Niobium Oxide Nanorods Obtained by Hydrothermal Synthesis—Structure, Morphology, and Electrochemical Detection of Oxygen Via Oxygen Reduction Reaction

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Abstract: Niobium oxides are promising materials for applications within various research fields, especially as electrocatalysts for various chemical reactions. The tuning of the synthetic parameters can achieve a successful compromise between morphology and structure, aiming to obtain certain properties. Hence, this study aimed to investigate the influence of hydrothermal synthesis parameters on the morphology and structure of niobium oxide growth on a niobium metallic plate. The effect of annealing on the material performance was also evaluated. Afterward, the most crystalline sample was tested for the electrochemical determination of dissolved oxygen, a fundamental reaction in corrosion, biomedicine, and environmental monitoring. This is the first work using this material configuration as an electrochemical sensor. The hydrothermal synthesis produced nanorods formed by poorly crystalline, acidic, hydrated Nb$_2$O$_5$. Increasing the mineralizer concentration could increase the crystallinity and the nanorod growth rate, but it could also promote a lack of structural and morphological uniformity throughout the surface. Heat treatment allowed the increase in crystallinity and favored orthorhombic Nb$_2$O$_5$. Raman spectroscopy revealed that, at the first moment, acidic, hydrated niobium oxide structures were formed as precursors of crystalline niobium oxide that would be developed with longer reaction times and a higher mineralizer concentration. The obtained niobium oxide showed electrocatalytic activity toward the oxygen reduction reaction, with comparable performance between the samples with and without heat treatment. At all analyzed pH values, the amperometric response was linearly correlated with the dissolved oxygen concentration. pH influenced the sensitivity of the material; a maximum sensitivity of 0.0417 mA/cm$^2$·mg/L O$_2$ was achieved at pH = 6. The participation of the acidic functionalities of the surface in the ORR reaction was confirmed by Raman spectroscopy.

Keywords: niobium; niobium oxide; nanorods; electrochemical sensor; dissolved oxygen

1. Introduction

Niobium oxides possess a wide variety of properties due to their oxidation states (0, 2+, 4+, and 5+) and allotropic forms [1–3]. As niobium is a very reactive metal and stoichiometric and non-stoichiometric phases can be formed, niobium oxide systems tend
to be complex, even though synthesizing a unique phase is very difficult [4]. A mixture of metastable phases or crystal structures can usually be found after synthesis. Due to their catalytic and semiconductive properties, these materials play an important role in developing sensors and electrocatalysts [5]. Additionally, niobium oxides can remarkably perform at a nanometric scale, and different nanostructured morphologies can be obtained depending on the synthesis routes and the precursors. Hence, niobium- and niobium oxide-based materials have become relevant in the last decades due to their applicability in the electronics industry [6,7].

The formation of niobium oxides with different crystal structures is highly dependent on the temperature [5,8]. At relatively low temperatures, the obtained niobium oxide is amorphous; at temperatures of ~500 °C, pseudohexagonal or orthorhombic structures can be obtained; and a tetragonal crystal structure is predominant after synthesis at ~800 °C and monoclinic at ~1000 °C [5]. However, the synthesis route, precursor material, impurities, other reactants, and atmosphere can impact the synthesized material morphology and structure [8].

Among the processes employed for obtaining nanostructured materials, hydrothermal synthesis is one of the most interesting ones, considering the low temperature, low energy consumption, and low costs, and the ability to obtain a well-controlled size of the crystals and nanostructures [9]. Hydrothermal synthesis is conducted in autoclaves, and the process variables, such as pH, temperature, and autogenous pressure, and concentrations of reactants and additives will determine the final structure and morphology of the product [5,10].

Other synthesis routes, such as colloidal synthesis [11], need an inert atmosphere, employ toxic organic solvents, especially during purification, and follow several steps, but yield very well-tuned structures and morphologies. Solvothermal syntheses can yield niobium oxides with different surface acidities that can impact their performance as catalysts for organic reactions [12]. Sol-gel and the Pechini method have formerly been applied for obtaining nanoparticles; however, obtaining only one phase or crystal structure is only possible through heat treatment [3,13]. Anodizing has also been reported as a technique for obtaining highly organized niobium oxide nanotubes, employing a niobium plate with a bath of glycerol in the presence of NH₄F [14]. Other authors used an alumina template to obtain columnar niobium oxide nanostructures [15,16]. Nb₂O₅ nanoparticles have been synthesized via laser ablation for further heat treatment to obtain niobium nitrides [17].

Thus, this work aims to study the influence of the hydrothermal synthesis parameters in the structure and morphology of niobium oxide nanorods. The studied parameters include the temperature, time of reaction, and concentration of the electrolyte. NH₄F was employed as a mineralizer in the hydrothermal process to avoid using HF. With the hydrothermal synthesis method, it is possible to obtain a very well-tuned morphology in the nanoscale [18]. However, in many cases concerning niobium oxides, the structure tends to be amorphous or hydrated, and to achieve a preferential crystal structure, heat treatment needs to be conducted. For this reason, the influence of heat treatment will also be evaluated. Finally, the sample with the most crystalline structure was submitted to electrochemical tests to assess its sensitivity toward the oxygen reduction reaction as a means of dissolved oxygen quantification.

The measurement of dissolved oxygen is essential environmentally, medically, and industrially, as the amount of dissolved oxygen influences many reactions and biological processes. The most common dissolved oxygen sensor used is the Clark-type electrode, an electrochemical sensor [19], but due to their limitations, optical sensors have received significant attention recently. Compared with other techniques for dissolved oxygen determination, such as optical methods, electrochemical sensors are especially attractive because of their remarkable detectability, experimental simplicity, and low cost [1]. The working principle of the Clark electrode is the oxygen reduction reaction (ORR). This is one of the fundamental reactions because it participates in many processes, e.g., corrosion, fuel cells, and biochemistry. However, ORR presents one of the slowest kinetics and different
groups devote considerable efforts in the catalyst design to enhance the reaction rate and mechanism.

Most of the works reported in the literature employ niobium oxide as a support for tuning the selectivity and avoiding the poisoning of catalysts [20]. However, its capability has been demonstrated to catalyze fundamental reactions, such as oxygen reduction [17,21]. Compared with Pt, niobium oxides have not received much attention as catalysts for ORR; however, they have been employed as catalyst supports, with promising results [20,22,23], or as co-catalysts [24]. In the work of Rohib et al. [17], the authors reported the synthesis of an Nb4N5-NbOx core–shell structure that catalyzed ORR in acidic medium. Other researchers [25] pointed out the need for heat treatment in a reducing atmosphere for enhancing the ORR electrocatalytic performance due to the distribution of defects. On the other hand, the literature also remarks on the stable behavior of niobium oxides toward the oxygen evolution reaction [26]. Carbon-supported Nb2O5 was found to produce important amounts of H2O2 via ORR for the degradation of pharmaceutical compounds [27].

In this work, niobium oxide nanorods were grown on a niobium plate; hence, the need for support was overcome. To the best of our knowledge, this is the first work to employ this morphology obtained by hydrothermal synthesis (HS), with and without annealing (HT), in dissolved oxygen sensing. In addition, this is one of the few works to report the performance of the obtained oxides along a wide pH range (2.5–11) [17]. This work also provides insights into the formation of acidic niobium oxide structures as intermediates in niobium oxide crystal formation, as well as the consumption of acidic functions in the ORR.

2. Experimental

Niobium samples (CBMM, 99.8 wt%) of dimensions 1 mm × 15 mm × 15 mm were manually ground with sandpapers (#80 to #5000), washed in an ultrasonic bath with deionized water, and detergent, acetone, ethanol, and deionized water, and dried with cold air. The Nb2O5 nanorods were synthesized by hydrothermal synthesis based on the procedure described by other authors [4]. The methodology is the matter of a patent deposited before the Brazilian Intellectual Property Institute (INPI) number BR10 2019 020527 0 [6]. The samples were placed in ammonium fluoride (NH4F, Neon p.a.) solution (0.02 or 0.05 M) in a Teflon-lined autoclave and kept at the process temperature (130, 140, or 150 °C), employing a heating jacket. The samples were washed with deionized water after the reaction time (20 or 40 h). Annealing was carried out in a tubular furnace at 450 °C for 2 h under N2 atmosphere (HS + HT).

The nanostructured surface was observed with a TESCAN—MIRA3 field-emission scanning electron microscope (FEG-SEM) (TESCAN Group a.s., Brno, Czechia) operating at 10 and 15 kV. Optical microscopy images were acquired with ZEISS Axio Lab A1 (Carl Zeiss Microscopy GmbH, Jena, Germany). Crystalline phases were identified by X-ray diffraction (XRD) (Philips X’pert MPD, Amsterdam, The Netherlands) using CuKα radiation. Raman spectra were obtained on a Renishaw InVia, using a 532 nm laser. The image analysis software ImageJ (https://imagej.nih.gov/ij/download.html, accessed on 25 August 2023) was employed for the determination of nanorod diameters. Twenty measurements of the diameters per image were taken, and the mean ± 1 standard deviation values were presented.

All cyclic voltammetry measurements were carried out on a three-electrode electrochemical cell containing 0.5 M LiClO4 (Sigma Aldrich, St. Louis, MI, USA, ACS reagent, ≥95.0%) as the electrolyte. The working electrode was the obtained nanostructured niobium oxide, a saturated calomel electrode (SCE) (0.240 V vs. SHE) for acidic to neutral solutions and an Ag/AgCl/KCl sat (0.180 V vs. SHE) electrode for alkaline solutions were used as reference electrodes, and a platinum wire was used as an auxiliary electrode. All the potentials are reported vs. standard hydrogen electrode (SHE) after normalization, employing the equation:

\[ E_{SHE} = E_{measured} + E^0_{RE} - 0.059pH \] (1)
Cyclic voltammetry was conducted on a Metrohm Autolab PGSTAT 302N and controlled by NOVA 1.11.1 software. The oxygen concentrations were measured using a Clark-type Akso DOEco dissolved oxygen meter. All experiments were carried out at room temperature (22 °C). Nitrogen gas (UltraAir, 99.99%, Rionegro, Colombia) was bubbled into the solution (1 L/min), and the O\(_2\) concentration was adjusted with the N\(_2\) bubbling time. A SANXIN MP521 pH meter was used to measure the solution pH. HCl and NaOH stock solutions were employed to adjust the pH to the studied values.

3. Results and Discussion

3.1. Structure and Morphology—Influence of the Synthesis Parameters

Figure 1 shows the FEG-SEM images for the samples obtained at the studied temperatures (130 °C and 140 °C) and mineralizing agent concentrations (0.02 M and 0.05 M) after 40 h of hydrothermal synthesis. Despite both tested temperatures and concentrations yielding nanostructures, a synergistic effect was observed: the increase in temperature and NH\(_4\)F concentration increased the nanorod diameter and density on the surface. The diameter of the nanorods was determined using ImageJ software, and the distributions can be observed in Figure S2. The lower NH\(_4\)F concentration allowed the growth of a layer of thin nanorods randomly dispersed over the substrate surface, with diameters of 11.52 nm (sd = 3.73 nm) for 130 °C and 18.09 nm (sd = 3.26 nm) for 140 °C, as determined by image analysis (Figure S2). The nanorods were thicker for the concentration of 0.05 M and the layer was denser. The diameters found for 0.05 M and 130 °C were 24.30 nm (sd = 4.51 nm), and for the same concentration and 140 °C, the diameter was 29.12 nm (sd = 6.55 nm) (Figure S2).

Figure 1. FEG-SEM images for the samples obtained after 40 h of hydrothermal synthesis at (a) 130 °C and 0.02 M NH\(_4\)F, (b) 130 °C and 0.05 M NH\(_4\)F, (c) 140 °C and 0.02 M NH\(_4\)F, and (d) 140 °C and 0.05 M NH\(_4\)F.
At a concentration of 0.05 M, the presence of huge crystals was observed, even through an optical microscope (Figure 2). The crystals presented a shape of distorted octahedra that seemed to grow on the surface of the other by solid diffusion processes. Other authors reported similar crystals and attributed this morphology to the $Pnma$ structure [28]. However, these samples presented a strongly attacked surface (Figure S1), and the surface was not uniform.

Figure 2. Optical microscopy and FEG-SEM images of the samples obtained by hydrothermal synthesis employing 0.05 M NH$_4$F and 40 h for both the studied temperatures: (a) 130 °C, (b) 140 °C.

The influence of time was more predominant at the low concentration studied, as observed in Figure 3: with 0.02 M, it was not possible to observe the growth of nanorods, but an etched surface after 20 h of hydrothermal synthesis at both 130 °C and 140 °C. Only a time of 40 h allowed the growth of nanorods for these mixed conditions of temperature and concentration. On the other hand, with the increase in the concentration to 0.05 M, it was possible to cover the substrate fully with nanorods with shorter reaction times. In the latter case, the nanorod diameter corresponded to 20.78 nm (sd = 4.12 nm) and 25.54 nm (sd = 3.38 nm) for 130 °C and 140 °C, respectively (Figure S3), with very similar values regarding the error values.

Other works report obtaining nanorods of Nb$_2$O$_5$ from pure niobium powder using water as the mineralizing agent [29] at 200 °C; however, the formation of nanorods was only evidenced after three days in the autoclave. According to their result, the presence of the mineralizing agent is essential for improving the process’s kinetics. In that case, the nanorods grew following the radial direction of the powder particles. In the present work, considering the marks of the sanding process as cylinders, the growth of the nanorods was also in the radial direction.
Raman spectroscopy also revealed the predominant influence of the NH$_4$F concentration on the crystal structure of the samples, as shown in Figure 4. This effect appeared to be more determinant for crystal structure than temperature. The peak centered at 660 cm$^{-1}$ related to Nb$_2$O$_5$ [30] was present in all the samples, but it was broader and less defined for the samples obtained with 0.02 M NH$_4$F. For this reason, the obtained compound could be identified as hydrated niobium oxide [31], which presented vibrations between 799 and 911 cm$^{-1}$ (Figure S4). The broad signal at $\sim$660 cm$^{-1}$ was assigned to the symmetric stretching mode of the niobia polyhedra, with its broad feature reflecting the distribution of the NbO$_6$, NbO$_7$, and NbO$_8$ sites in the structure of the amorphous Nb$_2$O$_5$ [12,30]. As the samples obtained with 0.02 M NH$_4$F presented less defined peaks, they could be considered amorphous, because they were constituted by a mixture of phases within the structure [30]. The shifting of this peak toward the right or the left could be attributed to its nanostructured morphology [32]. With time, the vibration at $\sim$660 cm$^{-1}$ increased in intensity, while those for the acidic structures moved towards lower shift values and their intensity decreased (Figure S4).

For a better understanding of the species formed on the surface, Lorentzian fitting was conducted for the spectral ranges between 50 and 350 cm$^{-1}$ (Figures S4–S6) and 450 and 1050 cm$^{-1}$ (Figures S4 and S6). For all the samples obtained with 0.05 M NH$_4$F, the contribution of vibrations between 880 and 1020 cm$^{-1}$ was elucidated (Figures S4 and S6) and could be assigned to the symmetric stretching mode of the Nb=O surface sites [30]. Due to the temperature of the formation of the present oxides, they were expected to be in a hydrated form [12]. According to another work [33], this band is promoted by distorted NbO$_6$ octahedra within an aqueous H$_x$Nb$_6$O$_{19-(8-x)}$(8−x)−. With the incorporation of O$^{2−}$ as part of the octahedral structure, the simultaneous formation of acidic sites H$^+$ occurs [31]. Hydrated niobium oxides (Nb$_2$O$_5$·nH$_2$O) contain both Lewis and Brønsted acidic sites, which can promote various electrochemical reactions. With the increase in the NH$_4$F concentration, spectra display bands in the region of 700–900 cm$^{-1}$, which are

![Figure 3. FEG-SEM images of the samples obtained after 20 h of hydrothermal synthesis.](image-url)
typical for some layered niobates, hydrated niobium oxides, or niobic acid (HNb$_3$O$_8$), with structures consisting of layers of edge- and corner-shared NbO$_6$ octahedra and cations intercalated between the layers [12,30,34,35].

More substantial differences can be observed at lower Raman shifts: the spectra presented similar bands. However, their different relative intensities could be attributed to the different ratios of these structures. This feature is in agreement with the structural disorder that has been reported by other authors [12]. The vibration at 123 cm$^{-1}$ corresponded to that coming from the octahedra, and the vibration at 235 cm$^{-1}$ to the Nb-O-Nb bonds [12], and they increased with the higher concentration of NH$_4$F and a longer reaction time (0.05 M NH$_4$F and 40 h) (Figures S4 and S5). This feature can suggest an increase in the crystallinity of the oxide, as analyzed by Raman spectroscopy.

The XRD results (Figure 5) confirm the Raman results and reveal that the samples obtained with a concentration of 0.05 M developed more crystallinity as the number of reflections increased between 20° and 70°, as reported by other authors [36]. The presence of the T-phase (orthorhombic structure) [37] and the presence of the pyrochlore phase, as indicated by the strong reflection in $\theta = 14^\circ$, typical of acidic niobium oxide [38], were confirmed. However, these phases were not very easy to distinguish, which is why both techniques, XRD and Raman spectroscopy, needed to be employed as complementary.
Other authors have reported the synthesis of similar acidic niobium oxides with niobic acid or ammonium niobium oxalate as the precursor or with oxalic acid in the reaction medium [37]. Other mixtures of pyrochlore and orthorhombic phases have been obtained by other authors [28] that follow the crystal groups Fd-3m and Pnma.

A higher concentration of mineralizing agent allowed more NbxOy to be obtained than acidic HNb3O8, which may have been due to the higher reaction rate, as detected by Raman spectroscopy. In addition, as some oxide peaks were observed on XRD, the oxide layer thickness could have been higher, since it could be detected even with the important influence of the niobium substrate. The present study also conducted a test with an even shorter time (10 h) to confirm this hypothesis, employing 0.05 M NH4F solution (Figure 6). This sample presented a more crystalline structure than those obtained at the same temperature and longer times, but with 0.02 M NH4F (Figure 5), confirming the effect of the mineralizing agent on the crystallinity.

**Figure 5.** XRD patterns obtained for the samples obtained at 130 °C and 20 h of reaction in the autoclave.

**Figure 6.** (a) FEG-SEM image and (b) X-ray diffractogram for the sample obtained at 130 °C, 10 h of reaction, and 0.05 M NH4F.
In the chemical synthesis of niobium oxide nanostructures, $F^-$ ions attack the metallic niobium to form the reaction intermediates. As reported in the literature, the ionic group $[\text{NbOF}_5]^2-$ is the predominant intermediate [4]. The formation of $(\text{NH}_4)_2\text{NbOF}_5$ that is transformed into $\text{NH}_4\text{NbOF}_4$ occurs, which becomes more stable with the release of an $\text{NH}_4\text{F}$ molecule under the conditions of the reactor. The formation of $\text{Nb}_2\text{O}_5$ takes place after the decomposition of $(\text{NH}_4)_2\text{NbOF}_5$, according to the following mechanism reported by [39]:

$$\text{Nb} + 5\text{NH}_4\text{F} + 1.25\text{O}_2 \rightarrow (\text{NH}_4)_2\text{NbOF}_5 + 3\text{NH}_3 + 1.5\text{H}_2\text{O}$$

$$(\text{NH}_4)_2\text{NbOF}_5 \rightarrow \text{NH}_4\text{NbOF}_4 + \text{NH}_4\text{F}$$

$$\text{H}_4\text{NbOF}_4 + 1.5\text{H}_2\text{O} \rightarrow 0.5\text{Nb}_2\text{O}_5 + \text{NH}_4\text{F} + 3\text{HF}$$

3.2. Structure and Morphology after Annealing

The crystal structures of the samples obtained with 0.05 M $\text{NH}_4\text{F}$ were more defined. Still, the lack of uniformity made the samples unsuitable for the electrochemical tests. A sample obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M $\text{NH}_4\text{F}$ was prepared and then annealed in a furnace at 450 °C under an $\text{N}_2$ atmosphere.

Figure 7 shows the FEG-SEM images of the sample after hydrothermal synthesis and the annealed sample after hydrothermal synthesis (+HT). Figure 7a shows a layer of uniform, high-density nanorods on the sample substrate after hydrothermal synthesis. These nanorods were about 20–50 nm in diameter, and the length could reach more than 0.5 μm. Figure 7b shows the FEG-SEM image of the sample obtained by hydrothermal synthesis + HT. The diameter of the nanorods remained the same (35.59 nm and $sd = 5.94$ nm for the sample without heat treatment and 30.56 nm with $sd = 5.27$ nm for the sample after heat treatment), according to the diameter distribution (Figure S8).

![Figure 7. FEG-SEM images of the samples obtained at (a) 150 °C, 40 h, and 0.02 M $\text{NH}_4\text{F}$ and (b) the same sample after annealing at 450 °C.](image_url)

Figure 8 shows the Raman spectra and XRD patterns of the samples. The Raman spectra (Figure 8a) for the sample obtained by hydrothermal synthesis corresponded to poorly crystalline hydrated $\text{Nb}_2\text{O}_5$ obtained by hydrothermal synthesis. Meanwhile, the sample obtained by hydrothermal synthesis + HT presented more resolved peaks between 150 and 300 cm$^{-1}$, indicating more crystallinity, particularly the increase in the signal at 235 cm$^{-1}$ (Nb-O-Nb) (Figure S4), which suggests the presence of more octahedra. The absence of vibrations at ~960 cm$^{-1}$ for this sample was related to the presence of fewer
acids, and tended to be present in more crystalline niobium oxides, as well as the smaller width of the peak at 690 cm$^{-1}$ (Figure S4) [32,40].

The XRD for the sample obtained only by HS (Figure 8b) showed a new diffraction signal at 21°, corresponding to the (0 0 1) crystal plane, and other reflections at 27.5° and 45.4°, corresponding to the same phase; this reflection could be indexed to the hexagonal structure of Nb$_2$O$_5$ (JCPDS #28-0317) and be assigned as the plane of preferential growth of the nanorods. The annealed sample showed a different XRD pattern, with reflection that could be indexed to the orthorhombic phase (JCPDS #27-1003). Our results are in agreement with those formerly reported in the literature [4,30], and the predominant crystal structures were hexagonal or orthorhombic.

The presence of niobium nitrides (Nb$_x$N$_y$) was not detected through the XRD pattern. The signals reported in JCPDS # 038-1155 for NbN (35, 41, 59, 71°) were not found in our XRD data. Other authors [41] report that nitrogen insertion into the crystal structure of niobium is already possible between 500 and 600 °C in N$_2$. Still, XRD signals corresponding to the formation of Nb$_x$N$_y$ appeared at temperatures of 800, 1000, and 1100 °C. In other work [42], similar XRD patterns were found for Nb$_2$O$_5$ samples annealed in air and N$_2$ atmosphere; the authors did not attribute any signal to Nb$_x$N$_y$. Nb$_4$N$_5$ was synthesized by the heat treatment of Nb$_2$O$_5$ in a mixture of NH$_3$ and N$_2$ atmosphere at temperatures between 700 and 900 °C.

### 3.3. Electrochemical Characterization

Figure 9 shows the electrochemical response for the obtained niobium oxide samples from hydrothermal synthesis at different dissolved oxygen concentrations and pH values based on their corresponding cyclic voltammograms (Figures 9 and 10). Cyclic voltammograms on a pure niobium plate were obtained at different pH values and did not develop any ORR reaction peak (Figure S9). Oxygen reduction reaction (ORR) was irreversible, as observed by the asymmetric form of the curves (Figure S5). The ORR potential shifted towards more negative values with the increase in pH (Figure 9a), as expected from the Pourbaix diagrams [43]. In contrast, the cathodic peak current density increased with the increase in the oxygen concentration (Figure 9b).
Figure 9. Cyclic voltammograms for the sample obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M NH₄F at different pH: (a) 2.5, (b) 3.65, (c) 6.00, and (d) 10.97, and concentrations of dissolved oxygen. LiClO₄ electrolyte: 0.5 mol/L, scan rate: 20 mV/s, 22 °C.

The sample obtained by hydrothermal synthesis only allowed the evolution of an oxidation peak at pH 6.0 and 11 (Figure 9). This feature could be related to the incomplete ORR and the hydrogen peroxide formation as a reaction intermediate [19] or to the surface acidity slightly neutralized by the OH⁻ species. The sample after heat treatment did not display any peaks in the anodic part of the curve (Figure 10), which could be associated with the completion of the ORR and the improvement in the sensing performance. For the sample obtained by hydrothermal synthesis +HT, the potentials were slightly more positive than those of the sample without heat treatment (Figure 11a,b).
Figure 10. Cyclic voltammograms for the sample obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M NH₄F + HT at different pH: (a) 3.72, (b) 6.79, and (c) 10.08, and concentrations of dissolved oxygen. LiClO₄ electrolyte: 0.5 mol/L, scan rate: 20 mV/s, 22 °C.

Given the very strong influence of the dissolved oxygen concentration in the cyclic voltammogram shape and current peaks, this sensor is conceived as a voltammetric one. Thus, the characteristic current peak values were plotted vs. the dissolved oxygen concentration, and a linear fitting was conducted. The limit of detection (LOD) was calculated following Equation (2):

\[
\text{LOD} = \frac{3\sigma}{S}
\]

where \(\sigma\) is the standard deviation of the intercept, 3 is the signal-to-noise ratio (S/N), and S is the sensitivity. The sensitivity and limit of detection of the studied materials at all the pH values are reported in Table 1.
Figure 11. ORR peak current density vs. ORR potential or dissolved oxygen concentration for the samples obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M NH4F without (a,c) and after heat treatment (b,d).

Table 1. Sensitivity and limit of detection of the samples obtained by hydrothermal synthesis with and without annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>LOD (mg L⁻¹)</th>
<th>Sensitivity (mA cm⁻²·mg⁻¹ O₂ L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C-40 h-0.02 M NH₄F</td>
<td>2.5</td>
<td>0.916</td>
<td>0.00478</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>1.371</td>
<td>0.0035</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>1.070</td>
<td>0.0122</td>
</tr>
<tr>
<td></td>
<td>10.97</td>
<td>1.519</td>
<td>0.0264</td>
</tr>
<tr>
<td>150 °C-40 h-0.02 M NH₄F + HT</td>
<td>2.5</td>
<td>0.52</td>
<td>0.00443</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>1.726</td>
<td>0.0320</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.349</td>
<td>0.0417</td>
</tr>
<tr>
<td></td>
<td>10.97</td>
<td>0.06</td>
<td>0.0253</td>
</tr>
</tbody>
</table>

The ORR peak current density also increased with the pH for the corresponding dissolved oxygen concentrations. The sample obtained by hydrothermal synthesis at pH of 6.0 and 11 ORR peak current density showed similar values; at lower pH values, the peak current density was reduced by almost 50% (Figures 9 and 11c). The reduction in this peak current density for the sample obtained by hydrothermal synthesis +HT...
(Figures 10 and 11d) was observed only at pH 2.5; for pH 3.7, 6.0, and 11, the peak current densities were similar, which could be related to the less acidic surface when compared with the HS sample. This result reveals that the oxide obtained by hydrothermal synthesis successfully electrocatalyzed ORR and that the performance could be enhanced by annealing. Figure 11c,d also shows the linear variation in the current with the increase in concentration for both samples. Similar linear behavior was reported by other authors [21], but nothing was stated concerning pH variation. Considering the low dissolved oxygen concentration detection and the peak potential stability with pH variation (Figure 11, Table 1. Sensitivity and limit of detection of the samples obtained by hydrothermal synthesis with and without annealing), sample HS + HT was the most promising for dissolved oxygen application. However, the performance of the sample obtained only by hydrothermal synthesis was comparable when the sensitivities were evaluated. Both materials presented linear responses at the studied concentrations. Although the nanorod density on the sample surface diminished with the heat treatment (Figure 7), implying a reduction in the surface area, the crystallinity (Figure 8) and oxygen vacancies increased. As the sample developed less variation in the ORR potential after heat treatment and its peak current density values were higher (Figures 9–11), these improvements were attributed to the crystallinity more than any other feature.

As the intended application for the material is a voltammetric sensor and there is no need for the application of constant potential, chronoamperometric measurements were not judged adequate by the authors as a means for determining stability. However, after the samples were tested at pH 11, they tended to lose their catalytic activity, and the current peaks observed when immersed again in lower pH did not appear anymore. This phenomenon could be related to the neutralization of the acidic active sites, as has already been reported for niobic acid and acidic niobium oxide structures [36]. Raman spectroscopy before and after the electrochemical tests in a neutral medium was conducted to evaluate any electrochemically induced structural changes (Figure 12). The vibration at 782 cm$^{-1}$ was associated with acidic, layered niobic acid structures [12,33], which were present in the samples after hydrothermal synthesis, but absent in the sample after cyclic voltammetry, revealing that these species were consumed during ORR.

![Raman spectra for the samples obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M NH$_4$F before and after cyclic voltammetry in pH 6.00 0.5 M LiClO$_4$ electrolyte.](image_url)

**Figure 12.** Raman spectra for the samples obtained by hydrothermal synthesis at 150 °C, 40 h, and 0.02 M NH$_4$F before and after cyclic voltammetry in pH 6.00 0.5 M LiClO$_4$ electrolyte.
4. Conclusions

Hydrothermal synthesis allowed obtaining different structures of niobium oxide, depending on the synthetic parameters. The predominant morphology was nanorods and the oxide was hydrated with an acidic surface. This feature was predominant with a reaction time of 20 h and NH₄F concentration of 0.02 M, being the first intermediate formed for later crystallization. With the increase in time and mineralizer concentration (40 h and 0.05 M NH₄F), the density of nanorods formed and the sample crystallinity increased, as well as the density of octahedra on the surface. Higher crystallinity was achieved with 0.05 M NH₄F, but the coverage throughout the surface was not uniform. The material obtained by hydrothermal synthesis and heat treatment developed a preferentially orthorhombic phase. The increase in crystallinity and the acidity reduction observed with heat treatment allowed the material to promote higher current values for similar amounts of dissolved oxygen and stabilize the ORR potentials. Hydrothermal synthesis under the studied conditions allowed a nanostructured niobium oxide sensitive toward oxygen to be obtained by catalyzing the oxygen reduction reaction (ORR) at all the studied pH values, enhanced via annealing. Raman spectroscopy allowed the identification of acidic functional groups that participated in ORR and were consumed irreversibly by the reaction. The lowest detection limit was achieved for the sample without heat treatment at the lowest pH value (0.916 mg L⁻¹ at pH = 2.5); in contrast, the sample after heat treatment presented its lowest detection limit in alkaline medium (0.06 mg L⁻¹ at pH = 11).

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings13101786/s1, Figure S1: Images of the samples after removal from the autoclave. Dimension of the samples: 15 mm × 15 mm. Figure S2: Diameter distribution of the samples after hydrothermal synthesis (t = 40 h). Figure S3: Diameter distribution of the samples after hydrothermal synthesis (t = 20 h). Figure S4: Lorentzian deconvolutions for the Raman spectra of the samples obtained by hydrothermal synthesis at 130 °C and 0.02 M NH₄F. Spectral ranges: 50–450 cm⁻¹ and 500–1100 cm⁻¹. Figure S5: Raman spectra for the samples obtained at 130 and 140 °C and 0.05 M NH₄F. Spectral range: 50 to 350 cm⁻¹. Figure S6: Raman spectra for the samples obtained at 130 and 140 °C. Spectral range: 450 to 1050 cm⁻¹. Figure S7: Lorentzian deconvolution of the Raman spectra for the sample after hydrothermal process (HS). Spectral range of 100–350 cm⁻¹ (R² = 0.998). Figure S8: Diameter distribution of the nanorods obtained by only hydrothermal synthesis (150 °C, 40 h, 0.02 M NH₄F) and after heat treatment. Figure S9: Electrochemical behavior of niobium towards ORR at different pH values.


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