Correlation between pore size and reactivity of macro/mesoporous iron and copper hexacyanoferrates for H$_2$O$_2$ electrocatalysis

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1. Introduction

Close-packed arrays of monodisperse polystyrene or silica particles have been successful employed to develop electrochemical sensors and biosensors [1–7]. After removing the spherical particles, the resulting film is a true cast of the template structure. Following a similar methodology, surfactant micelles can also be used as templates instead of the colloidal particles. However, in this case, the resulting mesoporous structure presents dimensions comparable to the diameter of the used amphiphilic aggregates. Both strategies are interesting because they allow the formation of three-dimensional materials with high electroactive surface area/volume ratio, allowing good accessibility of the electrolyte to inner active sites and presenting electronic conductivity through the walls of the material up to the current collector [8–10].

For clinical electrochemical sensors, it is well known that direct H$_2$O$_2$ quantification can present significant signal interference. As a result, electrodes have been modified with metal-hexacyanoferrate-based electrocatalysts to produce high-selectivity H$_2$O$_2$ sensors capable of operating between −0.20 and 0.00 V (vs Ag/AgCl/KCl$_{sat}$) with fast and sensitive responses [11–14].

The present work utilizes close-packed arrays of spherical colloidal polystyrene particles and lyotropic liquid crystalline phases to produce macroporous and mesoporous metal-hexacyanoferrate-based sensors. In the first case, polystyrene spheres with diameters of 300, 460, 600 and 800 nm were used to synthesize a hybrid copper hexacyanoferrate/polypyrrole (CuHCNFe/Ppy) material. As described in previous works, the incorporation of a metal-hexacyanoferrate electrocatalyst into a conducting polymer could drastically improve the mechanical and electroanalytical properties of the resulting sensors [15,16]. Metal hexacyanoferrate-based sensors with pores at nanoscale were also produced.
through the immobilization of the electrocatalyst into mesoporous TiO₂ platforms previously synthesised around surfactant micelles templates in hexagonal phase [17,18]. In this case, TiO₂ with pore diameters of 13, 20 and 40 nm were modified with CuHCNFe and Prussian blue films by coordination-assisted layer-by-layer deposition.

The objective of the paper is to study the importance of pore size to H₂O₂ detection by macroporous and mesoporous Prussian blue type electrocatalysts. The paper is focused on the employment of Prussian blue, since it is very active and selective for H₂O₂ reduction, and also on copper hexacyanoferrate (CuHNCFe), since it is active in the presence Na⁺, which is a Prussian blue cation commonly found in biological samples. The comparison of both methodologies contributes to our understanding of the importance of pore size on H₂O₂ sensors performance, affecting both the wettability and reactivity of the electrocatalyst.

2. Methodology

2.1. Reagents

Polystyrene latex spheres with diameters of 300, 460, 600 and 800 nm were obtained from Aldrich as 10 wt% dispersions in water. All reagents were used as received except pyrrrole, which was distilled prior to use. H₂O₂ was purchased from Sigma–Aldrich as a 30 wt% aqueous solution. Purified water (UHQ Elga System 18 MΩ cm) was used to prepare the solutions.

2.2. Instrumentation

Cyclic voltammetry and chronoamperometry experiments were performed with an Autolab PGSTAT 30 (Eco Chemie). All potentials were referred to an Ag/AgCl/KCl sat electrode, while a platinum foil platforms was employed as the auxiliary electrode. The morphologic images were obtained from field emission scanning electron microscopy (FESEM, JSM-7401F from JEOL). The UV–Vis spectra were acquired on a HP8453 Hewlett–Packard spectrophotometer. Contact angle experiments were performed in a GBX Instrumentation Scientific instrument coupled to a Nikon PixeLink camera.

2.3. Deposition of macroporous and non-porous CuHNCFe/Ppy on glassy carbon electrode

The CuHNCFe/Ppy synthesis was performed in two electrochemical steps. The methodology was based on previous publications [2,3], but here the number of voltammetric cycles was controlled as a function of the desired deposition charge.

Briefly, polystyrene spheres were assembled over glassy carbon by adding 10 μL of a 0.5 wt% aqueous suspension containing 1.0 × 10⁻³ mol L⁻¹ Triton X-100. After slow evaporation of water, another 10 μL aliquot of the suspension was deposited over the previously layer and the water was slowly evaporated again. After that, the electrodes were placed in an oven at 100 °C for 4 h.

For CuHNCFe/Ppy deposition, the Fe(CN)₆³⁻ ions were initially incorporated in the polymer matrix by potential cycling a glassy carbon electrode in a solution containing 2.0 × 10⁻² mol L⁻¹ K₃Fe(CN)₆, 1.5 × 10⁻² mol L⁻¹ pyrrrole + 1.0 × 10⁻¹ mol L⁻¹ KCl. The electrode was cycled in a range of –0.25 to +0.95 V at 50 mV s⁻¹. The electrodeposition was started only after 30 min, in order to swell the interspaces among polystyrene particles by the deposition solution. The second step consisted of placing the Fe(CN)₆³⁻/Ppy modified electrode in a solution containing 2.0 × 10⁻² mol L⁻¹ CuCl₂ + 1.0 × 10⁻¹ mol L⁻¹ KCl for 2 h. This procedure was carried out to allow the insertion of Cu²⁺ ions into the Fe(CN)₆³⁻-doped polypyrrole network. After this time, the electrode was cycled in a potential range of –0.25 to +0.95 V at 50 mV s⁻¹. The polystyrene template was dissolved by soaking the electrode in stirred toluene for 24 h. After that, the modified electrode was washed and dried in a desiccator.

2.4. Synthesis of Prussian blue and CuHNCFe into mesoporous TiO₂ films

ITO electrodes (indium-tin oxide, one side coated glass by Delta Technologies Ltd., Rs <25 Ω) were used to deposit mesoporous TiO₂ films as described elsewhere [19,20]. This procedure allowed the synthesis of TiO₂ films with porous channels of 13 nm in diameter and thicknesses of 130, 200 and 260 nm. Not only thickness, but also the pore diameter could be modulated by changing the experimental procedure as described previously [17]. In this case, polypropylene glycol and tetrahydrofuran were used to produce two new mesoporous TiO₂ platforms, one formed by channels with 20 nm diameter and another formed by channels of 40 nm in diameter.

The immobilization of Prussian blue inside mesoporous TiO₂ films was performed using the methodology described previously [18]. Briefly, the bifunctional ligand 1,10-phenanthroline-5,6-dione was bind to the TiIV surface by immersing the TiO₂ platforms in a 5.0 × 10⁻¹ mol L⁻¹ ethanolic solution of the ligand for 24 h. After that, the nitrogen atoms on the ligand remained available for coordination. Thus, the substrate was immersed in a 5.0 × 10⁻¹ mol L⁻¹ FeSO₄ solution, where Fe²⁺ cation coordination was performed. Subsequent exposure of this modified electrode to a 5.0 × 10⁻¹ mol L⁻¹ K₃Fe(CN)₆ solution led to the formation of one layer of Prussian blue. The immersion sequence in Fe²⁺ and Fe(CN)₆³⁻ solutions could be then repeated in order to grow a new Prussian blue layer over the previously deposited.

This procedure was also adapted for CuHNCFe formation on the surface of mesoporous TiO₂ films. After immobilising the 1,10-phenanthroline-5,6-dione ligand, the electrode was immersed in an aqueous solution containing 5.0 × 10⁻¹ mol L⁻¹ CuCl₂ for 30 min and washed with deionised water. After the electrode was immersed for 30 min in a 5.0 × 10⁻¹ mol L⁻¹ aqueous solution of K₃Fe(CN)₆ and washed once more with deionised water. Repetition of the dipping process in CuCl₂ and K₃Fe(CN)₆ solutions was capable of forming another CuHNCFe monolayer on top of the previous one.

2.5. Electrochemical detection of H₂O₂

H₂O₂ electrochemical detection was performed with macroporous and mesoporous electrocatalysts by chronoamperometry. A solution containing 5 mL of 1.0 × 10⁻¹ mol L⁻¹ NaCl (or KCl – see caption of the figures) + 1.0 × 10⁻¹ mol L⁻¹ HCl was used with slight magnetic stirring. Initially, the electrodes were polarized to 0.00 V for 40 min to stabilize the background current.

3. Results and discussion

The FESEM images obtained after removing the template of polystyrene spherical particles are presented from Fig. 1A–D. All of the macroporous films were electrodeposited controlling the charge during synthesis, so that the electrodes were always modified with similar amounts of material. These films were electrochemically characterized in media containing only cations able to block Prussian blue electroactivity, such as Na⁺ and H⁺. As shown in Fig. S1 (ESI), it was possible to observe the reversible oxidation and reduction of the hybrid compound at different scan rates.

The analytical performance on H₂O₂ detection of non-porous CuHNCFe/Ppy electrodes was compared with the results obtained with macroporous films presenting 300, 460, 600 and 800 nm in
diameter. The obtained chronoamperograms are shown in Fig. S2 (ESI). The analytical parameters obtained using the curves are presented in Table 1. The detection limits are three times the standard deviation of the background current without analyte/sensitivity, and the response time was 90% of total current variation when \( \text{H}_2\text{O}_2 \) aliquots were added.

Surprisingly, there was not considerable variation in the performance of the macroporous electrocatalysts and, moreover, no difference was observed when the results were compared with the performance of the non-porous CuHCNFe/Ppy material. An explanation for these results required to determine whether detection of \( \text{H}_2\text{O}_2 \) by CuHCNFe/Ppy was a surface phenomenon or it was dependent on the amount of material present in the electrode. If the film was very permeable to \( \text{H}_2\text{O}_2 \), detection could occur throughout the electrocatalyst volume. Consequently, all the sensors could present the same performances because all the electrodes were modified with the same amount of electrocatalyst.

Table S1 (ESI) presents the measured sensitivities for four films with different amounts of non-porous CuHCNFe/Ppy that were used for \( \text{H}_2\text{O}_2 \) detection showing that the obtained sensitivities were very similar, regardless of the different charges observed during voltammetric deposition of non-porous CuHCNFe/Ppy. This result suggests that the reduction of \( \text{H}_2\text{O}_2 \) by CuHCNFe/Ppy does not depend on the volume of material but occurs mainly in the outer surface of the electrocatalyst.

Consequently, the determination of how much the surface is increased by using macroporous CuHCNFe/Ppy films becomes another important aspect for understanding the presented analytical results. With this purpose, the thicknesses of all macroporous electrocatalysts were determined by FESEM, as illustrated in Fig. S3 (ESI) and the results are summarized in Fig. 2.

It can be observed that CuHCNFe/Ppy electrocatalysts with larger pores were thicker than those synthesised around polystyrene spheres with smaller diameters. However, dividing the average thickness by the diameter of the sphere used as a template, it was possible to estimate that all macroporous CuHCNFe/Ppy were formed by approximately 2.5 porous layers. When a macroporous film of CuHCNFe/Ppy is compared with non-porous CuHCNFe/Ppy material, the theoretical value of the increase in surface area can

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**Table 1**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Non-nanostructured</th>
<th>300 nm</th>
<th>460 nm</th>
<th>600 nm</th>
<th>800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (( \mu \text{A cm}^{-2} \text{ mmol}^{-1} \text{ L} ))</td>
<td>(198 ± 6)</td>
<td>(180 ± 20)</td>
<td>(190 ± 30)</td>
<td>(200 ± 20)</td>
<td>(170 ± 30)</td>
</tr>
<tr>
<td>Detection limit (( \mu \text{mol} L^{-1} ))</td>
<td>(1.9 ± 0.1)</td>
<td>(3 ± 1)</td>
<td>(3 ± 2)</td>
<td>(1.0 ± 0.3)</td>
<td>(2 ± 1)</td>
</tr>
<tr>
<td>Linear range (mmol L(^{-1}))</td>
<td>(4.0 ± 0.2)</td>
<td>(3.2 ± 0.2)</td>
<td>(3.0 ± 0.5)</td>
<td>(2.2 ± 0.2)</td>
<td>(2.2 ± 0.2)</td>
</tr>
<tr>
<td>Response time (s)</td>
<td>(3.5 ± 0.7)</td>
<td>(3 ± 1)</td>
<td>(4 ± 1)</td>
<td>(5 ± 2)</td>
<td>(5 ± 3)</td>
</tr>
</tbody>
</table>
be estimated on the basis of geometric considerations, leading to Eq. 1, where \( f \) is the factor of increase in surface area when compared with a “flat” deposit, and “n” is the number of porous layers [21,22].

\[
f = n\pi \left( \frac{4}{3} \right)
\]

(1)

For \( n = 2.5 \), the factor of increased surface area corresponds to \( f = 9 \), which means that all macroporous CuHCNFe/Ppy films have a theoretical surface area approximately nine times greater than the non-porous CuHCNFe/Ppy. This might help to understand why the performance of all macroporous CuHCNFe/Ppy are similar to each other but does not explain why there is no advantage in using these macrostructures instead of the non-porous material. Because of that, the wettabilities of the macroporous and non-porous CuHCNFe/Ppy electrocatalysts were studied through contact angle measurements, with the purpose of understanding how difficult was the pore accessibility by the aqueous solutions where \( \text{H}_2\text{O}_2 \) tests were performed. [23–25], Fig. S4 (ESI) shows the images obtained when a drop of an aqueous solution containing \( 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{NaCl} + 1.0 \times 10^{-3} \text{ mol L}^{-1} \text{HCl} \) was placed on macroporous and non-porous CuHCNFe/Ppy electrocatalysts. These angles were greater than that of non-porous CuHCNFe/Ppy, indicating a hydrophobic surface.

As shown in Fig. 3, there is no significant difference between the contact angles of any of the macroporous CuHCNFe/Ppy, which were above 90° in all the cases, indicating a hydrophilic surface. These angles were greater than that of non-porous CuHCNFe/Ppy, which was approximately (65 ± 4)°. This difference is attributable to the air trapped within the pores, which indicates that the present porous system follows the behavior of the model proposed by Cassie and Baxter [23]. This phenomenon makes the access to the inner active sites of the macroporous CuHCNFe/Ppy by the electrolyte solution, more difficult. We therefore added the surfactant sodium dodecyl sulfate (SDS) to the 0.1 mol L\(^{-1}\) NaCl + 0.1 mol L\(^{-1}\) HCl solution to alter the surface tension and improve wettability of the macroporous electrocatalyst, causing complete filling of the pores [26]; Fig. S5 (ESI) presents the contact angle measurements carried out on macroporous CuHCNFe/Ppy:460 nm; the use of various concentrations of surfactant allowed an effective transition from a Cassie-Baxter to a Wenzel system. Experiments for \( \text{H}_2\text{O}_2 \) detection were repeated with CuHCNFe/Ppy-460 nm, in the presence of SDS surfactant. The experiments were performed with electrolyte solutions containing \( 1.0 \times 10^{-1} \), \( 1.0 \times 10^{-2} \) and \( 1.0 \times 10^{-4} \text{ mol L}^{-1} \) surfactant, to verify whether the number of amphiphilic molecules in the environment could alter the results. The obtained sensitivities are shown in Fig. S6 (ESI); the performances were again quite similar among all of the considered systems, suggesting that even with complete accessibility of the pores there is another factor affecting the results. This factor is related to kinetics and, as already demonstrated by Szamocki et al. [27], it plays a key role in the use of macroporous platforms for electrochemical sensors. For fast electrochemical kinetics, molecules react completely in the pores of the outer half layer before reaching the innermost pores. Once CuHCNFe/Ppy is an electrocatalyst poorly permeable to \( \text{H}_2\text{O}_2 \) reduction, only a small part of the outer macroporous CuHCNFe/Ppy area is used for the reaction, and as a result, the current is always constant. Alternatively, electrochemical reactions with slow kinetics allow the utilization of all porous layers.

These results are interesting because they show that efforts performed to increase surface area of porous electrodes do not always bring advantages to analytical performance of sensors. Consequently, to interpret the analytical application of porous films, it is important to answer the following questions: Does the sensor response depend on surface area or volume of the material? Can the inner pores be accessible by the analyte? Does the kinetic allow the utilization of inner pores or the reaction is so fast that occurs only at outer half pore?

We were also interested to observe how these questions were manifested in electrodes modified by Prussian blue type electrocatalysts with smaller pores, when the macroscale is diminished to the nanoscale. As shown recently [18], mesoporous TiO\(_2\) thin films presenting pore arrays with 13 nm in diameter and a thickness of 130 nm were functionalized with a bifunctional ligand (1,10-phenantroline-5,6-dione) that allowed the immobilization of Fe\(^{2+}\) ions with open coordination sites on the mesoporous surface. The system was exposed to a Fe(CN)\(_6^{3-}\) solution to assemble a monolayer of Prussian blue inside the mesoporous matrix. Alternating immersions in Fe\(^{2+}\) and Fe(CN)\(_6^{3-}\) solutions were repeated to add more Prussian blue layers to the mesoporous material, and the results achieved during \( \text{H}_2\text{O}_2 \) detection showed that the sensitivity of the sensor increased to up to 4 confined layers, presenting a good chronoamperometric result of (410 ± 20) \( \mu \text{A cm}^{-2} \text{ mmol}^{-1} \text{L}^{-1} \).

Different from CuHCNFe/Ppy, it is well known that Prussian blue alone presents a good permeability to \( \text{H}_2\text{O}_2 \), once there is no polypyrrole diminishing the hydrophilic character of the system [28,29]. So, experiments were carried out to study the way in which kinetics could affect the performance of the sensor. Because of that, mesoporous TiO\(_2\) electrodes formed by pore arrays with an average diameter of 13 nm were prepared with thickness of 130, 200 and 260 nm. These platforms were modified with 4 layers of Prussian blue and the results achieved for \( \text{H}_2\text{O}_2 \) detection using the films with different thickness are shown in Fig. S7 (ESI). The obtained sensitivities were similar and independent on the thickness of the employed mesoporous materials. It is noteworthy that, as in the case of macroporous CuHCNFe/Ppy, Prussian blue is also a catalyst for \( \text{H}_2\text{O}_2 \) electroreduction. Consequently, the fast kinetics of the reaction turns only the outer Prussian blue active sites responsible for reducing \( \text{H}_2\text{O}_2 \), even though the mesoporous material presents nanometer-scale film thickness while the macroporous CuHCNFe/Ppy thickness is on the micrometer scale.

In another set of experiments, the thickness was maintained at 130 nm and the pore size of mesoporous TiO\(_2\) films was changed. Platforms with 13, 20 and 40 nm in diameter were used to immobilize Prussian blue layers into their cavities. Then, electrodes were applied for \( \text{H}_2\text{O}_2 \) detection in \( 1.0 \times 10^{-1} \text{ mol L}^{-1} \text{KCl} + 1.0 \times 10^{-1} \) mol L\(^{-1}\) \text{HCl} \). The obtained sensitivities for each pore size in function of the number of immobilized Prussian blue layers are shown in Fig. 4.

Fig. 4 shows that when thickness was maintained at 130 nm, for each pore size, the sensitivities were dependent on the material volume and they increased until a specific number of immobilized layers before declining substantially. We have shown for the platform with 13 nm in diameter [18] that the values of the
sensitivities and their relation with the number of Prussian blue layers can be explained using UV–Vis spectroscopy and scanning electron microscopy data. When a few layers of Prussian blue were confined into the pores with 13 nm, FESEM images revealed that the pores remained open and accessible to H$_2$O$_2$, while UV–Vis data revealed a blue-shifted metal-to-metal charge transition, indicating an unusual and more reactive Prussian blue structure. Furthermore, the sensitivity increased until the immobilization of 4 layers because it was possible to confine the greatest amount of Prussian blue electrocatalyst inside the pores of 13 nm without blocking the cavities. Finally, the immobilization of the 5th Prussian blue layer made the sensitivity to decline because the pores were completely filled, leading to the loss of nanoporous morphology, as represented in Fig. S8A (ESI). The UV–Vis data obtained with electrocatalysts where pores were blocked also revealed that the metal-to-metal charge transition was very similar to that observed with a non-porous Prussian blue material, indicating that coordination of a large amount of layers diminishes the number of defects present in the material, as depicted in Fig. SBB (ESI).

This explanation can also be applied to the new platforms with 20 and 40 nm in diameter. However, note that the number of Prussian blue layers that can be immobilized before diminishing the sensitivity varied as a function of the pore diameter. For pores of 13 nm, it was possible to confine accessible and reactive active sites up to 4 layers, and the sensitivity reached (410 ± 20) µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$. For pores of 20 nm, the sensitivity increased until immobilizing 5 layers, where it reached a value of (940 ± 40) µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$. The possibility of increasing the number of deposited layers before losing the confinement effect was attributed to the fact that the platforms of 20 nm in diameter present pores with greater diameters than the systems with pores of 13 nm. This result becomes even more interesting when we observe the sensitivity of the films immobilized into the platforms with 40 nm in diameter, which increased until the 6th layer, before decreasing because the pores were completely obstructed. However, even with larger pores, the sensitivity obtained immobilizing 6 layers of Prussian blue into the pores of 40 nm was (790 ± 50) µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$; lower than that displayed by confining 5 Prussian blue layers into the pores of 20 nm. This original result indicates that the gain in accessibility achieved with the pores of 40 nm does not improve the analytical performance of the sensor during H$_2$O$_2$ detection when compared to the sensor prepared with pores of 20 nm. Consequently, it is necessary to consider a compromise between the amount of immobilized electrocatalyst and the accessibility of H$_2$O$_2$ in order to understand the analytical performance of the present mesoporous Prussian blue sensors.

Finally, many reports have shown that the activity of Prussian blue can be blocked in the presence of Na$^+$, H$^+$, Li$^+$ and the group II cations [30,31] depending on the conditions in which Prussian blue was deposited. An alternative to this limitation replaces Prussian blue with an analogue with larger vacancies in its inorganic structure, such as CuHCNFe. Maintaining the same strategy of electrocatalyst immobilization, sequential immersions in Cu$^{2+}$ and Fe(CN)$_6^{3-}$ solutions could be performed to control the number of CuHCNFe layers present in the TiO$_2$ mesostructure. Using this methodology, TiO$_2$ platforms with pore sizes of 13, 20 and 40 nm in diameter were used to confine 4, 5 and 6 layers of CuHCNFe, respectively. Fig. S9 (ESI) presents the sensitivities obtained when these electrocatalysts were applied to detect H$_2$O$_2$ in an electrolyte containing Prussian blue blocking cations. For comparative purposes, the graph also includes the sensitivities obtained in the same electrolyte using TiO$_2$ platforms with pore sizes of 13, 20 and 40 nm in diameter modified with 4, 5 and 6 layers of Prussian blue, respectively. The analytical curves achieved by confining 5 layers of CuHCNFe or Prussian blue into TiO$_2$ with pore sizes of 20 nm are presented in Fig. 5, in comparison with the result achieved with a conventionally non-porous Prussian blue material.

From Figs. S9 (ESI) and 5, it is possible to see that the sensitivities achieved with the nanoporous platforms modified with CuHCNFe (332 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ for pores of 13 nm, 637 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ for pores of 20 nm and 560 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ for pores of 40 nm) in media containing Na$^+$ and H$^+$ were extremely high, especially when compared to previously reported sensitivities. For example, a non-porous CuHCNFe film presents a sensitivity of 0.14 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ [16], while systems with CuHCNFe nanoparticles show sensitivities of 30.6 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ [32]. In spite of these results, an even more striking performance was obtained with the Prussian blue modified sensors in media containing Na$^+$ and H$^+$. Just as in media with K$^+$ ions, films with pores of 20 nm showed a better performance than pore sizes of 13 or 40 nm, reaching a sensitivity of (930 ± 50) µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$. To the best of our knowledge, this result is extremely satisfactory considering chronoamperometric experiments performed in medium containing Prussian blue blocking cations. Moreover, mesoporous Prussian blue also showed an improved performance when compared to the conventional electrodeposited Prussian blue, which sensitivity obtained in Na$^+$ was only 82 µA cm$^{-2}$ mol$^{-1}$ L$^{-1}$ and the linear range did not exceed 0.15 mmol L$^{-1}$ (one order of magnitude lower than that exhibited by mesoporous Prussian blue sensor). The limit of detection...
obtained with the mesoporous Prussian blue was 
(0.49 ± 0.08) μmol L⁻¹ (3 times the standard deviation of the background current without analyte/sensitivity), the response time was (6 ± 2) (90% of the current variation) and the linear range was up to (1.3 ± 0.1) μmol L⁻¹.

The results achieved here suggest that Prussian blue immobilised by coordination in the TiO₂ platforms with pores of 13, 20 or 40 nm presents an inorganic structure different from the displayed by the non-porous electrocatalyst. The spectra in the visible region shown in Fig. S8B (ESI) supports this hypothesis because the electronic transition of the mesoporous electrocatalyst was shifted to shorter wavelengths when compared to that currently exhibited by Prussian blue. This different structure contributes to the high reactivity of the material and allows insertion/removal of Na⁺ during charge compensation without losing electroactivity. It is important to emphasize that all porous Prussian blue materials were synthesised with the same experimental conditions, once incorporation of different M²⁺ cations during charge neutralization could also affect the energy of the charge-transfer band [33]. Moreover, as shown in Fig. S10 (ESI), the better wettability of this material also favors electrochemical experiments performed in aqueous solution. The low contact angle of (33 ± 2°) (number of angles measured = 4) indicates that this platform is hydrophilic, unlike the hydrophobic macroporous CuHCNFe/Ppy reported in Fig. 3, with contact angles above 90°. This difference in the contact angle measurements of the porous electrocatalysts can be explained as a function of the different physical–chemical natures of the materials and due to the greater amount of air trapped in the macroporous system.

For comparison, to the best of our knowledge, the highest sensitivity achieved with a Prussian blue based sensor was reported recently by Karyakin and col. [34], where a macroporous gold microelectrode was utilized for Prussian blue electrodeposition. The sensitivity obtained for H₂O₂ sensing was 8.8 ± 0.7 A mol L⁻¹ cm⁻² in a batch regime under stirring at 0.00 V; in a 0.05 mol L⁻¹ phosphate buffer solution, pH 7.0, and containing KCl 0.1 mol L⁻¹. Interestingly, when the pores of the microelectrode surface were completely filled with the electrocatalyst, the resulting sensor also showed a behavior similar to the non-porous microelectrode.

4. Conclusions

Efforts performed to increase surface area of porous electrodes do not always bring advantages to analytical performance of electrochemical sensors. In order to evaluate the situations where their use is recommended, important questions must be answered: does the sensor response depend on surface area or volume of the material? Can the inner pores be accessible by the analyte? Does the kinetic allow the utilization of inner pores or the reaction is so fast that occurs only at outer half pores?

Macroporous CuHCNFe/Ppy sensors with diameters from 300 to 800 nm, in spite of increasing the surface area/volume ratio when compared to the non-porous analogue, presented analytical results that indicate that kinetics involved in the electrochemical reaction made it occur only in the outer pores of the material. Once CuHCNFe/Ppy presented poor permeability to H₂O₂, the electrochemical responses were independent of the macropore size. Oppositely, porous Prussian blue based sensors prepared at nanoscale presented the ability to modulate the performance according to the size of the pore and number of immobilized layers. By changing these parameters, it was possible to observe the influence of the confinement effect on reactivity. Kinetic parameters also played an important role on mesoporous platforms, once it was shown that only the external active sites of the mesoporous Prussian blue were participating in H₂O₂ detection. However, the good permeability of the material to H₂O₂ created a compromise between accessibility and the amount of external immobilized layers of electrocatalyst, which allowed the achievement of a mesoporous Prussian blue sensor presenting a sensitivity of (930 ± 50) μA cm⁻² mmol L⁻¹, detection limit of (0.49 ± 0.08) μmol L⁻¹, response time of (6 ± 2) seconds and linear range up to (1.3 ± 0.1) mmol L⁻¹. This performance is extremely satisfactory considering sensors operating by chronoamperometry in Prussian blue blocking cations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jelechem.2013.07.029.

References


