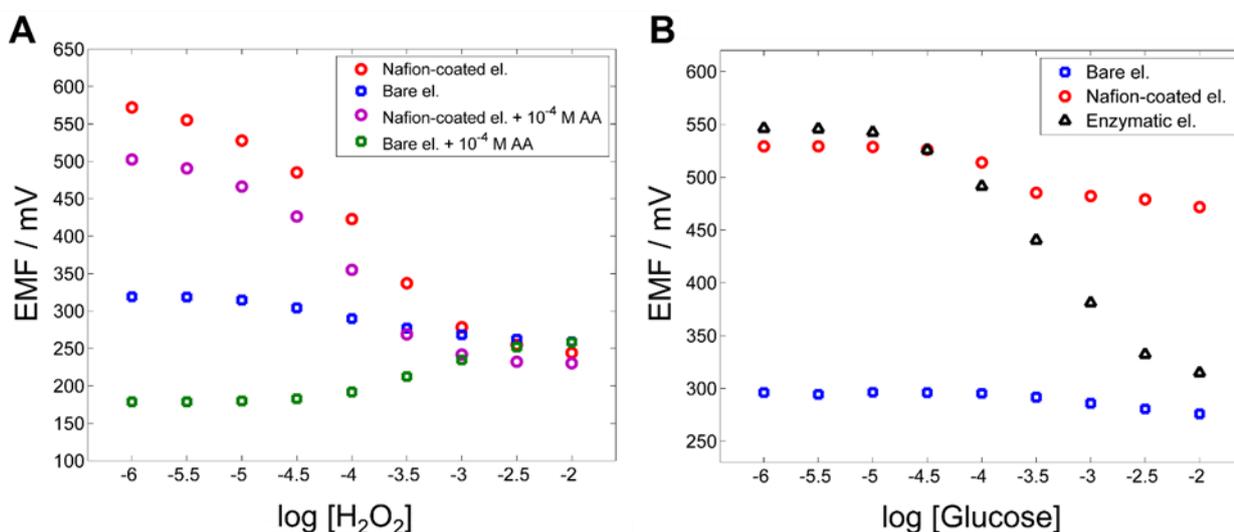


Fig. 6. (A) Evaluation of the addition of ascorbic acid (AA) in the cell for bare and Nafion-coated electrodes in 0.1 M PBS pH 7.2 at 25°C. (B) Calibration curve for increasing glucose concentration over time for bare, Nafion-coated and Nafion-coated enzymatic electrodes in 0.1 M PBS pH 7.4 at 25°C.

bulk solution and the interface of the Nafion membrane. Nafion membrane exhibited the typical Nyquist plot for a circuit with a resistor and a capacitor in parallel. The resistor is built up with the solution resistance and the resistance of the charge transfer. The double-layer capacitance is built up from the charges accumulation in the interface due to the sulphonate groups of Nafion polymer. In the Nyquist plot there is no Warburg resistance because the hydrated Nafion membrane is in completely equilibrium with the solution in the bulk. This resistance is smaller than what is observed in other conventional polymeric membranes electrodes [45], due to the electrical and structural characteristics of Nafion. Furthermore, Nafion membranes exhibit different selectivity coefficients to different counterions and more uniform exchange site environment than conventional sulfonate ion-exchange resins [22,46]. The perfluorosulfonate ionomer morphology was suggested to follow an oriented ionic nanochannels embedded within a locally aligned polymer matrix where sulfonate groups ($-\text{SO}_3^-$) coated channels are invoked to account for intercluster ion hopping of positive charge species but rejection of negative ions [40]. However, there are several current models describing the Nafion morphology and membrane behaviour, and the evidence is not yet conclusive [37]. Figure S2A of Supporting Information exhibits the rejection of negatively charge molecules thus performing a decrease in the oxidation and reduction peaks of the cyclic voltammogram. Besides, Figure S2B presents redox sensitivity for bare Pt electrode, as

expected, and remains insensitive for Nafion-coated electrode.

Even though mechanisms are still under debate, Nafion membranes have been extensively used in amperometric sensors as a permselective barrier against negatively charged redox species. Thus, the question remains on whether a similar effect could be used to improved potentiometric sensors. Figure 6A shows the results of the addition of ascorbic acid on the calibration plots for peroxide using coated and uncoated electrodes. Ascorbate is a reducing agent that is typically found as interference in biological fluids. Thus, when added to the solution at 100 μM level (normal upper range of the biological fluids) the bare Pt electrode becomes almost insensitive to the addition of peroxide (Figure 6A). Indeed, upon the addition of ascorbic the bare Pt electrodes register a drop of the initial potential, which remains almost constant until a higher concentration of peroxide is reached. The coated electrodes, on the other hand, show a significantly different behaviour (Figure 6A). Interestingly, all the electrodes merge to the final electrochemical potential that is governed by the redox potential of the peroxide solution.

Table 2: Comparison of analytical figures of merit for the determination of H_2O_2 with Nafion coated electrodes before and after the addition of Ascorbic acid in 0.1M PBS.

Test	No Ascorbate	100 μM Ascorbate
Sensitivity (mV decade ⁻¹)	-129.1	-132.3
Linear Range (M)	10^{-5} to 10^{-3}	10^{-5} to $10^{-3.5}$
LOD (M)	$10^{-5.3}$	$10^{-5.4}$

Table 2 compares the analytical parameters obtained for the coated electrodes before and after the addition of ascorbate. First, it can be seen that neither the sensitivity nor the limits of detection (LOD) show significant changes. The linear range shows a slight reduction, but it does not seem to be severely affected. The most significant change that can be observed is a decrease on the initial potential when ascorbate is added (Figure 6A). Evidently, an optimization of the Nafion layer could reduce these effects, and the development of suitable working protocols may help to further enhance the applicability of this approach. It has been suggested, for example, that a thickness of the Nafion membrane could be modified to improve the permselectivity towards negatively charged molecules [47]. Clearly, further work is needed in order to optimize these aspects. However, as a preliminary conclusion, the results suggest that the interference of the potentiometric detection caused by negatively charged redox species can be overcome when using the Nafion coating.

The results shown so far are extremely relevant, since they present a way to alleviate two of the major limitations of the potentiometric detection of peroxide in biological fluids, namely: limited sensitivity and severe interference caused by redox species. Regarding the sensitivity, the Nafion provides a way to produce an enhancement due to the presence of electrolytes. While it could be argued that this modulation of the sensitivity by electrolytes might be a problem for some applications, many biological fluids -such as blood or serum- have a high and constant concentration of ions. Therefore, this should be advantageous for the detection of peroxide. The problem of the interferences, which is also a major issue, can be also successfully overcome as it has been previously shown. The experimental results also show some other practical advantages of the use of Nafion, such as a better reproducibility between sensors and shorter stabilization times of the signal. It is well known that Pt surfaces can be easily contaminated, affecting the electrochemical response. Thus, Nafion might be acting as a barrier that limits this undesired effect.

There are significant implications of these findings in the field of biosensors. The use of oxidase enzymes, for example, that produce peroxide, could be used for the potentiometric detection of neutral molecules in a simple, sensitive and robust way. To prove this point, the enzyme glucose oxidase (GOx) was sandwiched between two layers of Nafion cast on a Pt electrode. The results of the addition of glucose to a bare Pt electrode, an electrode coated with Nafion, and an electrode

coated with Nafion containing the GOx enzyme are presented in Figure 6B. As the concentration of glucose is increased, peroxide is generated and potentiometrically detected, as shown previously. The results exhibit a slope of approximately 110 mV decade⁻¹ of glucose, with a linear range between 10⁻⁴ M to 10^{-2.5} M.

Clearly, these are just preliminary results, since a careful study and optimization of the enzymatic reaction must be performed. However, these initial results strongly encourage further research on this direction.

4 Conclusions

This manuscript demonstrates that permselective membranes -such as Nafion- can be used as an efficient enhancer for the sensitive and selective potentiometric detection of H₂O₂. The approach presented allows the detection of H₂O₂ based on the change of the redox potential of the solution, as well as through the additional contribution of a Donnan potential generated at the membrane-solution interface. Because of this, a modulation of the sensitivity based on the ionic strength and pH of the solution is possible. The maximum sensitivities are thus obtained in high ionic strength, which can be advantageous when dealing with biological fluids.

As a proof of principle, the direct application of this simple H₂O₂ detection through the use of an enzymatic reaction is demonstrated. Thus, the proof of principle for the construction of a simple enzymatic electrode with an enhanced potentiometric response using Nafion permselective membranes is demonstrated for the first time. This device should provide significant advantages when facing the challenge of developing simple, low-cost decentralized platforms.

5 Supporting Information

2 figures as noted in text. This material is available free of charge via the Internet.

6 Acknowledgements

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