Ultra-fast synthesis of Ti/Ru_{0.3}Ti_{0.7}O₂ anodes with superior electrochemical properties using an ionic liquid and laser calcination

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Abstract

Here, we combine CO₂ laser heating and an ionic liquid solvent (i.e., methylimidazolium hydrogensulfate HMIM⁺ HSO₄⁻) as an innovative route to produce Ti/Ru_{0.3}Ti_{0.7}O₂ anodes. For comparison purposes, the anodes were also prepared using conventional thermal treatment (in a furnace), and by the standard polymeric precursor method (also known as the Pechini method). For the laser heating, the anodes were heated at a power density of 0.4 W mm⁻² up to 550 °C and kept at this temperature for 40 seconds, followed by instantaneous cooling. Using these conditions, the total time spent to produce an anode (considering cooling) is just 9.7 min. It represents a remarkable reduction in 446-fold and 359-fold when compared with the conventional heating for Pechini and IL methods, respectively. The laser-prepared anodes presented an increase of 63.4% and 53.8% in the voltammetric charge, while the charge transfer resistance decreases 9.6-fold and 17.3-fold using IL and Pechini methods, respectively, when compared with their correspondent furnace-made ones. Finally, superior electrocatalytic activity toward the removal of the model pollutant atrazine is observed for the laser-prepared anodes. The anode produced using laser and the IL method is the most efficient, removing 81% of atrazine in 60 min, and presents the highest kinetic rate (0.062 min⁻¹) at the lowest energy consumption (0.179 kWh L⁻¹). The excellent electrocatalytic response of the anodes innovatively synthesized in this study characterizes them as an encouraging advance in the search for efficient materials to be applied in the electrochemical oxidation of organic compounds.

Keywords: wastewater treatment electrocatalytic activity; mixed metal oxide anodes; laser processing, atrazine.

1. Introduction

The electrochemical oxidation (EO) of toxic and recalcitrant organic compounds is an attractive alternative due to its simplicity, ease of automation, efficiency, and environmental compatibility [1]. A key aspect in EO, on a large scale, is the development of proper anode materials [2]. In this context, considerable progress has been achieved using low cost and stable mixed metal oxides (MMO) anodes for the treatment of recalcitrant organic compounds in an aqueous medium [3, 4]. Research on the synthesis of anodic materials with physical, electrochemical, and electrocatalytic enhanced properties is still essential for the industrial feasibility of these systems [5].

Among costs associated with components acquisition, the global cost of the anodes has also represented a drawback for the industrial application of electrochemical systems. In this sense, several studies have been carried out recently proposing alternative supports, synthesis routes, and solvents that seek to reduce costs related to anode synthesis [6-9]. Thus, one of the most direct routes for cost reduction is the modification in synthesis procedure; hence, sol-gel [10, 11] and polymeric precursors thermal decomposition (also known as Pechini) [12] methods have been studied. Recently, thermal decomposition using ionic liquids, especially the 1-methylimidazolium hydrogensulfate, as the solvent in the precursor solution preparation has been thoroughly assessed, showing increases in precursor solution viscosity with no compromise on anode physical features and electrochemical outcomes [2, 9, 13, 14]. Additionally, the use of ionic liquids is an emerging practice proven to reduce the number of repetitions in the synthesis process in most cases, consequently reducing total synthesis costs [9].

Alternative heating routes also promote a rapid solution to reduce global anode synthesis cost. Typically, conventional heating in a furnace is carried out through conduction and convection from the heat source to the anode, where the ‘mud-cracked’ formation is typically seen due to differences in expansion and contraction rates of the substrate and the

coating layers [15]. Although it requires straightforward and low-cost apparatus, the need for repetitive processing, along with the time spent with heating and cooling of the furnace between coatings, leads to the high final cost of obtaining these anodes [16].

Thus, seeking to reduce synthesis costs and promote enhancements in physical, electrochemical, and electrocatalytic properties of anodes, studies proposing alternative heating routes are of great interest. The use of CO₂ laser as a heating source for MMO anodes production is still scarcely reported in the literature, where laser heating was used for thermal decomposition of metallic chlorides dissolved in HCl solutions [17] or Pechini method [4, 18-20]. The main advantages of this heating procedure are centered on fast processing, high heating rates, and easy operation.

As has been pointed out, the electrocatalytic activity of the anodes is directly correlated to their method of synthesis. The evaluation of their performance for the treatment of water contaminated toward the removal of relevant model pollutants, such as atrazine is also of great interest. The herbicide atrazine is widely used to control broadleaf weeds, being frequently detected in water due to its moderate solubility (33 mg L⁻¹ at 20 °C) in water. Several studies have attempted to perform the degradation of atrazine through electrochemical oxidation processes, encountering considerable difficulties in obtaining high degradation rates [21-24]. Among the several problems reported, the formation of intermediates that reduces the treatment efficiency by adsorbing on the surface of the anodes [21], the high current densities required for the treatment [22], the need for additives in the treatment [23], among other influential factors have been analyzed to improve degradation rates in these systems.

In this sense, here we propose the synthesis and characterization of anodes with the Ti/Ru_{0.3}Ti_{0.7}O₂ nominal composition employing two different heating procedures (conventional furnace and laser heating) and by the Pechini and the ionic liquid (IL) synthesis methods. The as-prepared materials were characterized employing cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) coupled

with energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction analysis (XRD). Furthermore, the performance of the anodes materials was tested, evaluating the removal of atrazine (model pollutant), analyzed by high-performance liquid chromatography (HPLC).

2. Experimental

2.1 Materials

The following reagents were used for the synthesis, the pre-treatment of Ti substrates, and the electrochemical characterizations: ruthenium chloride (III) hydrate (99.99%), titanium (IV) butoxide (97%), ethylene glycol (EG), anhydrous citric acid (CA) (99.5%), sulfuric acid (95.0–98.0%) and isopropyl alcohol (99.8%), from Sigma-Aldrich®, oxalic acid (99.5%), and anhydrous citric acid (CA) (99.5%), from Vetec®, hydrochloric acid (38.0%) from Neon®. All solutions were prepared with an ultrapure (Gehaka MS 2000) system with a resistivity lower than $18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C .

2.2 Synthesis of the anodes

The precursor solutions were prepared using both the Pechini and IL methods. Thus, the metal precursors ruthenium chloride and titanium (IV) butoxide were weighted in molar concentrations of 0.3 mol L^{-1} of Ru and 0.7 mol L^{-1} of Ti, respectively, followed by dissolution in the home-made methylimidazolium hydrogensulfate ($\text{HMIM}^+ \text{HSO}_4^-$) ionic liquid, that was prepared according to a methodology previously described [11], whereas, for Pechini's method [12], the mixture of ethylene glycol (EG) and citric acid (CA) was the solvent, considering a molar ratio for EG:CA:metal chlorides was 10:3:1.

Titanium plates ($1 \text{ cm} \times 1 \text{ cm}$) were used as metallic support for MMOs deposition, with a geometric area of 2 cm^2 . Initially, the plates were polished with sanders of 220, followed by 320, and rinsed with ultrapure water. In order to ensure the removal of superficial impurities, the plates were submitted to thermal treatment in HCl (20% v/v) by boiling for 15 min,

followed by 10 min of thermal treatment in a $\text{C}_2\text{H}_2\text{O}_4$ (10% v/v) at 90 °C. Afterward, they were rinsed with ultrapure water. The precursor solutions were brushed on both sides of the pretreated titanium plates (1 cm $\times$ 1 cm $\times$ 0.1 cm).

The anodes were prepared using either an electric furnace or a CO_2 laser (operating in continuous mode) as the heating sources. For both methods, the final deposited mass reached 1.2 mg cm^{-2} . This value was adopted because a recent study proved to be a satisfactory mass for the production of RuO_2 -based MMOs [25]. The covering and subsequent heating procedure were repeated 8 times for all routes (Pechini and IL, regardless of the heating procedure), corresponding to a nominal thickness of around 2–3 μm [18].

The thermal treatment was made at 550 °C for both heating procedures, varying on heating mechanisms. For conventional heating, an EDG 3P-S furnace was used. For the IL method, a heating rate of 10 °C min^{-1} was used to reach 550 °C, which was then kept at this temperature for 10 min. For the Pechini method, a heating rate of 5 °C min^{-1} was used. In this methodology, the anodes were first treated at 130 °C for 30 min, followed by heating at 250 °C for 10 min, and finally calcined at 550 °C for 5 min. The final calcination procedure, for both IL and Pechini methods, was performed at the final temperature of 550 °C for 60 min [19]. The cooling was carried out naturally, and no control in the atmosphere was applied. For laser heating, a system composed of a CO_2 laser (GEM – 1001 – Coherent), mirrors, and a meniscus zinc selenite (ZnSe) lens was used. For the synthesis, the anodes were placed beyond the focal length of the lens so that the laser beam diameter could be adjusted to 1 cm, thus covering all superficial anode area. The temperature was measured using a type S thermocouple (cross-section = 0.25 mm) positioned at the center of the sample surface. In order to reach 550 °C, the power density of 0.4 W mm^{-2} was applied and kept constant for each layer for 40 seconds. The cooling occurred instantaneously. Finally, the final calcination procedure using laser heating consisted of keeping the anodes at 550 °C for 5 min.

Thus, the anodes were prepared by two different methods that, hereafter, will be denoted as CM (conventional heating method) and LM (laser heating method).

2.3 Physical Characterization

The surface morphology of the MMO films was accessed employing a field emission scanning electron microscope with high resolution. (FE-SEM; Zeiss GeminiSEM 500). The chemical composition of the obtained anodes was determined using EDX spectroscopy coupled to the SEM equipment. XRD experiments were performed using a Philips PW-1700 diffractometer with Cu K α radiation over a 2θ range between 20° and 80°, at a scan rate of 0.02° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were carried out by an Omicron (CHA-Concentric Hemisferica analyzer), spectrometer, a monochromated with Al K α X-ray source radiation ($h\nu = 1486.6$ eV) at a base pressure of 5×10^{-9} mbar. Binding energies of the spectra were referenced against the C 1 s component of adventitious carbon at 284.6 eV. Peak energies were given with an accuracy of 0.1 eV. The spectra were deconvoluted using a Levenberg–Marquardt algorithm of the CasaXPS software.

2.4 Electrochemical Characterization

A three-electrode glass cell was used for electrochemical measurements. The cell contained a platinum sheet as counter-electrode, a Ag/AgCl reference electrode, and the working electrode (anode - varying according to the heating procedure adopted). Analyses were carried using a Potentiostat/Galvanostat PGSTAT 302N from Methrom Autolab controlled by software Nova 2.1.

CV measurements were obtained from applying 50 mV s⁻¹, varying from 0.2 to 1.2 V in 3.7 g L⁻¹ (0.0064 mol L⁻¹) NaCl medium for all anodes. Morphology factor (ϕ) was determined following methodology in the literature [26], varying scan rate from 10 to 300 mV s⁻¹. EIS experiments were carried out in a 0.5 mol L⁻¹ H₂SO₄ solution, covering the frequency

range of 0.01 Hz – 10 kHz with a logarithmic distribution of 10 points per decade using an AC sine signal amplitude of 5 mV. Potential applied for EIS was the onset of the OER determined for each anode.

2.5 Electrolysis

The electrochemical oxidations of atrazine (10 mg L^{-1}) were carried out in a 0.1 L single electrochemical cell containing 3.7 g L^{-1} NaCl solution applying 20 mA cm^{-2} for 1 h.

Moreover, to confirm that there are no relevant effects of adsorption (what it may be expected because of the low surface area of diamond electrodes) electrolysis applying zero current in the solution of atrazine (20 mg L^{-1}) additional tests were carried out to evaluate if the solution of atrazine (20 mg L^{-1}) adsorbs onto the surface of the anode. Thus, linear voltammetry experiments (from 0 to -1.8 V), before and after adsorption tests were carried out using a boron-doped diamond (8000 ppm of boron) as a sensitive electrode to detect this contaminant. The concentration of the atrazine was evaluated by HPLC (Agilent 1100 series) coupled with a DAD detector. A Zorbax Eclipse Plus C-18 ($4.6 \text{ mm} \times 100 \text{ mm}$; $3.5 \text{ }\mu\text{m}$) analytical column was used, and its temperature was maintained at $25 \text{ }^{\circ}\text{C}$. The mobile phase consisted of a mixture of acetonitrile/water (containing 0.1 % formic acid) (55/45, v/v) at a flow rate of 0.6 mL min^{-1} . Detection was performed at 223 nm. The injection volume was $20.0 \text{ }\mu\text{L}$, and the retention time was around 2.7 min for atrazine.

The energy consumption (EC) was calculated by Eq. 1 during the electrolysis, the mean cell voltage (E_{cel}) in V, the current (I) in A, the electrolysis time (t) in hours, and the volume treated (V) in L.

$$\text{EC (kWh L}^{-1}\text{)} = (E_{\text{cell}} \times I \times t) / V \quad (1)$$

3. Results and Discussion

3.1 Physical Characterization

Fig. 1 displays the SEM images of the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anodes surface. As a general trend, the coating layer presents a structure commonly reported as mud-cracked morphology, which is related to the mechanical stress caused by the coating plasticity and the difference of the thermal expansion coefficient between the titanium substrate and the thin film formed [15, 27]. However, the laser-prepared anodes (Fig. 1b and 1d) display rougher morphology. The heating process using laser and furnace for the two different routes (Pechini and LI) is shown in Fig. 1e. In addition, Fig. S1 displays SEM images with a high magnification of $80.000\times$ of anodes prepared by the Pechini and IL methods after laser-based thermal treatment. The anode prepared by the Pechini method reveals a porous texture, with spherical and highly agglomerated particles; besides, particles of different sizes were observed in the sample (Fig. S1a). The anode prepared by IL, on the other hand, has a significantly smaller particle size (nanostructured surface) and uniform distribution. Thus, it was significant to characterize the material obtained after laser calcination to observe the differences in the microstructure generated by each technique.

Fig. 1: Scanning electron micrographs (insets represent magnifications of 5000 $\times$) of (a, b) Pechini-prepared anodes and (c, d) IL-prepared anodes obtained after conventional (a, c) and laser (b, d) heating and (e) representative scheme of the heating process in CO₂ laser and furnace for the different routes (Pechini and IL).

Analyses by EDX allows determining the real proportion of the oxides on the anode surface. As a result, a good correlation is seen between the nominal and real compositions (Table 1). Also, below each SEM image presented in Fig. 1a-d, the elemental mapping of each studied anode is provided. In these images, brightness changes are related to different concentrations of elements.

It is important to emphasize that as titanium is also the substrate component, in these images, regions with enhanced brightness can be related to the coating and be related to the

areas where titanium substrate can be easily accessed, such as cracks. Hence, the IL-produced anodes, regardless of the heat treatment employed, present a more homogeneous distribution. This result shows that although a mud-cracked morphology was favored, the cracks observed are shallow, which is the main challenge when producing such kind of materials by thermal decomposition [3].

On the other hand, although the Pechini method is well-known for the high homogeneity of the anode, it is commonly reported that deep cracks can occur when working at high temperatures [2, 14], which is in accordance with the present findings.

Table 1: EDX determination of the metals in the oxide film, full width at half maximum (FWHM) of the (110) diffraction peak, and mean crystallite size values for the anodes obtained after conventional and laser heat treatments for Pechini method and IL method, through XRD analysis.

Anode	Composition (mol%)		FWHM (110)	Crystallite Size
	Ru/M _T ^a	Ti/M _T ^a		
Conventional - Ionic Liquid	30	70	0.768	10.7
Conventional - Pechini	25.4	74.5	0.691	11.8
Laser - Ionic Liquid	31	69	1.504	5.4
Laser - Pechini	31.4	68.5	0.774	10.6

^a Total metal content, M_T = Ru + Ti

XRD data of the Ti/Ru_{0.3}Ti_{0.7}O₂ anodes obtained after conventional and laser heating are shown in Fig. 2. Both anodes, produced by Pechini (Fig. 2a) and IL (Fig. 2b) methods, exhibit the RuO₂ (JCPDS - PDF 40-1290) and TiO₂ (JCPDS - PDF 01-1292) peaks related to rutile-like structure. All XRD patterns were normalized to 1 by the intensity of the (110) reflection (~27.5°) and vertically shifted for laser samples. The splitting of the (101) peak

means that a meta-stable solid-solution of the two components can be formed for $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ coating or an extremely finely dispersed mixture of the two phases [28]. A solid solution between RuO_2 and TiO_2 rutile is expected since the constituent oxides satisfy the requirements of the Hume-Rothery rules for solid solution formation [29, 30]. Similar results have been reported in the literature for the formation of meta-stable solid-solution between RuO_2 and TiO_2 at the same proportion here studied (i.e., 30% RuO_2 : 70% TiO_2), regardless of the synthesis methodology [28-31].

Fig. 2: XRD diffraction patterns of a) Pechini-prepared anodes and b) IL-prepared anodes obtained after conventional and laser calcination.

Additional peaks corresponding to the titanium metal substrate appear as expected, frequently pointed out as characteristic of thin films, allowing X-ray penetration through coating [5, 18, 32, 33]. The average crystallite size of the oxides in the coatings was calculated using the Scherrer equation and are summarized in Table 1. The full width at half maximum (FWHM) of the (110) diffraction peak located at around 28.5° was used. The crystallite size of samples reduces from 10.7 nm to 5.4 nm for the IL anodes and from 11.8 nm to 10.6 nm for Pechini anodes when the laser heating method is used. The smaller crystallite size of the laser-

prepared anodes is in good agreement with the results presented by Santos and coworkers for RuO₂-IrO₂ laser-prepared anodes [18].

XPS analyses were carried out to explore the surface composition and oxidations states of the Ti/Ru_{0.3}Ti_{0.7}O₂ anodes obtained after conventional and laser heating. The XPS survey scans identified all the constituents of the coating (Fig. S2), showing an overlap of the C 1s peak of carbon with the Ru 3d spectrum of ruthenium, as well as Ru 3p_{3/2} and Ti 2p spectra. Excluding the carbon contribution, Table 2 confirmed the presence of ruthenium and titanium oxides as the most abundant phases.

Table 2: Elemental composition of the Ti/Ru_{0.3}Ti_{0.7}O₂ anodes obtained by XPS.

Anode	Element	At %
Conventional - Ionic Liquid	C 1s	31.27
	O 1s	37.90
	Ti 2p	17.14
	Ru 3d	12.78
Laser - Ionic Liquid	C 1s	35.06
	O 1s	34.93
	Ti 2p	17.82
	Ru 3d	12.01
Conventional - Pechini	C 1s	41.61
	O 1s	32.38
	Ti 2p	15.18
	Ru 3d	10.84
Laser - Pechini	C 1s	39.38
	O 1s	31.54
	Ti 2p	18.24
	Ru 3d	10.93

The deconvolution of the O 1s high-resolution spectra is shown in Fig. S3. The most intense peak can be attributed to the M–O bond, where M = Ru and/or Ti, confirming the

formation of metal oxides [34]. The second peak can be related to O–H groups adsorbed on the surface of the electrodes, while the smallest peak, identified only in the electrodes prepared by laser heating (Fig. 3Sb and 3Sd), can be attributed and related to the M–O–H group [34].

The deconvolution of the high-resolution spectra of Ru 3d/C 1s (Ru 3d_{5/2} and Ru 3d_{3/2}) and Ti 2p/Ru 3p are shown in Fig. 3. Several phases of Ru on the electrode surface have been identified: RuO₂, RuO₃, and RuOH [35-38], the latter being present only in the electrodes prepared by laser heating (Fig 3b and 3d), in accordance with the peaks observed in the O 1s spectra (Fig S3b and S3d). In addition, the binding energy of Ru 3d_{3/2} was superimposed with that of C 1s; thus, the oxidation state of Ru was assessed from the Ru 3d_{5/2} emission line. The Ru 3d_{5/2} peak indicated similar proportions of RuO₂ for the electrodes. The high-resolution XPS spectra for Ti 2p showed multiple peaks. The most intense peaks, located between 458.3 and 458.8 eV attributed to Ti 2p_{3/2} and the other between 464.1 and 464.5 eV corresponding to Ti 2p_{1/2}, which is consistent with TiO₂ [35-38].

Fig. 3: High-resolution XPS spectrum of Ru 3d/C 1s and Ti 2p/Ru 3p for Ti/Ru_{0.3}Ti_{0.7}O₂ anodes made using conventional and laser heat treatments and for the Pechini and IL methods.

3.2 Electrochemical characterization

Fig. 4 shows the CVs obtained for the as-prepared anodes in the potential interval of 0.2–1.2 V vs. Ag/AgCl in a 3.7 g L⁻¹ NaCl solution. All currents were normalized by the geometric area of the working electrode. The voltammograms showed pseudo-capacitive behavior. The electrochemically active area of the anode, a relative measure of the number of active sites, was estimated by integrating the voltammetric curves in the double layer domain ($\Delta E = 0.2$ –1.2 V vs. Ag/AgCl) [39, 40]. Values of voltammetric charge, q^* , are summarized in Table 3. The presence of more active sites for the laser-prepared anodes, regardless of the solvent employed, can be directly related to the oxide structure on the surface layer. This result agrees with the previous discussion on differences in the crystallite sizes varying with the synthesis conditions and can be strongly correlated with the XPS results, which showed the hydrous

ruthenium oxide phase (i.e., RuOH) only for the laser-prepared anodes. Although previous literature found an increase in active sites when the mean crystallite size is reduced [18, 41, 42], as seen here, the formation of this hydrous phase is also well-known to contribute to the higher electronic conductivity and the increase in the voltammetric charge when present in the coating, due to the fast deprotonation/protonation reaction [34, 43-45].

Fig. 4: Cyclic voltammograms made at 50 mV s^{-1} in $3.7 \text{ g L}^{-1} \text{ NaCl}$ for the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anodes obtained after conventional and laser heat treatments for (a) Pechini and (b) IL methods.

According to the literature, at low scan rates, reactions occur in all active sites because the electrolyte can diffuse throughout the catalytic layer [26]. However, at high scan rates,

reactions occur only at the most accessible active sites. The morphology factor (ϕ) was determined in the capacitive potential interval of 0.9–1.0 V vs. Ag/AgCl. The profiles of the studied anodes are shown in Fig. S4. The value of ϕ can vary between 0 and 1; when the anode tends to 0, it indicates that the internal sites of the anode have a small or negligible influence on the total differential capacitance.

Conversely, values near 1 indicate that the anode has a large internal area. For all anodes, the ϕ was ≤ 0.3 , indicating a compact coating surface, corroborating with SEM images (Fig. 1). This overall response in a low number of internal sites is expected and agrees with other studies that pointed out that high calcination temperatures (as the 550 °C used in this work) favor coalescence due to sintering effects. The effect of heat treatment temperature on the Ti/RuO₂-TiO₂ coatings was also reported by Moradi et al. [30]. They showed that the electrochemical porosity, as an indicator of internal active sites, decreases for high thermal treatment temperatures due to enhanced sintering and crystal growth inside the coating [30].

EIS measurements were carried out at the potential corresponding to the OER onset potential for each studied anode. The choice of the potential was based on linear sweep voltammetry data (Fig. S5). Fig. 5 shows the Nyquist plot of the four prepared anodes. All impedance spectra exhibited well-developed semicircles typically related to the charge-transfer process for the OER. The spectra were fitted using an equivalent circuit composed of one capacitive loop, represented by $R_s(R_{ct}Q_{dl})$, in which R_s is the cell resistance, including the connections, R_{ct} is the charge-transfer resistance, and Q_{dl} corresponds to the pseudo-capacitance. The constant phase element (CPE) is often used to replace Q_{dl} , considering the roughness and heterogeneous nature of the anode surface [46].

Fig. 5: Nyquist diagrams recorded for $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anodes made using conventional and laser heat treatments and for the Pechini and IL methods.

The values of R_Ω , R_{ct} , n , and CPE obtained by the fitting procedure are listed in Table 3. It can be noted that the charge transfer resistance for laser-prepared anodes is approximately 10 (IL) and 17 (Pechini) times smaller than the conventionally produced ones in the furnace. These results indicate that laser calcination substantially improves the ability to charge transfer, which is supported by CV data that showed increased active sites. This behavior can be attributed to the very fast heating and cooling rates, which avoids the formation of TiO_2 insulating interlayer between the substrate and the coating, as reported by Shao et al. [47]. It is essential to point out that the laser penetration is of about a few micrometers, and the thermal heating process is ultra-fast. Thus, there is a considerable temperature gradient between the coating surface and the titanium substrate; therefore, it is not directly heated by the laser radiation but by the conduction of heat from the coating layer. Besides, the laser beam is just a small heat source, and thus, the heat dissipation is fast, avoiding the rise of temperature on

titanium substrate, and as a consequence, the substrate oxidation is prevented. Therefore, in laser-prepared anodes, it is expected that the properties in which TiO₂ layers are harmful are avoided.

Table 3: Voltammetric charge and summary of fitted EIS data for Ti/Ru_{0.3}Ti_{0.7}O₂ anodes calcined using conventional and laser heat treatments for the Pechini method and IL method.

Method	Anode	q^* (mC cm ⁻²)	E (V)	R_s (Ohm)	R_{CT} (Ohm)	n	CPE	χ^2
Conventional	CM - Ionic	15.8	1.23	1.6	95.38	0.94	0.03	2.1×10^{-4}
	Liquid							
	CM -	12.6	1.22	2.9	214.1	0.95	1.15	1.1×10^{-4}
	Pechini							
Laser	LM - Ionic	24.9	1.20	0.9	9.9	0.90	0.05	8.7×10^{-4}
	Liquid							
	LM -	23.4	1.23	1.02	12.4	0.92	0.05	8.0×10^{-4}
	Pechini							

3.3 Economic considerations

Some essential aspects must be studied to accomplish practical applications, including the time spent on the preparation of the material. The synthesis of MMOs by thermal decomposition methods requires several coating layers; thus, several steps of heating and cooling are necessary. In that context, to obtain the desired oxide coating mass (1.2 mg cm⁻²), all anodes prepared in this work required 8 steps of heat treatment and cooling. For conventional heat treatment, the anodes prepared by the Pechini method and the IL method followed heating rates, as explained in the methodology, and reported by Santos et al. [19] and Santos et al. [41], respectively. After heating, the material remains inside the furnace for cooling until room

temperature. Thus, the electrodes prepared by conventional heating using the Pechini method and the Ionic Liquid method presented a total synthesis time of 71.3 h and 59.0 h, respectively (Fig. 6a). For thermal treatment by laser, an exceptionally brief time (40 s) is necessary to obtain each layer. At this point, we remind that cooling occurs almost instantaneously. It means that laser heating used for the production of the $\text{Ti/Ru}_{0.3}\text{-Ti}_{0.7}\text{O}_2$ anodes regardless of the route (Pechini or IL method) results in remarkable reductions in the synthesis time, which are approximately 446 and 369 times lower than for the conventionally-prepared ones.

Moreover, considering the average laser and furnace electric power, the electric energy consumed using the laser calcination was about 100 and 41 times lower than for the conventional calcination for Pechini and IL methods (Fig 6b). Therefore, the use of the laser to produce MMO anodes becomes advantageous due to its lower energy consumption, fast processing time, and the enhanced electrochemical properties of the MMO anodes compared with the respective conventional anodes.

Fig. 6: Total processing time, considering the heating and cooling time for conventional and laser calcination.

3.4 Electrolysis

Generally, the low performance of anodes demands high current densities be applied to overcome the energetic demand required to degrade the atrazine molecule. In this sense, the

novel materials proposed here were analyzed to evaluate their performance in this challenging scenario. Therefore, atrazine degradation (10 mg L^{-1}) in 3.7 g L^{-1} NaCl was assessed for the synthesized anodes. Also, most of the target pollutants concentrations used in most studies are orders of magnitude higher than those found in real matrixes [48]. Here, the chosen concentration of atrazine was fixed in 10 mg L^{-1} in order to have more realistically concentrations that do not exceed this concentration in natural waters. Fig. 7 shows that all synthesized anodes were able to remove atrazine, and the laser-synthesized ones showed higher removal rates, and consequently, faster kinetics.

Fig. 7: Atrazine removal with time during electrochemical oxidation using the four anodes with a composition of $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (a) and kinetics analysis considering a pseudo-first-order reaction (b). Electrolyte: 3.7 g L^{-1} NaCl, j : 20 mA cm^{-2} , cathode: Pt, reference electrode: Ag/AgCl.

Fig. 7 evidently shows that both the thermal heating process and the precursor solution composition strongly influences the final electrocatalytic performance of the obtained anodes. Hence, the laser-produced anodes yield a higher degradation rate for atrazine (81% for LM - Ionic Liquid), removing up to 2-folds more than the conventionally synthesized ones (49% for CM - Ionic Liquid). The higher electrocatalytic activity achieved by the IL laser-prepared anodes is in accordance with data indicating significant improvement in the conductivity (from

EIS measurements) and higher voltammetric charges (from VC data), as presented in Fig. 5 and Table 3. At this point, it is worthy of commenting on the mechanism of degradation in the system. In this sense, adsorption tests were conducted to prove that this mechanism does not contribute to the decrease in atrazine concentration. Atrazine is an electroactive compound presenting a peak maximum at a negative potential (around -1.0 V vs. Ag/AgCl), which can be detected by boron-doped diamond electrode employing linear voltammetry [49]. Thus, linear voltammetries were recorded at 50 mV s⁻¹ in the potential range from 0 to -1.8 V of the synthetic solution containing 20 mg L⁻¹ of atrazine recorded before and after adsorption tests electrochemical oxidation without applied current (Fig. S6). As a result, no evidence of adsorption of atrazine on the anode surface is observed, which demonstrates that this mechanism is not present-taking place and is not responsible for promoting the removal of the contaminant. Some studies on the electrochemical oxidation using carbon-based materials have performed such experiments to clarify if some portion of the contaminant adsorbs onto the electrode surface, since these materials present a large surface area and porosity. For example, Zhu et al. (2018) studied the anodic oxidation of atrazine and, according to additional experiments, showed that atrazine is not adsorbed by graphite [50]. In another study, carbon-felt was employed as the anode and was submerged for three days on different concentrations of the contaminant (adsorption experiments) and concluded that atrazine was not absorbed [51]. Regarding non-carbon-based electrodes, Garza-Campos and coworkers coupling solar photoelectro-Fenton and heterogeneous solar photocatalysis; previous tests of a 20 mg L⁻¹ atrazine solution (in the darkness) demonstrated insignificant adsorption of atrazine onto the TiO₂ film [52].

Therefore, the main mechanisms involved in the degradation of atrazine are expected to occur by two routes occurring simultaneously, according to a model proposed in the literature by Comninellis [6]. In the first route, the oxidation reactions occur directly on the anode M(*OH) by forming hydroxyl radicals (*OH) adsorbed chemically. Moreover, for the active

anodes (as the MMOs here studied), due to the strong interaction with the $\cdot\text{OH}$, a superior oxide or superoxide (MO) can be formed ($[\text{M} (\cdot\text{OH}) \rightarrow \text{MO} + \text{H}^\bullet + \text{e}^-]$) when a superior oxidation state is available for the metallic oxide anode. Thus, for active anodes, the redox pair MO/M acts as a mediator of organic oxidation $[\text{MO} + \text{R} \rightarrow \text{RO} + \text{M}]$. In the second route, oxidation occurs indirectly, by intermediation of electroactive oxidative species formed on the anode, in which active chlorine is expected to be formed from chloride solutions [6].

In order to further estimate the catalytic performance of these anodes, the kinetic degradation constant was calculated by applying Eq. 2 [53, 54], in which C is the initial concentration of atrazine and $\frac{\partial C}{\partial t}$ is the concentration change as a function of the electrolysis time.

$$\frac{\partial C}{\partial t} = -k C \quad (2)$$

The k values for atrazine degradation (Table 4) were estimated between 0.009 and 0.062 min^{-1} . The reaction rate was 5.6-folds higher for laser-prepared anodes when compared to their respective conventionally-prepared anodes. In addition, the anode prepared by laser using IL as solvent had the highest atrazine removal (81%), as well as the highest kinetic constant (0.062 min^{-1}).

Table 4: Atrazine removal, pseudo-first-order rate constant, and energy consumption obtained for electrochemical oxidation of 10 mg L^{-1} of atrazine in 3.7 g L^{-1} NaCl solution at a current density of 20 mA cm^{-1} using the four anodes with a composition of $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

Method	Anode	Atrazine Removal (%)	k (min^{-1}) 1)	R^2	EC (kWh L^{-1}) 1)
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Conventional	CM - Ionic	49	0.011	0.970	0.189
	Liquid				
	CM - Pechini	37	0.009	0.991	0.205
Laser	LM - Ionic Liquid	81	0.062	0.982	0.179
	LM - Pechini	67	0.051	0.986	0.185

The efficiency of the process was also evaluated regarding energy consumption (EC), which expresses the amount of energy consumed during the process. The results were estimated between 0.205 and 0.179 kWh L⁻¹, and the lowest values were found for the laser-calcined anodes produced by both IL (0.179 kWh L⁻¹) and Pechini (0.185 kWh L⁻¹) methods. These data corroborate with the EIS measurements, in which the laser-prepared anodes presented lower charge transfer resistance. Moreover, a study carried out by Zaviska et al. [22] shows that in order to obtain similarly high electrocatalytic performance by using Ti/IrO₂ anodes, up to 10 kWh L⁻¹ can be demanded to perform the electrochemical degradation of atrazine. This high energy demand is also pointed out in studies developed using Ti/Ru_{0.7}Ir_{0.3}O₂ to treat samples collected from an advanced water treatment plant in Bundamba, Australia. They found that in order to obtain 80% removal of atrazine, at least 150 A m⁻² of current density needs to be applied for a period of 8 h [55]. Here, it is worthwhile to note that the high rates of removal were obtained under considerably lower current density (20 mA cm⁻²) in just 1 h of reaction time.

In addition, it is worthwhile to mention that direct comparison of the results found for electrochemical oxidation of atrazine with those found in the available literature is difficult because of the different conditions employed (i.e., current density, electrolyte, initial

concentration of the contaminant, etc.) and scarce literature on EO of this compound. Nevertheless, from the results obtained in this work (see Table 4), it is clear that the anode produced here is competitive compared to other MMOs applied in EO of atrazine. As shown in Table 5, the anodes that led to a complete atrazine removal required a longer electrolysis time (120 min) and a smaller treated volume (40 mL) compared with the conditions employed in our study. Moreover, the kinetic rate value ($k = 0.062 \text{ min}^{-1}$) found for the removal of atrazine using the anode prepared by laser using IL as solvent was much higher than those values reported by Contreras et al. [56] ($k = 0.01086 \text{ min}^{-1}$), which treated soil washing effluents polluted with atrazine by electrochemical oxidation.

Table 5 Comparison of the performance of different anodes for the oxidation atrazine in aqueous media.

Anode	Experimental conditions	Removal	Reference
Ti/RuO ₂ -Sb ₂ O ₅	$j = 20 \text{ mA cm}^{-2}$; $C_0 = 10 \text{ mg L}^{-1}$; Electrolyte = 0.1 mol L^{-1} Na ₂ SO ₄ ; Anode area: 2 cm^2 $V = 0.4 \text{ L}$ $t = 100 \text{ min}$	100% atrazine	[14]
	$j = 15 \text{ mA cm}^{-2}$; $C_0 = 40 \text{ mg L}^{-1}$, Electrolyte = groundwater medium with 84 mg dm^{-3} NaCl, Anode area= 78 cm^2 , $V = 5.0 \text{ L}$, flow rate = 15 mL s^{-1}	72% atrazine after 20 A h dm ⁻³ $k = 0.01086 \text{ min}^{-1}$	[56]
	$j = 1 \text{ mA cm}^{-2}$; $C_0 = 10 \text{ mg L}^{-1}$, Electrolyte = 0.033 mol L^{-1} Na ₂ SO ₄ , Anode area: 2 cm^2 $V = 0. \text{ L}$ and $t = 60 \text{ min}$	58% atrazine	[57]
	$j = 20 \text{ mA cm}^{-2}$,	100 % atrazine	[2]

$C_0 = 10 \text{ mg L}^{-1}$, Electrolyte = 0.1 mol L^{-1} NaCl, Anode area: 2 cm^2 $V = 0.04 \text{ L}$ and $t = 120 \text{ min}$			
Laser-made	$j = 20 \text{ mA cm}^{-2}$;		
Ti/RuO₂–	$C_0 = 10 \text{ mg L}^{-1}$; Electrolyte = 3.7 g L^{-1}	81% atrazine	This work
TiO₂	NaCl,	$k = 0.062 \text{ min}^{-1}$	
	$V = 0.1 \text{ L}$, $t = 60 \text{ min}$.		

4. Conclusions

This study reports, for the first time, the combination of ionic liquid as a solvent precursor and CO₂ laser as the only heating source to prepare the Ti/Ru_{0.3}Ti_{0.7}O₂ anodes. When compared with conventionally prepared (in a furnace), the anode prepared by laser heating showed better adhesion and excellent homogeneity of the oxide metals onto the anode surface. Solid-solution formation is observed for all anodes produced, but reduced crystallite sizes were observed for the laser-prepared anodes, consistent with increased voltammetric charges. The laser heating also provoked a significant reduction in the charge-transfer resistance in 9.6 and 17.3-fold for Pechini and an ionic liquid method, respectively. The anode produced using the laser and the IL presented the highest efficiencies towards electrochemical oxidation of the atrazine at the lowest energy consumption. Finally, the method using an ionic liquid as the solvent and CO₂ laser as the primary heating source appears as a promising alternative to prepare Ti/Ru_{0.3}Ti_{0.7}O₂ anodes. The importance of developing faster and cost-effective methods to produced anodes with improved electrocatalytic properties makes the proposed method quite attractive, especially when compared with conventional heating in furnaces.

Acknowledgments

The authors thank the Brazilian National Counsel of Technological and Scientific Development-CNPq (grants: 305438/2018-2, 409017/2016-7, 142034/2020-7 and 311856/2019-5), to the Coordination for the Improvement of Higher Education Personnel - CAPES (grant: 001), to Sergipe State Research and Technological Innovation Foundation (FAPITEC/SE) and the Spanish Agencia Estatal de Investigación and European Union through project PID2019-107271RB-I00 (AEI/FEDER, UE) for the scholarships and financial support for this work. We also acknowledge the MSc. Caio Vinícius da Silva Almeida, MSc. Angela Moratalla and Eduardo Prado García-Consuegra for their contributions to XPS and MEV data acquisition and processing.

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