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Title: New laser-based method for the synthesis of stable and active Ti/SnO₂-Sb anodes

Article Type: Research Paper

Keywords: Mixed metal oxides; Ti/SnO₂-Sb anodes; CO₂ laser; electrolysis

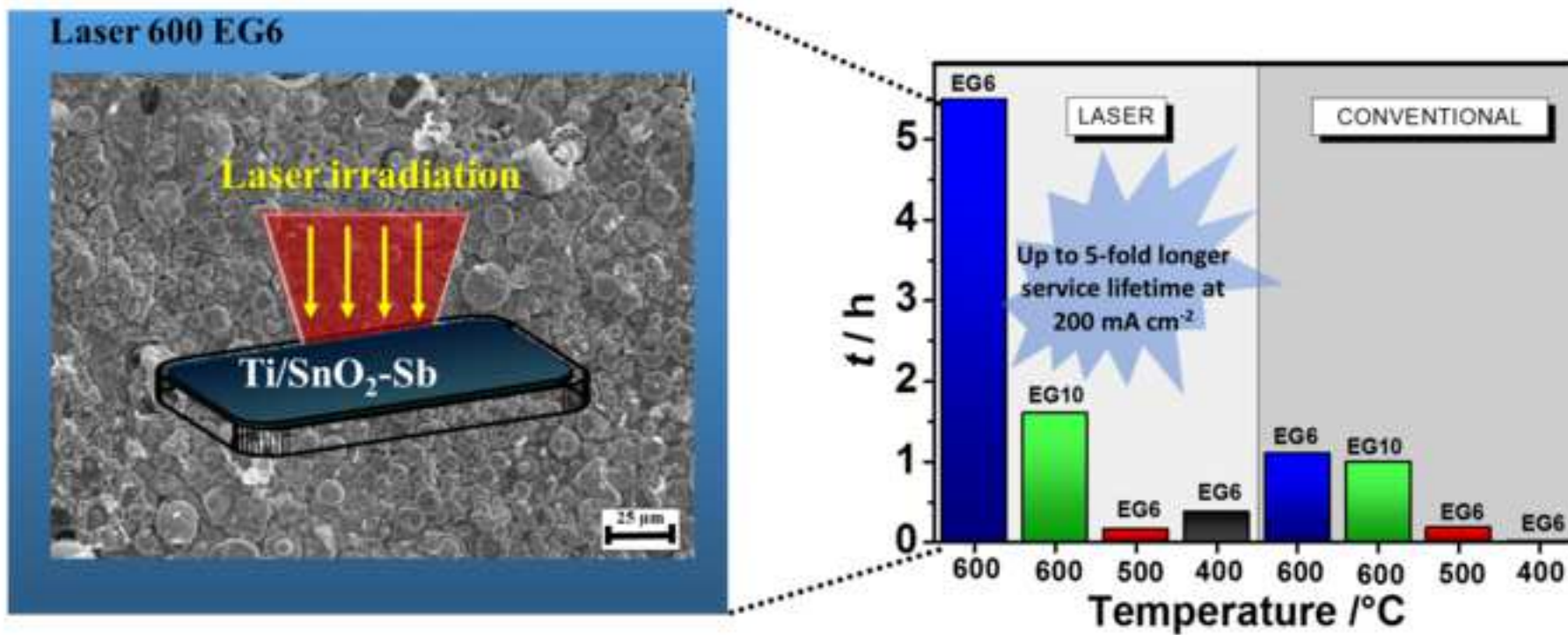
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Abstract: The main drawback impairing the application of highly electrocatalytic SnO₂-Sb anodes in the removal of recalcitrant pollutants from wastewater is their short service life. Here, we report the synthesis of Ti/SnO₂-Sb anodes with improved stability through a CO₂ laser as the primary heating source. The influence of different calcination temperatures (400, 500, 600 °C), and varied composition of the solvent in the precursor solution, on the stability and activity of the anodes, were investigated. Notably, the use of the CO₂ laser heating method at 600 °C improves the service life up to 5-fold as compared to the conventionally prepared anodes. The laser-made Ti/SnO₂-Sb anode calcined at 600 °C exhibits the best electrocatalytic performance with the fastest color removal rates in the oxidation of methylene blue dye. Therefore, for the first time, Ti/SnO₂-Sb anodes with superior properties were produced by a fast method employing CO₂ laser, envisaging its future applications in wastewater treatment.



Highlights

- Ti/SnO₂Sb anodes with improved stability and electrochemical properties were made using a CO₂ laser
- Laser-made anodes have a homogenous distribution of metallic oxides and improved surface coverage
- The calcination temperature (400, 500 and 600 °C) influences the performance of the anodes
- The higher the temperature, the higher the service life and better is the charge transfer capacity
- The laser-made Ti/SnO₂Sb (600 °C) displays the fastest kinetics of methylene blue dye removal



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To Prof. Sotiris Sotiropoulos, *Electrochimica Acta* Editor

Dept. of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece.

29th December 2019.

Dear Prof. Sotiris,

Please find attached a copy of the manuscript entitled “**New laser-based method for the synthesis of stable and active Ti/SnO₂-Sb anodes**”, by Géssica de O. S. Santos, Vanessa M. Vasconcelos, Ronaldo S. da Silva, Manuel A. Rodrigo, Katlin I. B. Eguiluz and Giancarlo R. Salazar-Banda to be reconsidered for publication in *Electrochimica Acta*.

We have corrected the manuscript following all the suggestions of the reviewers (the corrections were highlighted in yellow). Besides, we have also answered all the questions and/or comments of the reviewers (please find it in attachment).

Finally, the authors state that the submitted work is original, it was not published previously, and it is not under consideration for publication elsewhere. Moreover, all authors have approved this submission. There is no conflict of interest. If the article is accepted, the same will not be published elsewhere in the same form, in any language, without the written consent of the publisher.

I look forward to hearing from you

Yours sincerely,

Ph.D. Giancarlo Richard Salazar Banda

Response to Reviewers

Initially, we would like to thank the reviewer for the opportune comments provided. We have corrected the text following all the suggestions of the reviewer (the corrections were highlighted in yellow) and we have also answered the questions as detailed below.

Reviewer #1 Comments:

Authors presented an original application of CO₂ laser for synthesis Ti/SnO₂-Sb anode catalysts for wastewater treatment process, and up to 5-fold improvement their lifetime. SnO₂-Sb, as well as Ti/SnO₂-Sb system, are materials of great importance as being applied for oxygen evolution reaction (OER) catalysts. Although the manuscript provides attractive results and I recommend considering its publication in EA, it needs to be carefully and rigorously revised with regard to following remarks. The English must be proofread and corrected by native speaker (many typos).

Answer: Thanks for your careful review. We have tried our best to improve the manuscript, and the changes are marked with a yellow highlight in the revised paper.

Typos e.g. 'Ti/SnO₂Sb' -> 'Ti/SnO₂-Sb', 'Mixed metal anodes (MMO)' -> Mixed metal oxides (MMO)

Answer: Thanks for detecting these typos. These typos were corrected, and the document was thoroughly revised, editing such mistakes, as suggested.

Highlights:

3rd: the higher temperature ('up to 600C'). Analyzed temperature range should be pointed out.

Answer: Corrections were made, as suggested.

Detailed remarks: Results of the research on the lifetime aspect of Ti/SnO₂-Sb catalysts should be broader commented in the Introduction. Authors proved that CO₂ laser treated Ti/SnO₂-Sb reached up to 5-fold increment of the lifetime what is

a great improvement if related to conventional ones, but is the 5h service life of the catalyst impressive enough from the application point of view? What are the expectations for ideal catalyst in that application?

Answer: In order to address the reviewer's comments, we understand that more references regarding research focused on the lifetime aspect of Ti/SnO₂-Sb anodes can benefit the introduction. Thus, the introduction was completed as follows (please see page 3):

Although Sb-doped SnO₂ presents interesting properties to produce physisorbed hydroxyl radical (M([•]OH)), its significant drawback is still the short service lifetime, which is attributed to the formation of a certain degree of non-stoichiometry SnO_(2-x) during the oxygen evolution reaction (OER) [2], which hinders further application. Therefore, to enhance its stability, much research has been done, exploring different strategies. Recent studies indicate that by doping with different metals into the oxide coating may have a positive effect on the stability of the anode [4,20,21]. Also, efforts by insertion of an intermediate layer [22], and by the formation of TiO₂ nanotubes (TiO₂-NTs) that cover [9,23] and protects the Ti substrate has been also reported [24]. These studies point out the relevance of this material and the importance of finding a practical and straightforward approach, at low cost to enhance the lifetime of Ti/SnO₂-Sb anodes.

[4] L.M. Da Silva, G.O.S. Santos, M.M.S. Pupo, K.I.B. Eguiluz, G.R. Salazar-Banda, Influence of heating rate on the physical and electrochemical properties of mixed metal oxides anodes synthesized by thermal decomposition method applying an ionic liquid, J. Electroanal. Chem. 813 (2018) 127–133. doi:10.1016/j.jelechem.2018.02.026.

[9] T. Duan, L. Ma, Y. Chen, X. Ma, J. Hou, C. Lin, M. Sun, Morphology-dependent activities of TiO₂-NTs@Sb-SnO₂ electrodes for efficient electrocatalytic methyl orange decolorization, J. Solid State Electrochem. (2018). doi:10.1007/s10008-018-3895-1.

[20] M.M.S. Pupo, L. Mirella, G. O. S. Santos, K.I. Eguluz, G.R. Salazar-banda, Synthesis and characterization of ternary metallic oxide electrodes containing $(\text{SnO}_2)_{93}\text{Sb}_5\text{M}_2$ (M = Ce , Ta , Bi , Gd) using an ionic liquid as the precursor solvent, Chem. Eng. Commun. (2019) 1–19. doi:10.1080/00986445.2019.1680367.

[21] R. Berenguer, J.M. Sieben, C. Quijada, E. Morallón, Pt- and Ru-Doped SnO_2 – Sb Anodes with High Stability in Alkaline Medium *Rau 1*, Appl. Mater. Interfaces. 6 (2014) 22778–22789.

[22] Q. Bi, W. Guan, Y. Gao, Y. Cui, S. Ma, J. Xue, Study of the mechanisms underlying the effects of composite intermediate layers on the performance of Ti/ SnO_2 – Sb-La electrodes, Electrochim. Acta. 306 (2019) 667–679. doi:10.1016/j.electacta.2019.03.122.

[23] A. Xu, X. Dai, K. Wei, W. Han, J. Li, X. Sun, J. Shen, L. Wang, Preparation and characterization of a TiO_2 -NT/ SnO_2 -Sb tubular porous electrode with long service lifetime for wastewater treatment process, RSC Adv. 7 (2017) 37806–37814. doi:10.1039/c7ra05127a.

[24] D. Shao, W. Yan, X. Li, H. Yang, H. Xu, A Highly Stable Ti/ TiH_x /Sb– SnO_2 Anode: Preparation , Characterization and Application, Ind. Eng. Chem. Res. 53 (2014) 3898–3907.

For the second question of the reviewer, we reinforce that electrochemical stability tests were carried out, focusing on the understanding of the overall electrode response to highly aggressive media. The choice to carry out stability tests under these conditions is based on literature [18, 52], which intends to understand the operational limit of the electrode. On the other hand, carrying out these tests under milder conditions, like the one proposed in section 3.3, would present a highly specific and limiting outcome for the material proposed. Here, the intention is not only determining the lifetime inside the system proposed but also provide insight on the applicability of these anodes under various conditions (different pH, cations and anions interference, etc.), which are commonly seen as the result of electro-oxidation of organic compounds. Thus, in order to clarify this point out the following paragraph was inserted (please see pages 14/15):

Also, it is essential to point out that the accelerated lifetime tests were carried out that severe conditions (i.e., acid solution and high current density), under normal milder operating conditions the real service life of the anode will be expected to be much longer than the 5.5 h measured in the drastic conditions used here.

[18] Q. Zhuo, S. Deng, B. Yang, J. Huang, G. Yu, Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO₂-Sb-Bi anode, Environ. Sci. Technol. 45 (2011) 2973–2979. doi:10.1021/es1024542.

[51] D. Shao, X. Li, H. Xu, W. Yan, A simply improved Ti/Sb-SnO₂ electrode with stable and high performance in electrochemical oxidation process, RSC Adv. 4 (2014) 21230–21237. doi:10.1039/C4RA01990C.

[52] D. Lim, Y. Kim, D. Nam, S. Hwang, S.E. Shim, S. Baeck, Influence of the Sb content in Ti/SnO₂-Sb electrodes on the electrocatalytic behaviour for the degradation of organic matter, J. Clean. Prod. 197 (2018) 1268–1274. doi:10.1016/j.jclepro.2018.06.301.

Reviewer #2: Summary and general comment:

The mixed metal anode is a promising material for the wastewater treatment. Mixed metal anodes consist of a mixture of two or more metal oxides forming new stable compounds, in which the unique catalytic activity and stability of the composite raw material are integrated in one. This contribution studies a Ti/SnO₂Sb anode that is prepared by CO₂ laser. The CO₂ laser made anodes show, in terms of materials characteristics, improved stability and electrochemical properties and, in terms of material fabrication, a homogenous distribution of metallic oxides and improved surface coverage. The following fabrication study of the CO₂ laser made Ti/SnO₂Sb anode indicate that a high temperature gives a better service life and charge transfer capacity. A few comments below are listed for the authors as a reference.

Additional Comments:

1. The authors should be commended for giving a detailed experimental section. Moreover, in this manuscript, the experimental data are supported with analytical results or scientific discussion, following by the authors' comments and statements. Findings and results are supported with suitable citations.

Answer: We were delighted in receiving such a comment and hope that our work will contribute to the academic field of research by presenting a method to fabricate improved SnO₂-Sb anodes envisaging its future practical application in wastewater treatment.

2. The figure caption of Figure 1 tells that 1000× magnification is used. However, the SEM images shown in Figure 1 have two different scale bars as 50 and 25μm for the

same magnification. The SEM images inserted in Figures 1e and 1g do not have their scale bars. Please correct the mistakes.

Answer: Thanks for noticing this mistake. A new figure with elemental mapping was added with correct scale bars. Besides, the old Figure 1 was moved to the Supplementary information section, with the correct scale bars.

3. Why the Ti XRD peaks shown at ~ 38 degree sometimes show as one peak, while sometimes showing as two peaks? Also, Why the Ti XRD peaks shown at ~ 38 degree change their intensity ratios after the calcinations?

Answer: Thanks for perceiving it. The reason why we can see two peaks (sometimes looks like as one) is because of the signal at 38 degrees also corresponds to the peak (111) for the SnO₂, which was initially non-identified by the software. This peak was identified as (111) in Fig. 2 as well as in the text as follows:

From XRD patterns taken for the different anodes prepared (Fig. 2), where diffraction peaks were compared with patterns from the JCPDS, it could be confirmed that all the anodes presented the tetragonal rutile-type structure of SnO₂ with peaks corresponding to (110), (111), (101), (210), (211), (220), (310) and (321) (JCPDS 41-1445).

Answer: Moreover, complementary comments on the Ti peaks and its changes were inserted as follows (please see pages 10/11):

As can be noted, Ti peaks related to the substrate can decrease after different temperatures of calcination. The most marked decrease of these peaks indicated a more uniform coverage of the Ti substrate and was observed for the anodes obtained at the solvent proportion of 6:3 of EG:AC.

4. Please provide the high frequency region of the EIS data as an insertion in Figure 6.

Answer: The data required was included in Figure 6 in the corrected version of the paper, as suggested.

5. Please show the EDS and elemental mapping results of the Ti/SnO₂Sb anodes. Thanks.

Answer: Please see Figure 1 in which we inserted the elemental mapping for four primary samples. A proper discussion based on the elemental mapping was also inserted in the corrected manuscript (please see the last paragraph of page 9).

6. Some minor errors:

Page 2 - line 12 : Mixed metal anodes "(MMOs) stand out" as "promising materials" to apply in wastewater treatment.

Answer: The typo was corrected.

Page 5 - line 36 : "The anode production" was carried out ...

Answer: The typo was corrected.

Page 8 - line 38 : ... the Ti/SnO₂-Sb "anodes' surface."

Answer: The typo was corrected.

Page 9 - line 31 : According to "the literature," the metallic composition of the oxide layer may be different from the "precursor solutions' composition."

Answer: The typo was corrected.

Page 11 - line 48 : ... where "values approaching 0 indicate" that ...

Answer: The typo was corrected.

Page 15 - line 7 : From "study the calcination temperature," laser prepared ...

Answer: The typo was corrected.

Page 26 - Figure 1 : ... laser (b, d, f, and h) calcination. Figure symbols : Please make the formats and fronts of the plots consistent.

Answer: Corrections were made as suggested.

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New laser-based method for the synthesis of stable and active Ti/SnO₂-Sb anodes

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Abstract

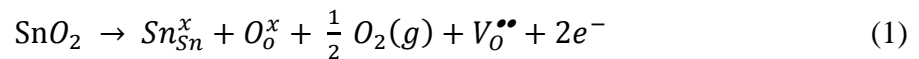
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2 The main drawback impairing the application of highly electrocatalytic SnO₂-Sb anodes in
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4 the removal of recalcitrant pollutants from wastewater is their short service life. Here, we
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6 report the synthesis of Ti/SnO₂-Sb anodes with improved stability through a CO₂ laser as the
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8 primary heating source. The influence of different calcination temperatures (400, 500, 600
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10 °C), and varied composition of the solvent in the precursor solution, on the stability and
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12 activity of the anodes, were investigated. Notably, the use of the CO₂ laser heating method at
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14 600 °C improves the service life up to 5-fold as compared to the conventionally prepared
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16 anodes. The laser-made Ti/SnO₂-Sb anode calcined at 600 °C exhibits the best
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18 electrocatalytic performance with the fastest color removal rates in the oxidation of methylene
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20 blue dye. Therefore, for the first time, Ti/SnO₂-Sb anodes with superior properties were
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22 produced by a fast method employing CO₂ laser, envisaging its future applications in
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24 wastewater treatment.
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43 **Keywords:** Mixed metal oxides; Ti/SnO₂-Sb anodes; CO₂ laser; electrolysis.
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1. Introduction

Electrochemical oxidation has been commonly referred to as an environmentally friendly method for the treatment of wastewater containing complex organic compounds. In this field, the development of anodes with high oxygen evolution overpotential, high physical and chemical stability and low operational cost, has been the focus of several studies [1–3].

Mixed metal oxides (MMO) anodes stand out as promising materials to apply in wastewater treatment. MMOs consist of a mixture of two or more metal oxides forming new stable compounds, some of which exhibit significant improvement in the catalytic activity and stability over their respective single-component metal oxide [4–7]. The MMO Ti/SnO₂–Sb is one of the most attractive alternatives displaying high oxygen evolution overpotential because it favors the generation of •OH radicals that act in the indirect oxidation of organic compounds. Besides, it simultaneously presents a considerably lower cost of precursors' metals compared to other MMOs [3]. Among the MMOs most commonly studied, the development of SnO₂-based anodes has been receiving considerable attention in the last years [4,8–11]. In its pure form, SnO₂ is an *n*-type semiconductor with a wide band-gap (3.87–4.3 eV), due to the existence of distortions created by the oxygen vacancies, according to Eq. (1), where Sn_{Sn}^x and O_O^x are elements in their position with no charges, and V_O^{••} is the oxygen vacancy with two positive charges.



Thus, oxygen vacancies and free electrons are responsible for the increase of SnO₂ conductivity. However, before being applied onto the metallic substrate, tin oxide must be doped to improve its conductivity and chemical stability [12]. Among possible SnO₂ dopants,

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antimony (Sb) is often used, maintaining the high oxygen and chlorine evolution overpotentials and electrocatalytic activity for the oxidation of organic pollutants [13–16].

In this sense, the addition to SnO₂ of a trivalent cation such as Sb³⁺ increases the number of oxygen vacancies, and, in consequence, it increases the material conductivity according to Eq. (2), where Sb_{Sn^x} represents an Sb occupying a Sn position. On the other hand, if Sb⁵⁺ is present, the SnO₂ conductivity will be increased due to the presence of free electrons (Eq. (3)) [11].



In both cases, antimony cations will form a solid solution with tin oxide [11,17]. Many authors have shown that SnO₂ anodes doped with small amounts of Sb (ranging from 3 to 10 mol%), possess high overpotential to oxygen evolution (around 1.9 V vs. RHE), and are highly effective toward electrochemical oxidation of aqueous pollutants [14,18,19]. Although Sb-doped SnO₂ presents interesting properties to produce physisorbed hydroxyl radical (M([•]OH)), its significant drawback is still the short service lifetime, which is attributed to the formation of a certain degree of non-stoichiometry SnO_(2-x) during the oxygen evolution reaction (OER) [2], which hinders further application. Therefore, to enhance its stability, much research has been done, exploring different strategies. Recent studies indicate that by doping with different metals into the oxide coating may have a positive effect on the stability of the anode [4,20,21]. Also, efforts by insertion of an intermediate layer [22], and by the formation of TiO₂ nanotubes (TiO₂-NTs) that cover [9,23] and protects the Ti substrate has been also reported [24]. These studies point out the relevance of this material and the

1 importance of finding a practical and straightforward approach, at low cost to enhance the
2 lifetime of Ti/SnO₂-Sb anodes.
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4 Thus, being widely reported that the performance of SnO₂-Sb anodes depends on the
5 method and conditions employed in the synthesis procedure [4,8-11], among several
6 processes to produce the Ti/SnO₂-Sb coating [12,16-18], the most studied is the sol-gel and
7 the thermal decomposition of polymeric precursor solutions (also called Pechini method)
8 [12,25,26]. Pechini method, have been successfully used to produce SnO₂-Sb films with
9 controlled stoichiometry [7]. In this method, the metallic cations precursors are dissolved in a
10 mixture of a carboxylic acid (citric acid) and a polyhydroxilic alcohol (ethylene glycol).
11 When this solution is heated up to a controlled temperature, an esterification reaction takes
12 place, and the metallic cations are homogeneously incorporated in the formed polymer,
13 preventing then their evaporation during the calcination step [19].
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29 In recent years, laser technology has been used as an alternative sintering method to
30 produce dense and crack-free ceramics with better or improved properties [27,28]. However,
31 the most common method of heating employs furnaces, which is still an expensive and time-
32 consuming process. Many advantages are promoting laser technology as an attractive
33 technique to produce MMO anodes, such as fast processing times, rapid heating and cooling
34 rates, and ease of laser parameter optimization. To the best of our knowledge, the synthesis of
35 Ti/SnO₂-Sb anodes produced using the CO₂ laser as the primary heating source was not
36 reported yet. Therefore, here we report the synthesis of Ti/SnO₂-Sb anodes made by a novel
37 and fast laser calcination procedure. The influence of the different calcination temperatures
38 (400 °C, 500 °C and 600 °C), as well as the modification of the molar ratio between ethylene
39 glycol (EG) and citric acid (CA) in the precursor solutions, were investigated. Besides, similar
40 anodes were conventionally prepared in an electric furnace, for comparison. The anodes were
41 physically characterized by scanning electron microscopy coupled with energy dispersive
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1 spectroscopy (SEM-EDS), and X-ray diffraction (XRD) analyses. Cyclic voltammetry (CV),
2 linear sweep voltammetry (LSV), morphology factor determination, accelerated service life
3 tests, and electrochemical impedance spectroscopy (EIS) were also considered to analyze the
4 electrochemical properties of the prepared anodes. Finally, electrochemical oxidation of
5 Methylene Blue (MB), used in this work as a model pollutant, was performed to compare the
6 electrocatalytic activity of these anodes.
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17 **2. Materials and Methods**

18 **2.1 Preparation of the MMO anodes**

19 The Ti/SnO₂-Sb solutions were prepared using ultrapure water (Gehaka MS 2000 system)
20 and, as chemical precursors, SnCl₂ (99.99%), SbCl₃ (99.99%), anhydrous citric acid (99%),
21 Methylene Blue (MB) (C₁₆H₁₈ClN₃S) (82%), ethylene glycol (99.8%) and sulfuric acid (95–
22 98% all purchased from Sigma-Aldrich[®]. Hydrochloric acid (38% - Vetec[®]) and oxalic acid
23 (99.5% - Neon[®]) were employed for the pre-treatment of the Ti substrate.
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34 The titanium (Ti) plates (10 mm × 10 mm × 1 mm), used as the substrates, were first
35 pretreated as previously reported [4]. This pre-treatment intended to increase the surface
36 roughness and improve the coating adhesion, also removing impurities found on the material
37 surface. The precursor solution was prepared by dissolving citric acid (CA) into ethylene
38 glycol (EG) at 60 °C, according to the molar ratio EG/CA summarized in Table 1. After that,
39 the metallic precursors (SnCl₂ and SbCl₃) were added and then the solution was heated up to
40 90 °C and kept under mechanical stirring until complete dissolution of the metallic salts. The
41 precursor solution was then spread by brushing, over both sides of the pretreated Ti plates.
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The production of the anodes was carried out using initially a furnace (denoted hereafter as a conventional method – CM) and then a CO₂ laser (denoted henceforth as LM) (GEM-100L – Coherent).

1 Seeking to improve LM synthesis, adaptations on the methodology previously
2 reported by our group were carried out [29]. The adopted strategy was to keep the laser beam
3 (diameter of 10 ± 0.5 mm) oriented toward the center of the sample and held at this location
4 throughout the process. When heating, the power density was raised at a linear rate of 0.01
5 W/mm^2 s, reaching a power density of 0.22–0.30 W/mm^2 , which was kept constant for 15
6 min. At the above-cited conditions, the maximum temperature achieved was between 400 °C
7 and 600 °C. A type S thermocouple (cross-section = 0.25 mm) was positioned to measure the
8 temperature at the center of the sample surface. Afterward, the cooling process occurs almost
9 instantaneously. Four repeated brush-pyrolysis stages were done. It is essential to point out
10 that the first film layer was calcined using the furnace as a heating source, and the remaining
11 three layers were calcined by laser heating only. The loading amount of coating for both
12 electrodes was controlled at ~ 1.2 mg cm^{-2} . For comparison, Ti/SnO₂–Sb anodes were
13 produced using the furnace exclusively, under the same conditions.
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31 **2.2 Physical characterization**

32 The morphological characteristics of the anodes were evaluated using a JEOL (JSM-6510LV)
33 scanning electron microscope, in both secondary electron (SE) and backscatter electron (BSE)
34 modes. The local chemical composition was determined by means of energy-dispersive X-ray
35 spectroscopy (EDS) measurements, coupled with the SEM equipment. XRD measurements
36 were carried out by using a Bruker-D8 Advance X-ray diffractometer with Cu K_α radiation
37 over a 2θ range between 20° and 80°, at a scan rate of 0.02° min^{-1} . Phase identification was
38 performed using the Joint Committee on Powder Diffraction Standards (JCPDS) database.
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54 **2.3 Electrochemical measurements**

55 Electrochemical measurements were carried out using an Autolab PGSTAT302N (Metrohm -
56 Pensalab) Potentiostat in a conventional three-electrode glass cell at room temperature. The
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1 working electrodes were the Ti/SnO₂-Sb anodes (geometric area = 2 cm²), the counter
2 electrode was a platinum plate of 2 cm², and an Ag/AgCl (KCl 3.0 mol L⁻¹) was used as the
3 reference electrode. CV measurements were performed with potential limits of 0.2–2.0 V with
4 a scan rate of 50 mV s⁻¹ in a 0.1 mol L⁻¹ Na₂SO₄ solution. The total voltammetric charges
5 (*q*^{*}) corresponding to electrochemically active surface areas were calculated by integrating
6 the area of the cyclic voltammograms [21]. Following the methodology proposed by da Silva
7 *et al.* [30], continuous voltammetric curves were recorded at several scan rates (10–300 mV s⁻¹)
8 in a Na₂SO₄ solution, to determine the morphology factor of each anode prepared [31].
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19 The electrocatalytic activity of the anodes towards the OER was investigated using
20 LSV performed from 0.2 to 2.3 V at 10 mV s⁻¹ in a 0.5 mol L⁻¹ H₂SO₄ solution. EIS
21 measurements were also carried out in a 0.5 mol L⁻¹ H₂SO₄ solution, applying a potential
22 determined by LSV analysis corresponding to the OER onset potential for each studied anode.
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The OER onset potential was established as the intercept potential between the linear extrapolation of the fast rise in current due to OER and the linear extrapolation of the baseline in linear voltammetry experiments. The measurements were obtained covering the frequency range 0.1–1000 Hz using an amplitude signal of 5 mV, and the results were fitted using Zview software 2.3. In this program, an equivalent circuit is created, which generates a theoretical curve to be fitted to the experimental data in order to obtain the values of the elements of the circuit.

Accelerated service life tests were carried out using chronopotentiometry applying a current density of 200 mA cm⁻² in 0.5 mol L⁻¹ H₂SO₄ solutions. The anodes were considered deactivated when the measured potential reached 10.0 V.

2.4 Electrolysis

1 To evaluate the electrocatalytic activity of the developed anodes, the electrochemical
2 oxidation of 20 mg L⁻¹ of MB dye (model pollutant without further purification) in aqueous
3 solution, was carried out in 80 mL solution in 0.1 mol L⁻¹ Na₂SO₄ supporting electrolyte and
4 with the addition of NaCl to produce a 0.02 mol L⁻¹ solution. In order to monitor the
5 absorbance of MB dye solution, spectra from 200 nm to 800 nm were monitored at certain
6 time intervals using **a** UV-vis spectrophotometer (UV-Vis Hach DR 5000). The MB
7 concentration was monitored by using a calibration curve of MB concentrations versus
8 absorbance at 664 nm.
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12 The color removal efficiency was expressed as η , according to Eq. (4) [32], where A_0
13 and A_t are the absorbance at an initial time and time t , respectively.
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$$\eta (\%) = \left[\frac{A_0 - A_t}{A_0} \right] \times 100 \quad (4)$$

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32 The specific electrical energy consumption (EC) per treated volume was calculated according
33 to Eq (5), where E_{cell} is the average cell potential (V), I is the applied current (A), t is the
34 electrolysis time (h), and V is the solution volume (dm³).
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$$EC (\text{kWh } dm^{-3}) = \frac{E_{cell} \times I \times t}{V} \quad (5)$$

42 43 44 45 46 47 **3. Results and discussion**

48 49 50 **3.1 Physical characterization**

51
52 Fig. 1 (left side) displays the representative SEM images (SE mode) from the surface of the
53 Ti/SnO₂-Sb anodes. The CM anodes (Fig. 1a and b) presented the typical mud cracked aspect
54 with morphological inhomogeneity. This aspect is commonly related to the mechanical stress
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caused by the coating plasticity and the difference of the thermal expansion coefficient between the substrate and the film [33,34].

On the other hand, LM anodes (Fig. 1c and d) presented a rough and more compact surface for all conditions, i.e., a reduction of the deep cracks and pores concentration. Amongst the temperatures studied, the samples treated at 600 °C showed more compact surfaces than those prepared at 400 °C and 500 °C (Fig. S1). This behavior can be attributed to the grain growth (coalescence effect) and agglomeration of the particles at higher temperatures, which is commonly reported in the literature for coatings deposited by using thermal decomposition at different temperatures [31,35]. Additionally, the reduction in the molar ratio EG/CA from 10:3 (Figure 1a and b) to 6:3 (Fig. 1c and d) seem to affect the morphology positively, improving the anode homogeneity. This improvement may be attributed to the higher amount of electroactive material dispersed into a smaller volume (EG/CA = 6:3), which favors the fixation of the layer as compared to the proportion often employed for Pechini method (EG/CA = 10:3). At this point, it is worth to remember that Aguilar *et al.* 2018 [36] changed the proportion between the organic chemicals (EG/CA = 16:0.12 and EG/CA=3.2/0.024) for Ti/Ir–Sn–Sb anodes, prepared by Pechini method, obtaining that the lower amounts of organic compounds enhanced the homogeneity of the coating and favored the Sn deposition.

In general, contrary to the CM anodes prepared by the Pechini method in a furnace that present typical cracked-mud morphology, the LM anodes present a more compact structure and poorly defined cracks, as pointed out previously for Ti/RuO₂–IrO₂ obtained by laser [29].

According to the literature, the metallic composition of the oxide layer may be different from the composition of the precursor solutions [12,37]. The right side in Fig. 1 shows the EDS spectra and elemental mapping (BSE mode) of the four main studied samples,

1 calcined at 600 °C by both methods. In these images, brightness differences are associated
2 with different element proportions; i.e, darker regions indicate a lower concentration of the
3 observed element. Note that in CM samples (Fig. 1a and 1b) there are some darker regions in
4 Sn and Sb elemental mapping while for LM samples these darker regions are less evidenced.
5 This result indicates a better ion homogeneity in LM anodes.

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12 Additionally, the real composition of the oxide layers was semi-qualitatively analyzed
13 by EDS, as summarized in Table 2. The percentage of the metallic components (Sb:Sn
14 proportion) for the Ti/SnO₂-Sb anodes is uniformly distributed over the surface. Moreover,
15 the Sb:Sn proportion, for different Sb contents, shows a good correlation between real and
16 nominal values. Nevertheless, slight discrepancies in Sb:Sn proportion, observed for some
17 LM and CM anodes, have been reported to occur at low doping levels. This behavior can
18 result from the small separation energy between the Sn and Sb spectral lines [4,37,38].
19 According to Rodrigues and Olivi, SnO₂-Sb anodes could be prepared at controlled
20 stoichiometry, showing excellent correlation between the real and the nominal compositions,
21 using the Pechini method [39].

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36 From XRD patterns taken for the different anodes prepared (Fig. 2), where diffraction
37 peaks were compared with patterns from the JCPDS, it could be confirmed that all the anodes
38 presented the tetragonal rutile-type structure of SnO₂ with peaks corresponding to (110),
39 (111), (101), (210), (211), (220), (310) and (321) (JCPDS 41-1445). It should be pointed out
40 that the dopant introduction in SnO₂ coating is commonly reported and does not cause
41 noticeable changes in the XRD patterns [40,41]. Similarly, here, no diffraction peaks of Sb
42 were detected, indicating that there was a low doping level, and the incorporation of the
43 doping ions into SnO₂ lattice occurred. In that sense, Sb is expected to enter the SnO₂ lattice
44 in the form of interstitial, replacement, or being dispersed in the middle of the SnO₂ particles
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1 [42]. In such cases, the presence of dopants with small doping levels must be verified by other
2 methods, such as EDX spectroscopy.
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5 Additionally, Ti related peaks were also detected, associated with the titanium support,
6 often reported for thin films [4,43]. As can be noted, Ti peaks related to the substrate can
7 decrease after different temperatures of calcination. The most marked decrease of these peaks
8 indicated a more uniform coverage of the Ti substrate and was observed for the anodes
9 obtained at the solvent proportion of 6:3 of EG:AC.
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19 **3.2 Electrochemical measurements**

20 **3.2.1 Cyclic voltammetry**

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22 The electrochemical behavior of the MMO anodes was analyzed firstly by cyclic voltammetry
23 (CV) measurements in a potential interval of 0.2–2.0 V *versus* Ag/AgCl (Fig. 3). All anodes
24 display a sharp current rise, corresponding to the OER, at potentials above 1.6 V *versus*
25 Ag/AgCl, which is a behavior commonly seen at this potential range for non-active
26 electrodes. These materials are known for the production of $\bullet\text{OH}$ on the surface and low
27 capability of superficial chemical reactions, differing from active electrodes (*e.g.*, Ti–Ru)
28 which are capable of degrading chemical compounds using physisorption and chemisorption
29 on the anode surface [4,44,45].
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43 The voltammetric charge values, q^* , obtained by the integration of the CV curves
44 between oxygen and hydrogen evolution, are shown in Table 3. The voltammetric charge
45 increases up to 7-fold as the calcination temperature increases from 400 °C to 500 °C. At high
46 temperatures, CM-600 and LM-600, the voltammetric charge decreases, which may be
47 attributed to the grain expansion, better crystallization, and gradual disappearance of porous
48 morphology of oxide layer [31,46]. Besides, the reduction in the voltammetric charge for laser
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1 anodes can be explained in terms of the more compact surfaces previously observed in SEM
2 images (Figure 1).
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4 To further investigate the coatings, the morphology factor of oxide layers was
5 estimated. Data of the total (C_d), external ($C_{d,e}$) and internal ($C_{d,i}$) differential capacitances
6 (Table 3) provides information about both the degree of roughness of the film and its surface
7 accessibility to the anode (internal and external surface), allowing to calculate the
8 "electrochemical porosity" [47,48] described here by the morphology factor (ϕ) [30,32].
9

10 It is worth mentioning that to ensure the measure of only the capacitive contribution, a
11 small potential interval of 200 mV was chosen to record the capacitive current density
12 according to the methodology described by Da Silva *et al.*, [30]. After that, the angular
13 coefficients of the linear segments of the profile versus v , observed in the regions of the low
14 and high values, respectively, provide the respective values of the C_d and $C_{d,e}$. Thus, the
15 internal differential capacitance, $C_{d,i}$, can be obtained according to Eq. (6). After that, ϕ values
16 can be determined as the ratio shown in Eq. 7.
17

$$18 \quad C_{d,i} = C_d - C_{d,e} \quad (6)$$

$$19 \quad \phi_m = C_{d,i}/C_d \quad (7)$$

20 The value of ϕ can vary between 0 and 1, where values approaching 0, indicates that
21 the internal sites of the small electrode influence on the total surface area, whereas values
22 close to 1 indicates a large internal area of the coating [30,49].
23

24 Fig. 4 shows the capacitive current density, j_c , versus v graphs of the Ti/SnO₂-Sb
25 anodes obtained in this study. The graph shows two linear segments, located, respectively, in
26 the low and high scan rate domains. These two segments result from the two distinct surface
27 regions typically exhibited in highly rough films [31,48].
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As a result, for LM and CM anodes prepared at a higher temperature, the morphology factor changes insignificantly, indicating a similar ratio between internal accessible sites and total capacitance ($\varphi_m = 0.08\text{--}0.18$). On the other hand, for lower synthesis temperatures, LM and CM anodes display higher morphology factors, which may be easily correlated to SEM images (Fig. 1), where increased temperature favors the sintering of the surface and, as a consequence, reduces the porosity.

3.2.2 Linear sweep voltammetry and electrochemical impedance spectroscopy

LSV experiments from 0.2 to 2.0 V at 10 mV s^{-1} in $0.5\text{ mol L}^{-1}\text{ H}_2\text{SO}_4$ electrolyte for each Ti/SnO₂-Sb anode, were performed to determinate the OER onset potential. Thus, Nyquist plots were recorded at each OER onset potential for each anode. For all anodes, a well-defined semi-circle is observed (Fig. 6). As previously reported in the literature [50], one capacitive loop for all frequencies on Nyquist complex plane indicates that only the OER takes place with negligible substrate/film interface contribution [51–53]. Here, data fit with a typical equivalent circuit to an electron transfer reaction represented by one capacitive loop, described as $R_\Omega (R_{ct} C_{dl})$, where R_Ω represents the cell resistance (including the connections, the electrolyte, and oxide deposit resistance); R_{ct} the charge transfer resistance for the OER and C_{dl} the double-layer capacitance. A constant phase element (CPE), was used to replace C_{dl} in order to take into account electrode roughness and heterogeneity [49,54].

Table 2 shows the equivalent circuit used (inset in Figure 6), as well as the R_Ω , R_{ct} , CPE, and n , obtained values. When $n = 1$, the CPE corresponds to a pure capacitance, which means that n values close to 0.9 for all potentials, confirms the pseudocapacitive behavior of the anodes. All impedance data fitted well with the proposed equivalent circuit with a fitting quality factor $\chi^2 < 5 \times 10^{-4}$, indicating the high quality of the fitting procedure.

1 For all samples, the R_{Ω} (cell resistance, including the connections, the electrolyte, and
2 the resistance of the deposited oxides) varies between 1.16 Ω and 3.36 Ω . Moreover, the
3 charge transfer resistance reduced for the LM anodes, suggesting facilitated electron transfer
4 (Table 4). These results indicate that laser calcination substantially improves the
5 electrochemical properties of the electrodes, which correlates well with SEM images data that
6 shows a more homogenous coating.
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14 **3.2 Accelerated service life tests**

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17 The physical stability of the Ti/SnO₂-Sb anodes was evaluated employing accelerated service
18 life tests, performed applying a current density of 200 mA cm⁻² (Fig. 7). The anodes were
19 considered to be deactivated when the anode potential response reaches a drastic potential of
20 10 V *versus* Ag/AgCl, being this time assumed as the accelerated service life of each
21 Ti/SnO₂-Sb anode. The anodes with best outcomes were LM-600EG06 and CM-600EG06
22 anodes, exhibiting higher stability of 5.5 and 1.1 h, respectively. The low service life can be a
23 result of a large number of cracks on the anode surface, which favors electrolyte penetration
24 and, consequently, a faster deactivation [55].
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39 Furthermore, the higher the temperature, the higher is the stability. Likewise, when the
40 proportion between EG/AC becomes higher, from 6:3 to 10:3, the anode stability decreases.
41 As pointed out before, the metallic precursors dissolved in a smaller volume produce better-
42 coated surfaces (higher amount of electroactive material dispersed on the film surface).
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49 Zhuo *et al.* investigated the stability of Ti/SnO₂-Sb and Ti/SnO₂-Sb-Bi anodes prepared by
50 Pechini method (molar ratio of 10:3:1 for EG:CA:metals) calcined at 600 °C for 1 h applying
51 100 mA cm⁻² in 0.5 mol L⁻¹ H₂SO₄ electrolyte [18]. As a result, the accelerated life for the
52 Ti/SnO₂-Sb was only 0.4 h, whereas Ti/SnO₂-Sb-Bi showed a more extended durability of
53 0.8 h under the same conditions. Moreover, a recent study from Lim *et al.* [56] has
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1 demonstrated the effect of dopant amount on SnO₂ lattice on the accelerated service life
2 carried out with a current density of 100 mA cm⁻² in a 0.5 mol L⁻¹ KOH solution. Thus,
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4 anodes prepared by traditional thermal decomposition of chlorides, calcined at 500 °C for 1 h,
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6 showed accelerated lifetimes of 0.14 s, 0.15 and 0.22 at a current density of 100 mA cm⁻², for
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8 the SnO₂-Sb anodes doped with 5, 10 and 15 % of Sb, respectively [56]. Compared to the
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10 above-cited studies, this work presents a considerable improvement in the service life of these
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12 anodes. Also, it is essential to point out that the accelerated lifetime tests were carried out that
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14 severe conditions (i.e., acid solution and high current density), under normal milder operating
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16 conditions the real service life of the anode will be expected to be much longer than the 5.5 h
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18 measured in the drastic conditions used here.
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27 3.3 Electrolysis

28 Methylene Blue (MB) dye solution was galvanostatically treated for 60 min at 40 mA cm⁻² to
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30 evaluate the electrocatalytic activity of the Ti/SnO₂-Sb anodes obtained at 600 °C, prepared
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32 by conventional and laser calcination, namely respectively - CM-600EG6 and LM-600EG6.
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34 Hence, the study of two different electrolytes (0.1 mol L⁻¹ Na₂SO₄ containing, or not, 0.02
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36 mol L⁻¹ NaCl) was carried out, in order to favor the effectiveness of the electrochemical
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38 oxidation by mediated oxidation processes. Among many factors, the presence of species able
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40 to act as mediators is known to seriously affect the process efficiency in the electrolysis of
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42 wastewater and the role of chlorine, sulfates, and many other types of salt anions have been
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44 reported in several studies on the electrochemical process due to generated *in situ* oxidative
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46 species depending on the electrolyte [2,3].
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53 Fig. 8a shows the color removal efficiency (η) calculated according to Eq (4) with the
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55 variation of time during 60 min electrolysis using LM-600EG6 and CM-600EG6 in 0.1 mol
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57 L⁻¹ Na₂SO₄ electrolyte without and with the addition of NaCl (0.02 mol L⁻¹). The results
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1 show that the efficiency of MB color removal increases from 37 % (LM-600EG6) in 60 min
2 to 100% in 15 min when 0.02 mol L⁻¹ NaCl was added to 0.1 mol L⁻¹ Na₂SO₄, while for CM-
3 600EG6, which reached 16 % in 60 min, attained total color removal in 20 min.
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7 It is worth to point out that the initial pH of 5.6 slightly changes during the treatment.
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9 According to Montonaro and Petrucci [57], pH values between 3.3 e 7.5 favor the formation
10 of HClO species, which are also known for their high oxidative capacity. The faster color
11 removal is in good agreement with the enhanced HClO formation when Cl⁻ ions are present in
12 the electrolyte. A small amount of NaCl (0.02 mol L⁻¹) allows mediated oxidation in the bulk
13 solution, as previously stated in the literature for color removal [58]. Del Río [59] studied
14 electrochemical treatment of Reactive Black 5 solutions on a Ti/SnO₂-Sb-Pt anode
15 employing a filter press reactor with two different configurations. In both cases, the kinetics
16 of color removal was of pseudo-first-order kinetics, and the addition of chloride (Na₂SO₄ 0.1
17 mol L⁻¹ with the addition of NaCl 0.1 mol L⁻¹) enhanced the efficiency of the process.
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31 The exponential profile of the MB dye absorbance curves as a function of the time
32 points out to a pseudo-first-order kinetic for the reactions involved in the electrochemical
33 oxidation of this dye. The apparent kinetic constants (k_{app}) can be related to the dye
34 concentration by Eq. (8) [60], where $[C_0]$ is the initial concentration of the dye, $[C_t]$ is the
35 concentration at a time t .
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$$46 \quad -\ln \frac{[C_0]}{[C_t]} = k_{app} \quad (8)$$

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51 The apparent kinetic rate constants for MB color removal on LM-600EG6 (0.0078
52 min⁻¹ in Na₂SO₄ media and 0.2642 min⁻¹ with the addition of chloride) is much higher than
53 those on CM-600EG6 (0.0029 min⁻¹ in Na₂SO₄ media and 0.2044 min⁻¹ with the addition of
54 chloride). These results reveal that laser use may increase the kinetic rate constant to a 2.7-
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1 and 1.3-fold, in Na₂SO₄ and with NaCl in media, respectively. Table 5 displays the k_{app}
2 observed for the anodes studied. The results obtained by estimating the energy consumptions
3 were compared to evaluate the efficiency of the process. Table 5 shows the energy
4 consumption required to reach the maximum of the color of MB dye in 60 min (100 % when
5 NaCl was added in the electrolyte), and to maximal removal achieved when only Na₂SO₄ as
6 an electrolyte was employed.
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14 As can be observed, energy consumption seems to depend on the electrocatalytic
15 material used. The values found for MB dye removal, respectively, in Na₂SO₄ medium only
16 and with the addition of a small amount of NaCl were 2.3 and 0.76 times lower for LM anode.
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18 The much lower energy consumption observed for medium containing NaCl compared to
19 only Na₂SO₄ can be attributed to the improved conductivity of the medium as well as the
20 indirect oxidation occurring in bulk, which in turn, as mentioned before, is related to the
21 electrogenerated chlorine species. However, as illustrated in Figure 9, the energy spent in the
22 medium with NaCl does not present a significant difference considering the anode employed.
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34 Therefore, the laser could be an alternative to prepare Ti/SnO₂-Sb anodes with enhanced
35 properties, to be applied in dye discoloration in chloride media more efficiently than that
36 conventional. Also, the effort on the electrode stability enhancement is meaningful,
37 considering we are working with a cost-effective environmental anode (Ti/SnO₂-Sb).
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39 Moreover, the reduced cost of synthesis and time for the production of these anodes makes
40 this technology even more attractive.
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51 **4. Conclusions**

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53 In this study, optimization of Ti/SnO₂-Sb synthesis by CO₂ laser heating as main heat source
54 allowed improved stability of this anode. From physical characterization, the formation of
55 SnO₂ and Sb incorporated in the coating at similar proportions of the precursor solutions
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1 indicates that both heating methods ensure the desired proportion of the coating layer.
2 Furthermore, electrochemical characterization showed that the laser method promotes a shift
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4 **in** the oxygen evolution overpotential onset to more positive values. Otherwise, when the
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6 molar ratio of EG was changed from 6 to 10, the negative effect was noted, which means that
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8 for SnO₂–Sb anodes, the more concentrated is the chloride precursor in the solution, the better
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10 are the coating properties and stability. **From the study the calcination temperature**, laser
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12 prepared Ti/SnO₂–Sb produced at 600 °C stands out as the most promising anode with better
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14 electrochemical properties and longer service life. Finally, the highest efficiencies towards
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16 electrochemical oxidation of methylene blue at lower energy consumption for this anode
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18 (LM-600EG6) open up the opportunity to its future applications in the electrochemical
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20 treatment of wastewaters polluted with complex organic compounds. Besides the advantages
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22 of fast processing time and ease of parameter optimization, the CO₂ laser can enhance the
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24 electrocatalytic properties.
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31 **Conflicts of interest**

32 There are no conflicts to declare.
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41 88887.142044/2017-00) and FAPITEC/SE.
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Figures

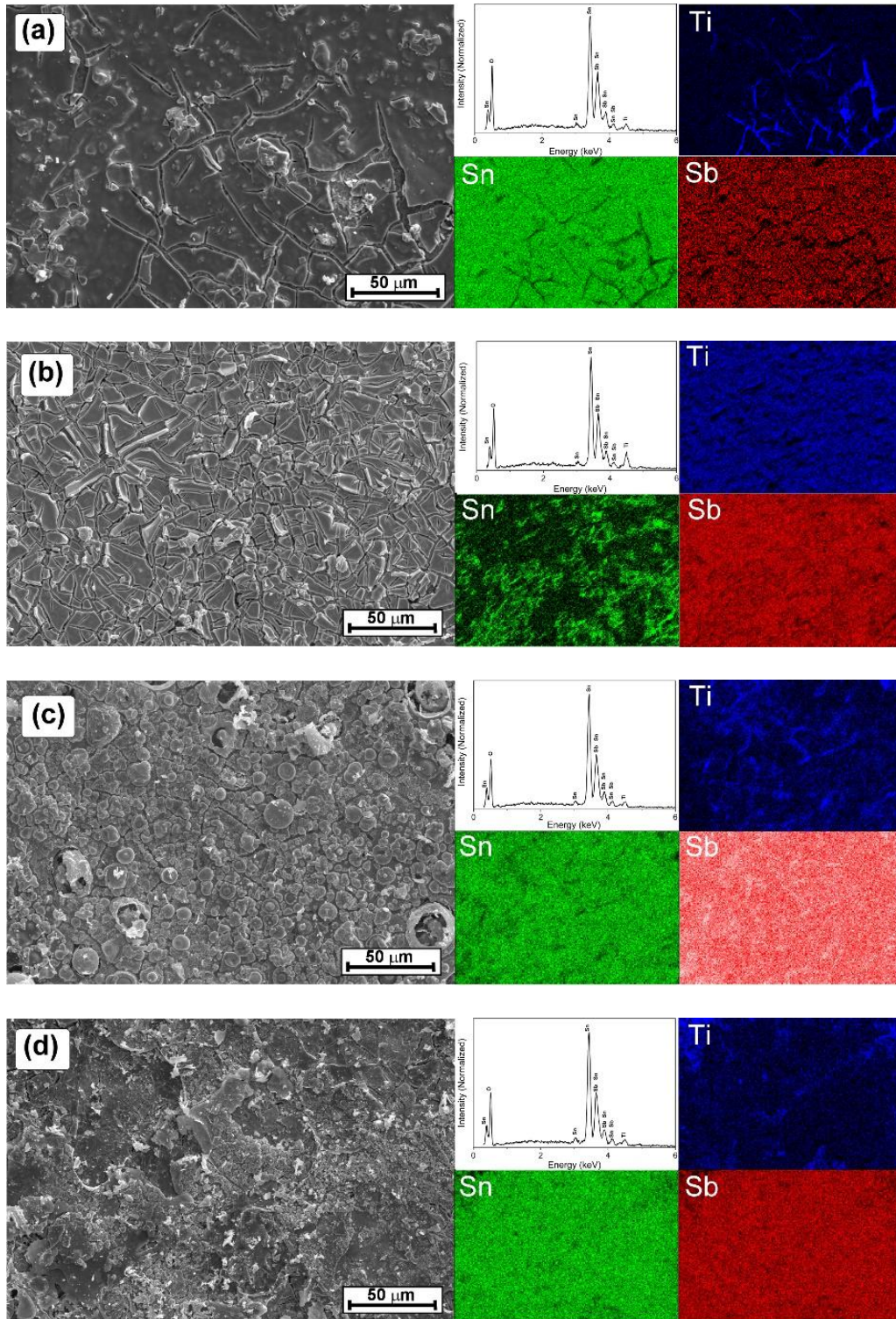


Fig. 1 – SEM image of the Ti/SnO₂-Sb anodes surface calcined at 600 °C. Left – Images obtained with BS mode; Right – EDS spectra and elemental mapping obtained in BSE mode. (a) CM anode (EG/CA = 6:3); (b) CM anode (EG/CA = 10:3); LM anode (EG/CA = 6:3); LM anode (EG/CA = 10:3);

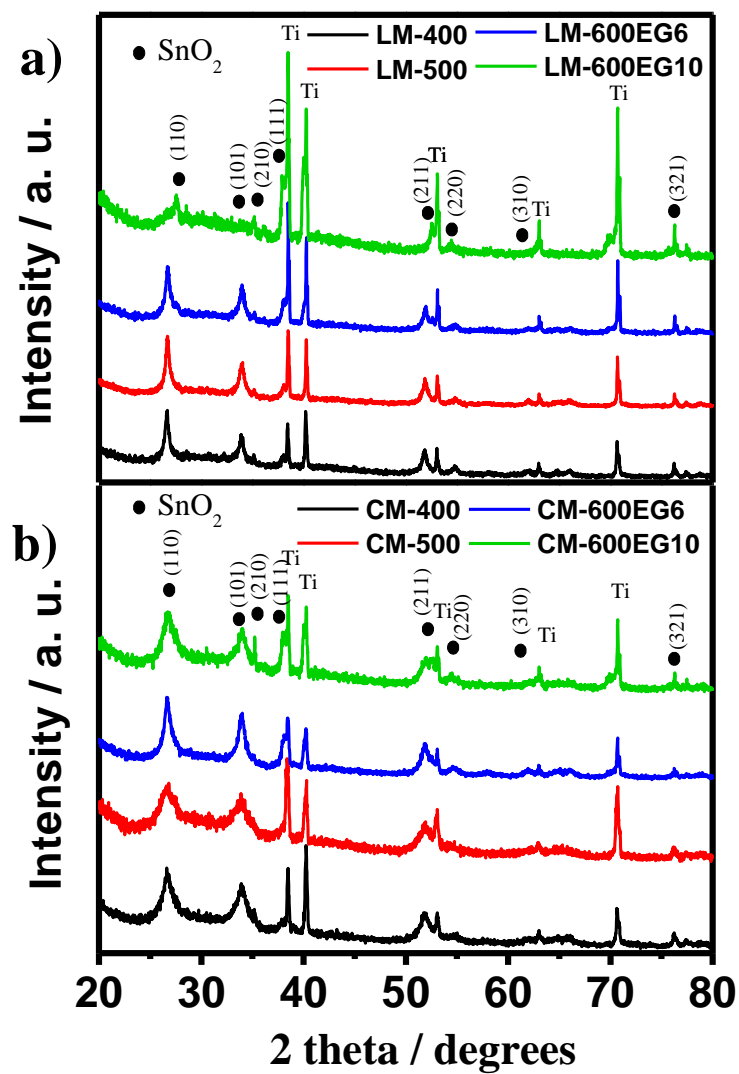


Fig. 2. XRD patterns of Ti/SnO₂-Sb anodes obtained after laser (a) a conventional (b) calcination.

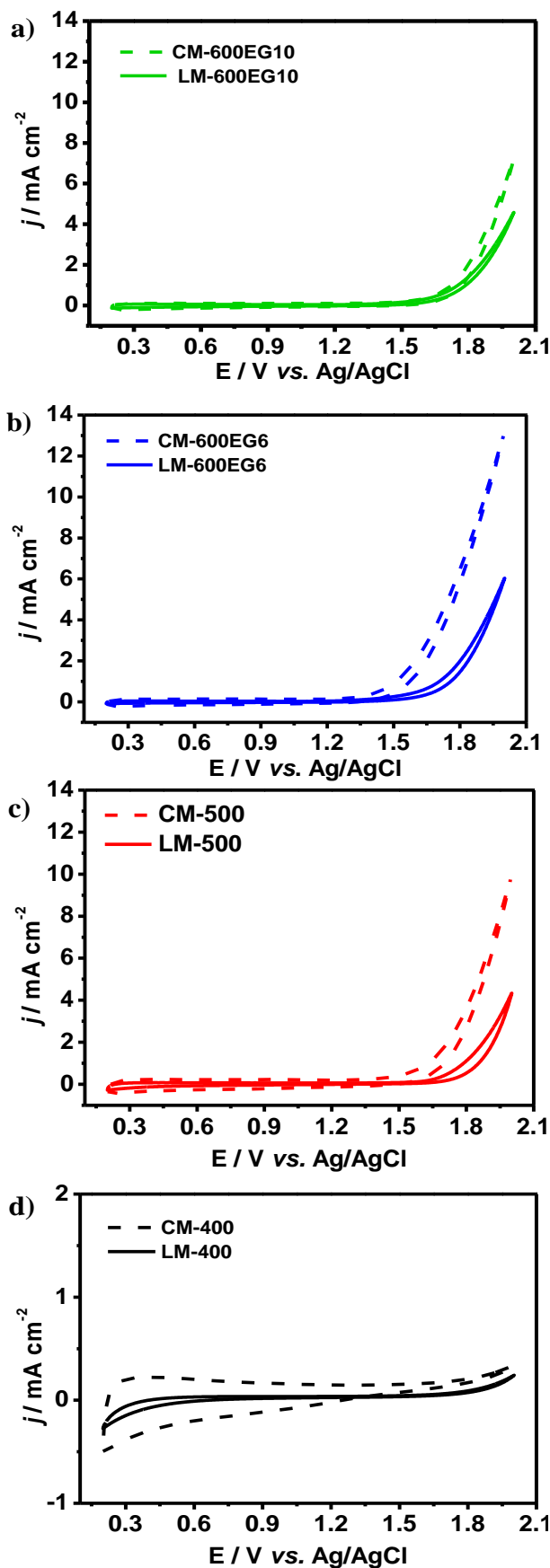


Fig. 3. Cyclic voltammograms recorded at 50 mV s^{-1} of $\text{Ti/SnO}_2\text{-Sb}$ anodes prepared using conventional and laser heating at 600 (EG/CA = 10:3) (a), 600 (EG/CA = 6:3) (b) 500 (c) and 400 °C (d) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte.

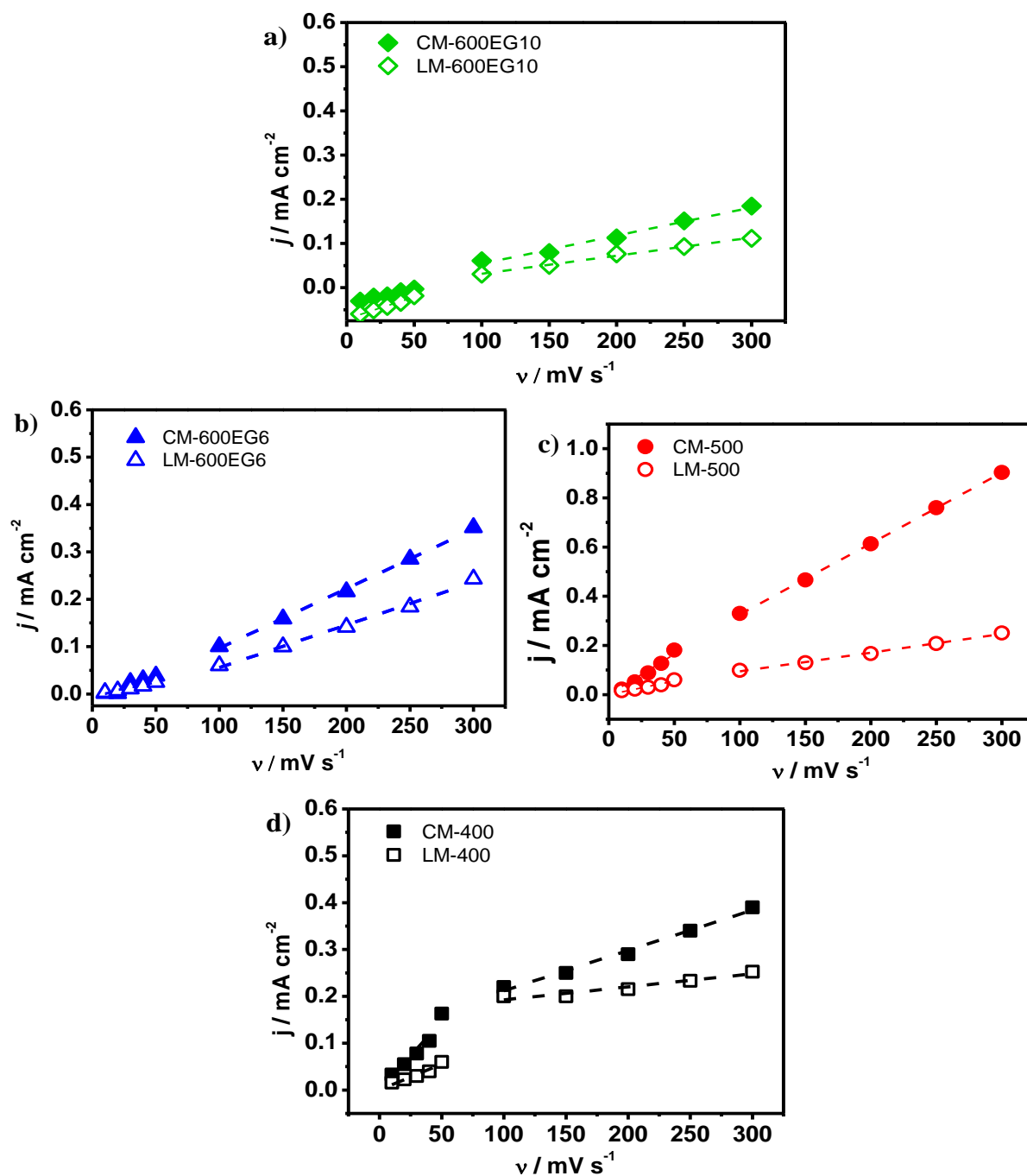


Fig. 4. Dependence of the capacitive voltammetric current density, j_c , on v of Ti/SnO₂-Sb anodes prepared at 600 °C and EG/AC = 10:3 (a) 600 °C and EG/AC = 6:3 (b), 500 °C (c) and 400 °C after conventional and laser calcination. Electrolyte: 0.1 mol L⁻¹ Na₂SO₄.

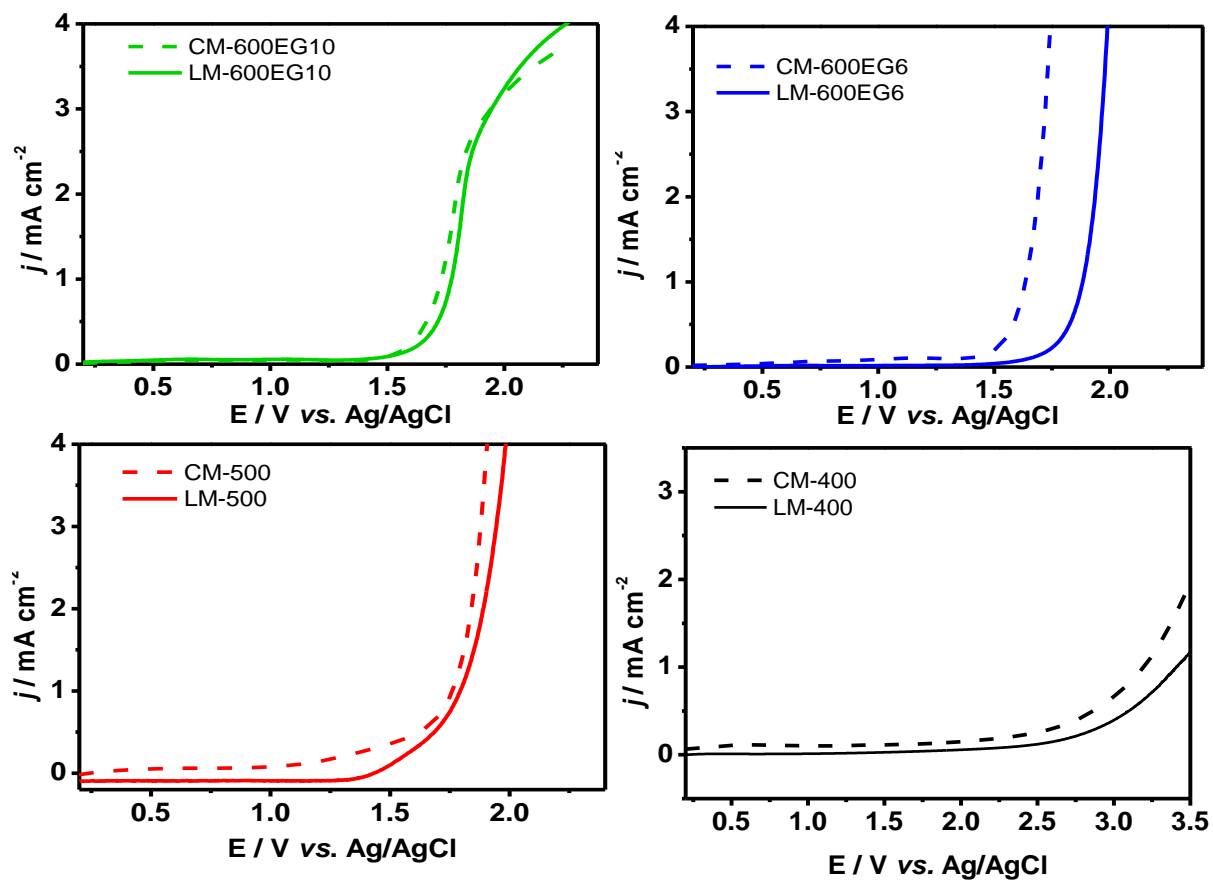


Fig. 5. Linear sweep voltammetry profiles of the Ti/SnO₂-Sb anodes prepared measured at a scan rate of 10 mV s⁻¹. Electrolyte: 0.5 mol L⁻¹ H₂SO₄.

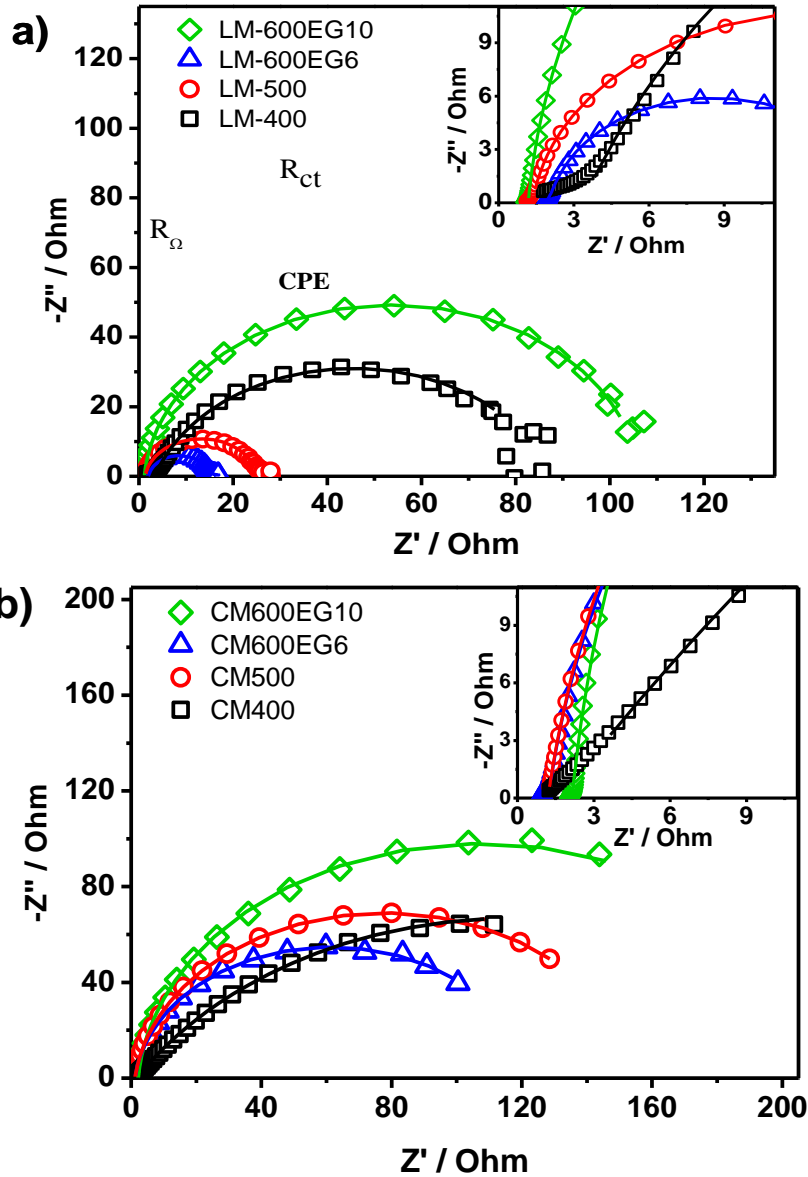


Fig. 6. Nyquist plots of Ti/SnO₂-Sb anodes prepared using the laser (a) and conventional (b) at different calcination temperatures at the OER onset potential (inset is the expanded view of the high-frequency region). Data obtained at 0.1–10⁴ Hz in 0.5 mol L⁻¹ H₂SO₄.

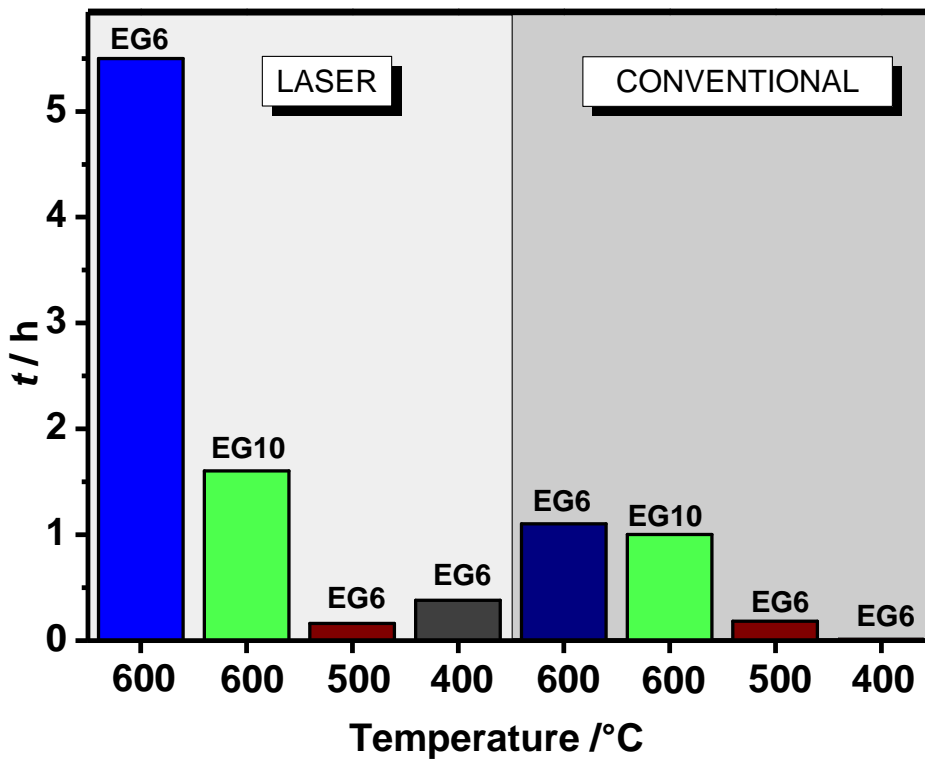


Fig. 7. Service life as a function of the Ti/SnO₂-Sb anodes after conventional and laser calcination (Conditions: 0.5 mol L⁻¹ H₂SO₄ at 200 mA cm⁻²). Molar ratio ethylene glycol/citric acid: 10:3 (EG10) and 6:3 (EG6).

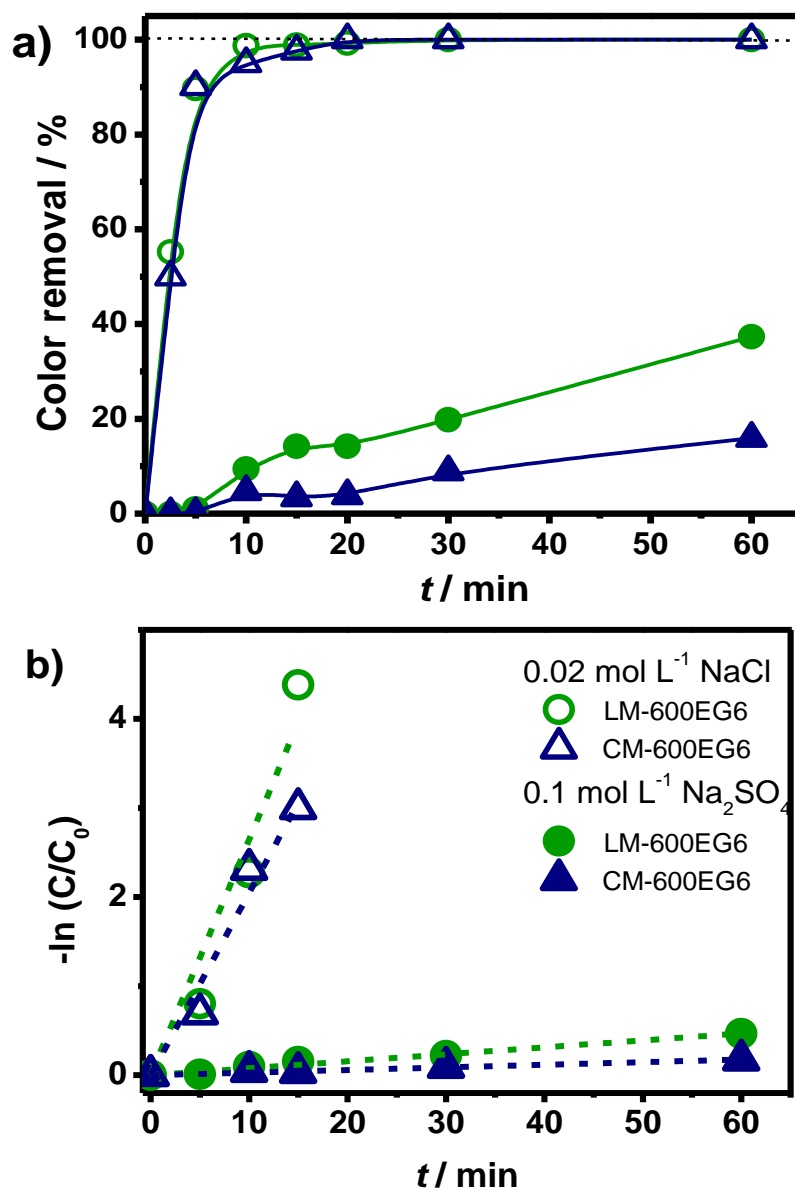


Fig. 8. Color removal of MB during electrolysis using LM-600EG6 (●, ○) and CM-600EG6 (▲ in 0.1 mol L⁻¹ Na₂SO₄ electrolyte (solid symbols) and with addition of 0.02 mol L⁻¹ NaCl (empty symbols) applying a fixed current of 40 mA cm⁻², for 60 min (a) and corresponding kinetic analysis related to the pseudo-first-order reaction kinetics (b).

Tab. 1.

Molar content of organic chemicals in the polymeric precursor solution employed for the preparation of different anodes. *LM* - laser method, *CM* - conventional method, *EG* - ethylene glycol and *CA* - citric acid.

Anode	Method	Temperature / °C	EG / mol	CA / mol
LM-600EG10	Laser	600	10	3
LM-600EG6	Laser	600	6	3
LM-500	Laser	500	6	3
LM-400	Laser	400	6	3
CM-600EG10	Conventional	600	10	3
CM-600EG6	Conventional	600	6	3
CM-500	Conventional	500	6	3
CM-400	Conventional	400	6	3

Tab. 2.Molar metallic percentages determined for all the developed Ti/SnO₂-Sb anodes.

Anode	EDX			
	Sn/M _T ^a		Sb/M _T ^a	
	Precursor solution (%)	Oxide layer (%)	Precursor solution (%)	Oxide layer (%)
LM-600EG10	94.0	96.13	6.0	3.87
LM-600EG6	94.0	96.0	6.0	4.0
LM-500	94.0	93.0	6.0	7.0
LM-400	94.0	96.0	6.0	4.0
CM-600EG10	94.0	97.0	6.0	3.0
CM-600EG6	94.0	96.0	6.0	4.0
CM-500	94.0	96.0	6.0	4.0
CM-400	94.0	94.4	6.0	5.6

^aTotal metal content, M_T = Sn + Sb

Tab. 3.

Dependence of voltammetric charge (q^*) and the total capacitance (C_d), external capacitance ($C_{d,e}$), and morphology factor (φ_m) with the thermal treatment used to prepare $\text{Ti/Ru}_x\text{Ir}_{x-1}\text{O}_2$ anodes.

Anode	q^* (mC cm ⁻²)	C_d	$C_{d,e}$	$C_{d,i}$	φ_m
LM-600EG10	5.0	0.67	0.64	0.04	0.08
LM-600EG6	5.6	0.99	0.89	0.1	0.10
LM-500	6.8	1.11	0.76	0.35	0.31
LM-400	1.0	1.11	0.35	0.76	0.68
CM-600EG10	9.50	1.33	1.19	0.14	0.11
CM-600EG6	12.98	1.26	1.03	0.23	0.18
CM-500	17.40	8.85	5.58	3.27	0.37
CM-400	8.51	2.93	0.31	2.62	0.89

Tab. 4.

Summary of fitted EIS data for Ti/SnO₂-Sb anodes prepared after conventional and laser calcination, recorded at OER potential for each anode.

Anode	E V vs Ag/AgCl / V	R _Ω / Ω	R _{ct} / Ω	Q _{dl} / F	n _{dl}
LM-600EG10	1.70	1.18	105.0	0.0016	0.96
LM-600EG6	1.90	1.16	13.17	0.0011	0.93
LM-500	1.80	1.36	23.74	0.0013	0.94
LM-400	2.80	3.36	84.25	0.015	0.80
CM-600EG10	1.68	2.14	210.6	0.004	0.95
CM-600EG6	1.70	1.20	120.5	0.006	0.94
CM-500	1.72	1.19	153.2	0.005	0.93
CM-400	2.80	1.60	235.3	0.002	0.66

Tab. 5.

The kinetic and energy consumption of color removal of methylene blue during electrolysis using Ti/SnO₂-Sb anodes obtained at 600 °C after conventional and laser calcination in different media.

Anode	Medium	k _{app} (min ⁻¹)	R ²	Energy consumption
				(Kw h / m ³)
LM-600EG6	0.1 mol L ⁻¹ Na ₂ SO ₄	0.0078	0.99	8.04
CM-600EG6		0.0029	0.98	18.86
LM-600EG6	0.1 mol L ⁻¹ Na ₂ SO ₄ + 20 mmol L ⁻¹ NaCl	0.2642	0.96	0.63
CM-600EG6		0.2044	0.98	0.83

Supplementary Materials

[Click here to download Supplementary Materials: Supporting information for the paper_corrected.docx](#)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

A handwritten signature in blue ink, appearing to be 'Law B', is located below the empty box.

CRedit author statement

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