

Photoelectrochemical Performance of Anodized Niobium for Hydrogen Production.

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Abstract. Nanoporous oxide on valve metals has received incredible attention due to its high surface area. The most studied nanoporous oxide is TiO₂; however niobium-based oxide presents electronic, textural and catalytic features similar to those of TiO₂, with the advantage of Brazil having the biggest niobium reserve. Since the beginning of this century, anodization has emerged as one of the most effective techniques for the fabrication of functional nanoporous oxide. In this study we evaluated two anodization parameters: fluoride ion concentration in the electrolytic bath and heat treatment after anodization. The samples were analysed morphologically by scanning electron microscopy (SEM). The structural characterization was performed by X-ray diffraction and the photoelectrochemical performance was monitored by photocurrent assay. The low fluoride concentration yielded an anodized niobium surface with morphology similar to nanotubes. Heat treatment induced the formation of Nb₂O₅ with a crystal structure compared to the non-treated samples, which were amorphous. The anodized niobium obtained in a bath with low fluoride concentration showed better photoelectrochemical performance compared to the anodized sample obtained in a bath with high fluoride concentration.

Key words

Anodization, niobium, Nb₂O₅, nanotubes, photoelectrochemical.

1. Introduction

The H₂ production has received attention very specifically in the area of clean energy, because it is a promising substitution for fossil fuel. It is well known that fossil fuels are non-renewable and their combustion yields the emission of greenhouse effect gases. Recently, an interesting source for H₂ production is the wastes of the biofuels industry, like glycerin. It makes a nice interface between renewable clean energy and wastewater treatment [1],[2].

Heterogeneous photocatalysts are commonly employed for hazardous wastewater treatment, aiming to transform especially organic compounds into less toxic substances like carbon dioxide and water. The most interesting idea is

to profit the solar energy that constantly arrives at the Earth surface with an average power of 700 W/m², to induce the rupture of the organic compounds present in wastewater through photocatalytic materials.

Among the photocatalytic materials, self-ordered metal oxide nanoporous arrays have stimulated great interest due to their potential technological application. Their unique architecture and large surface area make them promising structures for application in solar cells, gas sensors, energy storages, photocatalysis and medical materials [3],[4],[5],[6],[7],[8],[9].

Nanoporous metal oxide and nanotubular arrays can be formed by electrochemical oxidation of metallic films under specific conditions [10],[11]. It is very important to find the best parameters for anodic formation of the tube-like structures of each metal oxide. The formation of the tube-like structures during anodization is the result of a competition between the oxidation of the metal at the oxide/metal interface and the oxide dissolution at the electrolyte/oxide interface. The rates of the oxidation and dissolution reactions are strongly affected by the type of electrolyte, the applied voltage and the anodization temperature [12]. Therefore, the anodization current density and the composition of the electrolyte are the key parameters for the transition of the obtained structure from porous to tubular arrays [13].

The Nb₂O₅ has been studied as catalyst in reactions such as the esterification [14], hydrolysis [15], alkylation [16], and dehydrogenation [17] reactions. This material also presents absorption in the ultraviolet region. If tailored with the adequate electronic and textural properties, surface and morphology this material becomes potentially active for photocatalytic reactions, mainly H₂ production [18],[19],[20]. Nb₂O₅ is suitable for water splitting, catalysis, solar cells, chemical sensors, energy storage and photodetectors [21],[22],[23]. However, the Nb₂O₅ bandgap is higher than that of TiO₂ (3.4 eV and 3.2 eV respectively) [24].

The growth of self-organized Nb₂O₅ nanostructures by means of the electrochemical anodization method, was demonstrated for the first time by Schmuki et al. [25]. Results in the literature reported Nb₂O₅ structures obtained by anodization, which are only porous and present limited thickness [26].

The most appropriate morphology for photocatalysis is nanotubes; however, an organized porous layer can be optimized in order to better the performance, which can be achieved with the combination of the adequate anodization parameters. In this work, the influence of the fluoride concentration in the electrolytic bath for anodization, and the influence of heat treatment after anodization on the niobium oxide morphology were studied. In addition, photocatalytic activity of the obtained oxides was evaluated by photoelectrochemical measurements.

2. Material and Methods

A. Materials

Nanopores were grown on Nb foil supplied by the Companhia Brasileira de Metalurgia e Mineração, CBMM, (99.3 – purity: wt. %, 2 mm thickness), with dimensions of 1 cm × 1 cm. All samples were mechanically polished using silicon carbide sandpapers until grit size 4000. Before of the anodization process, the samples were cleaned by ultrasonic bath for 15 min in deionized water, then dried under cold air and cleaned of air plasma with 65W for 2 minutes.

The Nb foil was used as the working electrode and a platinum foil as counter electrode. The distance between these electrodes was about 2 cm and area of the working electrode was 0.32 cm². The anodization was performed at 90 V at a potential ramp of 9 V/min, 25 °C and 90 minutes and stirring of the electrolyte at 100 rpm. The organic electrolyte was a mixture of glycerol (Synth 99.5%) and water in 1:0.007 (wt./wt.) ratio and variable amounts of NH₄F (Synth 98.0%). Table I summarizes the experimental conditions. After anodization, some samples were heat-treated at 450°C (2 °C/min) for 60 minutes (Table I).

Table I. – Experimental conditions for nanoporous niobium production by the anodization process.

Sample	Glycerol:NH ₄ F (wt./wt.)	Heat treatment
A	1:0.012	No
ATT	1:0.012	Yes
B	1:0.035	No
BTT	1:0.035	Yes

C. Characterization

The anodized samples morphology was evaluated with a Field Emission Gun Scanning Electron Microscope (FEG-SEM) equipment MIRA3 by TESCAN operated at 15 kV.

The structural characterization was performed by X-ray diffraction. The analyses were performed with 2θ (5°) and the applied potential was 40 kV, with a current of 40 mA using Philips X-Ray Analytical Equipment X'Pert-MPD System, console PW3040/00 with X-ray tube PW3373/00. The software used for analysis and interpretation of results was X'Pert High Score.

The surface wettability was determined by the sessile drop method using a goniometer developed by the Corrosion Research Laboratory at the Federal University of Rio Grande do Sul (UFRGS). With this equipment, it was possible to determine the contact angle between a drop of water and glycerol and the analysed substrate. The contact angle was determined by image analyses using SURFTENS 4.5 software.

The photoelectrochemical measurements were performed using an Autolab PGSTAT302N potentiostat. The experiments were performed in a quartz cell using a three-electrode setup employing anodized niobium as the working electrode, a Pt wire as the counter electrode and an Hg/HgSO₄ electrode as reference electrode. The electrolyte was 0.1 M Na₂SO₄ solution. The photocurrent was measured under an irradiation from a 300 W Xe lamp (Oriel). The intensity of light source was calibrated with a Si diode (Newport) to simulate AM 1.5 illumination (100 mW.cm⁻²). Photocurrent tests were conducted as linear sweep voltammetry with scan rate of 10 mV s⁻¹. The photoresponse was evaluated under chopped light irradiation (light on/off cycles: 30 s for each) at a fixed electrode potential:

$$E_{app} = E_{light} - E_{dark} \quad (1)$$

where E_{light} is the potential with illumination and E_{dark} is the potential without light.

3. Results and Discussion

Transients of current density

Figure 1 shows the transient of the current density obtained during the samples anodization. After 10 minutes of anodization, when the potential reaches 90 V, the current density for the sample anodized in a higher fluoride concentration bath (Sample B) was lower than that developed by sample anodized in a lower fluoride concentration bath (Sample A). A study developed by Assaud et al. 2015 [27] showed that nanoporous surfaces (larger surface area) contribute to the increasing of the current density with decreasing of the surface resistance.

Figure 2 shows the XRD patterns of the samples only anodized and anodized samples with heat treatment at 450 °C (2 °C/min) for 60 minutes. The characteristic peak related to the Nb appears at 2θ = 38.1°, 2θ = 55.3° and 2θ = 69.3° in agreement with the standard JCPDS N°. 00-002-1108. In diffractograms of the samples ATT and BTT appear a peak in 2θ = 27.1° assigned to Nb₂O₅ (100) as reported by Galstyan et al. 2014 [28]. The peaks at 2θ = 21.5° correspond to orthorhombic Nb₂O₅ as indicated by Wei et al. 2012 [29]. For the samples ATT

and BTT the peaks at $2\theta = 48.8^\circ$ were associated to Nb_2O_5 (110) and the peaks at $2\theta = 54.4^\circ$ to Nb_2O_5 (102) [28,30]. According to Liu et al. 2016 [30], the peaks showed in samples ATT and BTT at $2\theta = 57.3^\circ$ and $2\theta = 68.4^\circ$ can be associated to Nb_2O_5 . Chan et al. 2017 [31] performed XRD analyses on heat treated niobium up to 500°C and found peaks in DRX 27° , 48° and 55° which were identified as Nb_2O_5 of pseudo-hexagonal crystal structure; in addition, these same authors found peaks around 60° and 70° indicated as Nb_2O_5 of distorted octahedral structure. Pseudo-hexagonal structure of Nb_2O_5 was also observed in the XRD results for the heat-treated samples. The anodized samples without heat treatment showed an amorphous oxide layer. The XRD results indicated that independently of the fluoride concentration in the anodization bath, the heat treatment promoted the formation of crystal oxide on both anodized surfaces.

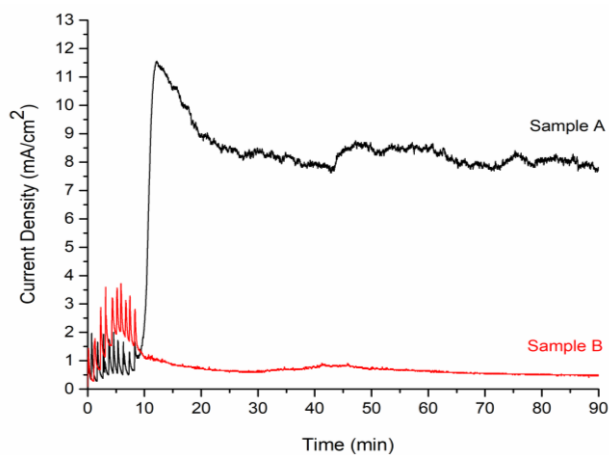


Fig. 1. Transients of current density of the anodized samples.

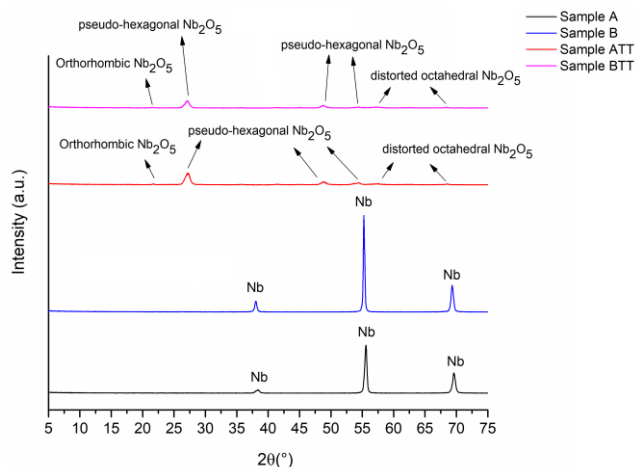


Fig. 2. XRD results of the anodized samples and anodized samples with heat treatment at 450°C ($2^\circ\text{C}/\text{min}$) for 60 minutes.

Figure 3 shows the FEG-SEM images of the anodized niobium that were obtained at different fluoride concentration (Sample A and Sample B) and anodized niobium with heat treatment at 450°C ($2^\circ\text{C}/\text{min}$), 60 min, (Sample ATT and Sample BTT). Sample with low fluoride concentration (Sample A) showed a nanoporous morphology similar to nanotubes; it is in agreement with the current transient (Figure 1), since the variation of the anodic dissolution and the oxide thickening competition promotes the formation of a porous texture [32]. Meanwhile, increasing of the fluoride concentration

contributes to a disordered surface. In relation to heat treated samples, no difference between both morphologies was observed. In both sample ATT and BTT the morphology showed a brittle oxide layer independently of the fluoride concentration. It shows that different fluoride concentrations in the anodization bath had an effect on the morphology of the niobium samples after anodizing process, but with the heat treatment this difference in morphology is no so perceptible; it made the morphology of the surfaces very similar.

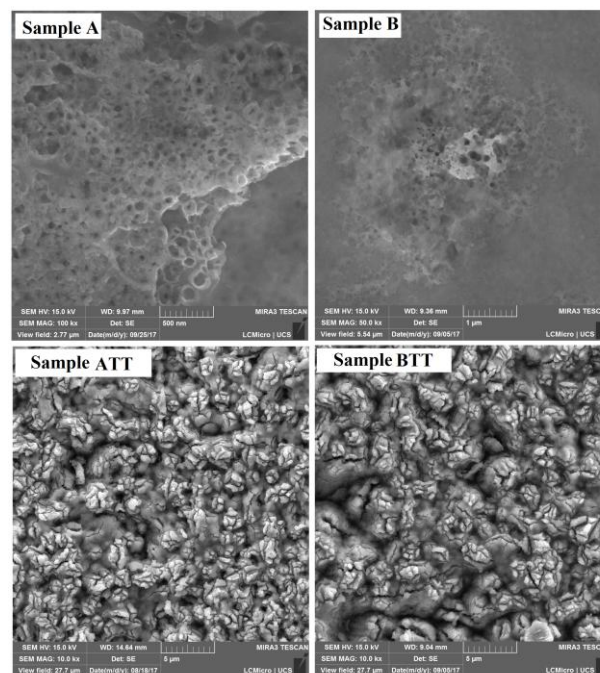


Fig. 3. FEG-SEM images of the anodized niobium samples (Samples A and B) and anodized samples after heat treatment at 450°C ($2^\circ\text{C}/\text{min}$), 60 min.

The best photoelectrochemical performance (greater photocurrent density values) within the electrochemical spectrum of the water reduction reaction for hydrogen production was obtained for sample ATT in clear region (with light) as showed in Fig. 4.

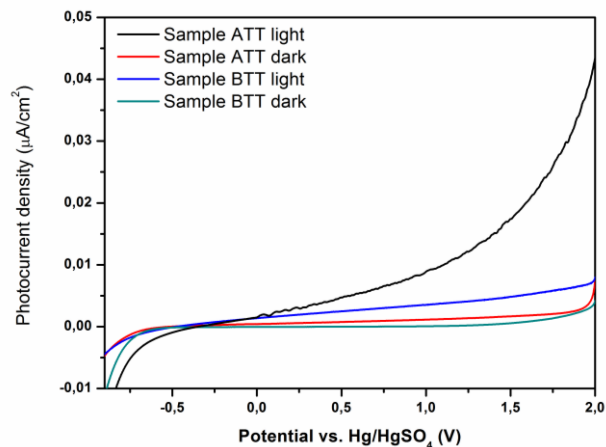


Fig. 4. Linear-sweep voltammograms of anodized niobium electrodes in different fluoride concentration with heat treatment at 450°C ($2^\circ\text{C}/\text{min}$), 60 min, in dark and under illumination. Scan rate is 10 mV/s and supporting electrolyte is $0.1\text{ M Na}_2\text{SO}_4$.

This result can be related to the morphology similar to nanotubes and lower fluoride concentration present on the sample after anodization process and before heat treatment. Furthermore, the sample ATT in clear region (with light), when increasing the applied potential, yielded the highest photocurrent density values. This behavior can be associated with its crystal structure enhanced by the heat treatment and its porous structure. The photocurrent density values presented in this study for the sample ATT in the light were higher than the values of photocurrent density already presented in the literature for niobium, as shown by Liu et al [33], who obtained for Nb₂O₅ nanoplates with hexagonal-like geometry results of photocurrent under illumination on the order of 59.9 μ A. While Fang et al. [34] studied the effect of Nb₂O₅ nanobelts on the photocurrent, finding values around 51.3 μ A.

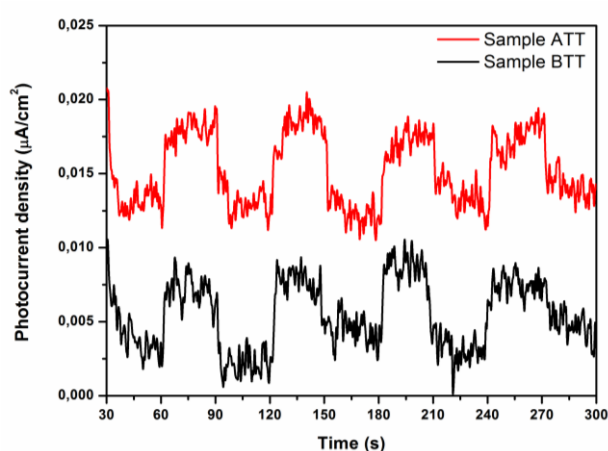


Fig. 5. Corresponding amperometric *i*-*t* curves at an applied potential of 0.09 V vs. Hg/HgSO₄ to Sample A and 0.07 V vs. Hg/HgSO₄ to Samples B under illumination with 30 s light on/off cycles with or without dyes.

The results of chronoamperometry are presented in Fig.5, where the sample ATT presented greater photocurrent density values. It indicates that the morphology similar to nanotubes favored obtaining higher photocurrent density values and the stability of the photocurrent in relation to the applied potential, when compared to the BTT sample. Besides, the development of higher current density can also be related to higher electrochemically active surface area, enhanced by the more organized structure of sample ATT.

4. Conclusion

The anodized sample obtained in a bath with lower fluoride concentration presents a surface with nanoporous structure which contributed to increase the photoelectrochemical performance compared to anodized sample obtained in a bath with higher fluoride concentration. After heat treatment no differences were observed between the morphologies of the samples, all the samples presented pseudo-hexagonal structure of Nb₂O₅.

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References

- [1] Z. Zhang, Y., G. Shi, Y. Fang, L. Linhong, H. Ding and L. Jin, *Environmental Science and Technology* 2007, 41, 6259–6263.
- [2] G. K. Mor, K. O. Varghese, M. Paulose, K. Shankar, C. A. Grimer, *Sol. Energy Mater. Sol. Cells*, 2006, 90, 2011–2075.
- [3] P. Roy, S. Berger and P. Schmuki, *Angew. Chem., Int. Ed.*, 2011, 50, 2904–2939.
- [4] O. K. Varghese, M. Paulose and C. A. Grimes, *Nat. Nanotechnol.*, 2009, 4, 592–597.
- [5] V. Galstyan, A. Vomiero, I. Concina, A. Braga, M. Brisotto, E. Bontempi, G. Faglia and G. Sberveglieri, *Small*, 2011, 7, 2437–2442.
- [6] V. Galstyan, E. Comini, G. Faglia, A. Vomiero, L. Borgese, E. Bontempi and G. Sberveglieri, *Nanotechnology*, 2012, 23, 235706.
- [7] N. A. Kyremateng, F. Vacandio, M. T. Sougrati, H. Martinez, J. C. Jumas, P. Knauth and T. Djenizian, *J. Power Sources*, 2013, 224, 269–277.
- [8] B. L. Ellis, P. Knauth and T. Djenizian, *Adv. Mater.*, 2014, 26, 3368–3397.
- [9] P. Lv, W. Fu, H. Yang, H. Sun, Y. Chen, J. Ma, X. Zhou, L. Tian, W. Zhang, M. Li, H. Yao and D. Wu, *Cryst Eng Comm*, 2013, 15, 7548–7555.
- [10] R. V. Goncalves, P. Migowski, H. Wender, A. F. Feil, M. J. M. Zapata, S. Khan, F. Bernardi, G. M. Azevedo and S. R. Teixeira, *CrystEngComm*, 2014, 16, 797–804.
- [11] A. M. M. Jani, D. Losic and N. H. Voelcker, *Prog. Mater. Sci.*, 2013, 58, 636–704.
- [12] W. Lee, R. Scholz and U. Goesele, *Nano Letters*, 2008, 8, 2155–2160.
- [13] V. Galstyan, E. Comini, G. Faglia and G. Sberveglieri, *Sensors*, 2013, 13, 14813–14838.
- [14] R. F. Brandão, R. L. Quirino, V. M. Mello, A. P. Tavares, A. C. Peres, F. Guinhos, J. C. Rubim and P. A. Z. Suarez, *J. Braz. Chem. Soc.*, 2009, 20, 954–966.
- [15] K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. N. Kondo, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2011, 133, 4224–4227.
- [16] K. Yamashita, M. Hirano, K. Okumura and M. Niwa, *Catalysis Today*, 2006, 118, 385–391.
- [17] D. A. G. Aranda, A. D. Ramos, F. B. Passos and M. Schmal, *Catalysis Today*, 1996, 28, 119–125.
- [18] X. Liu, R. Yuan, Y. Liu, S. Zhu, J. Lin and X. Chen, *New J. Chem.*, 2016, 40, 6276–6280.
- [19] V. Galstyan, E. Comini, G. Faglia and G. Sberveglieri, *CrystEngComm*, 2014, 16, 10273–10279.
- [20] L. Pei, M. Yang, D. Zhang, L. Zhang, P. Chen, Y. Song, *RSC Adv.*, 2015, 5, 9138–9142.
- [21] J. Z. Ou, R. A. Rani, M.-H. Ham, M. R. Field, Y. Zhang, H. Zheng, P. Reece, S. Zhuiykov, S. Sriram, M. Bhaskaran, R. B. Kanee and K. Kalantar-Zadeh, *ACS Nano*, 2012, 6, 4045–4053.
- [22] J. Z. Ou, R. A. Rani, M.-H. Ham, M. R. Field, Y. Zhang, H. Zheng, P. Reece, S. Zhuiykov, S. Sriram, M.

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- Bhaskaran, R. B. Kaner and K. Kalantar-zadeh, *ACS Nano*, 2012, 6, 5737–5737.
- [23] Z. Wang, Y. Hu, W. Wang, X. Zhang, B. Wang, H. Tian, Y. Wang, J. Guan and H. Gu, *Int. J. Hydrogen Energy*, 2012, 37, 4526–4532.
- [24] C. Yan and D. Xue, *Adv. Mater.*, 2008, 20, 1055–1058.
- [25] I. Sieber, H. Hildebrand, A. Friedrich and P. Schmuki, *Electrochem. Commun.*, 2005, 7, 97–100.
- [26] K. Lee, Y. Yang, M. Yang and P. Schmuki, *Chem. – Eur. J.*, 2012, 18, 9521–9524.
- [27] L. Assaud, J. Schumacher, A. Tafel, S. Bochmann, S. Christiansen and J. Bachmann, Systematic increase of electrocatalytic turnover at nanoporous platinum surfaces prepared by atomic layer deposition, *J. Mater. Chem. A*, 2015, 3, 8450–8458.
- [28] V. Galstyan, E. Comini, G. Faglia, G. Sberveglieri. Synthesis of self-ordered and well-aligned Nb₂O₅ nanotubes, *CrystEngComm*, v. 16, pp. 10273–10279, 2014.
- [29] W. Wei, K. Lee, S. Shaw, P. Schmuki. Anodic formation of high aspect ratio, self-ordered Nb₂O₅ nanotubes. *Chem. Commun.*, v. 48, 2012, pp. 4244–4246, 2012.
- [30] X. Liu, R. Yuan, Y. Liu, S. Zhu, J. Lin, X. Chen. Niobium pentoxide nanotube poder for efficient dye-sensitized solar cells. *New J. Chem.*, v. 40, pp. 6276–6280, 2016.
- [31] X. Chan, T. Pu, X. Chen, A. James, J. Lee, J. B. Parise, D. H. Kim, T. Kim. Effect of niobium oxide phase on the furfuryl alcohol dehydration. *Catalysis Communications*, v. 97, pp. 65–69, 2017.
- [32] L. M. Antonini. Superfícies nanoestruturadas de titânio e tratamento superficial com filmes Diamond Like Carbon (DLC). Dissertação Mestrado, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil, 2012.
- [33] H. Liu, N. Gao, M. Liao and X. Fang, Hexagonal-like Nb₂O₅ nonoplates-based photodetectors and photocatalyst with high performances, *Scientific Reports*, 5: 7716, 2015.
- [34] Fang, X. S. et al. New ultraviolet photodetector based on individual Nb₂O₅ nanobelts. *Adv. Funct. Mater.* 21, 3907–3915, 2011.