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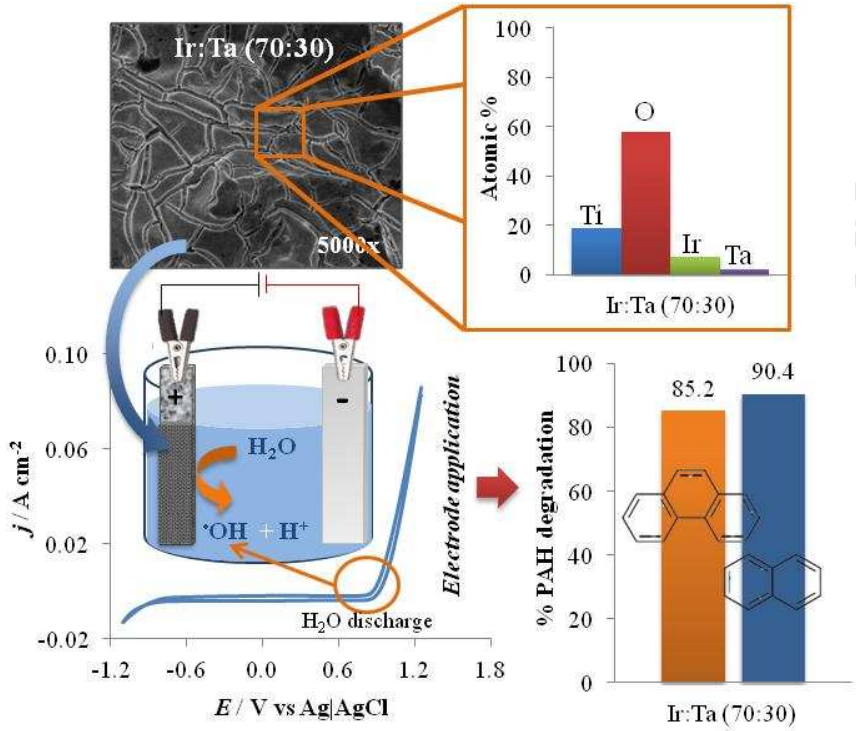
GRAHICAL ABSTRACT



IrO_2-Ta_2O_5|Ti electrodes prepared by electrodeposition from different Ir:Ta ratios for the degradation of polycyclic aromatic hydrocarbons

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Abstract

This work investigates the feasibility of producing IrO_2-Ta_2O_5|Ti electrodes by electrodeposition. Using precursor solutions with Ir:Ta molar ratios from 0:100 to 100:0, followed by thermal treatment, the goal was to find the optimal composition for enhancing the formation of hydroxyl radicals and providing long service lives. Scanning electron microscopy (SEM), coupled with energy dispersive X-ray spectroscopy (EDX), revealed that the production of homogeneous coatings with a good surface coverage and absence of agglomerates was only possible for electrodes with 70% or 100% Ir. The potential for O_2 evolution was similar for all the electrodes containing Ir, at about 0.90 V vs Ag|AgCl. However, the ability to produce M($^{\bullet}$OH) clearly increased with increasing Ir in the Ir:Ta ratios (100:0 > 70:30 > 30:70 > 0:100). This observation was confirmed by the transformation of coumarin to 7-hydroxycoumarin as determined by spectroscopic and chromatographic techniques after treatment. Once manufactured and characterized, the electrodes were tested, as anodes, for the electro-oxidation of polycyclic aromatic hydrocarbons in aqueous solutions at natural pH (i.e., without pH adjustment). The anodes prepared from 70:30 and 100:0 ratios produced the fastest and highest removal rates, reaching 86% and 93% for phenanthrene and naphthalene, respectively, after 120 min at 50 mA. This was accompanied by a high degree of mineralization, as the result of direct and M($^{\bullet}$OH)-mediated oxidation, with some refractory intermediates remaining in the final solutions. The interaction between IrO_2 and Ta_2O_5 oxides appeared to be important. The 100:0 anode provided high electrocatalytic effectiveness, whereas the anode with the 70:30 ratio provided improved long-term stability, as confirmed by its service life of about 93 h.

Keywords: Dimensionally stable anode; Electro-oxidation; Hydroxyl radical; PAHs; Water treatment

1. Introduction

Interest in electrochemical science and technology is growing worldwide, in large part because of their ability to devise new systems that ensure significant societal progress as they can lower negative environmental impacts when compared to old and well established processes [1]. The electrochemical technologies for water treatment are a clear example of this since they combine high efficiency, with low resource consumption, by using the electron as a 'clean reagent' [2]. Within this field, the so-called electrochemical advanced oxidation processes (EAOPs) have proven most successful for the degradation of organic pollutants. In many cases it is possible to achieve the complete detoxification of water streams with their use [3,4]. This outstanding performance, when coupled with reduced energy consumption in properly designed cell configurations and the appropriate electrode materials are chosen, follows from their ability to produce reactive oxygen species (ROS), like the hydroxyl radical ($^{\bullet}OH$), in-situ and in controlled ways with the correct modulation of the electrolytic conditions.

Boron-doped diamond (BDD) is considered the most powerful anode for removing organic contaminants from aqueous solutions by the production of quasi-free hydroxyl radicals through the oxidation of water at a high electrode potential following the Reaction (1) [5]:

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (1)$$

Despite its potential, BDD has several significant drawbacks that hamper its wider implementation on a large scale. It is expensive and very few substrate materials can be used to support stable thin films of BDD for use as anode. Additionally, the electrodes are brittle or exhibit poor electrical conductivity meaning that they are not acceptable for large scale industrial or municipal applications [6].

The need to reduce the cost of electrode materials has led to the synthesis of photoanodes, which allow the treatment of pollutants by an EAOP called photoelectrocatalysis [7], where artificial UV light, or natural sunlight, stimulate the production of hydroxyl radicals on the surface

of the photocatalysts. Alternatively, non photoactive but highly oxidizing dimensionally stable anodes suitable for O_2 or Cl_2 evolution have been manufactured by preparing mixtures of different metal oxides [8]. These anodes employ an electrocatalytic oxide film, usually based on RuO_2 or IrO_2, deposited on a suitable metal substrate like titanium (Ti). These anodes exhibit appealing technological properties including long-term mechanical and chemical stability and high catalytic activity [2]. Aiming to increase the film stability, other oxides (e.g., TiO_2, SnO_2, Ta_2O_5) are added, thus obtaining a greater corrosion resistance and diminishing the amount of the catalytic oxide needed which, in turn, minimizes production costs [9,10]. Single- and mixed-metal oxides are then employed for the electro-oxidation (EO) of organic pollutants. EO is the paradigm of sustainability among the EAOPs, since no addition of processing chemicals is needed. Its operational simplicity, combined with high effectiveness, has led to wider implementation when compared to other EAOPs. In EO, adsorbed M($^{\bullet}$OH) are produced by Reaction (1), with these being further transformed into a less powerful oxidant like chemisorbed "superoxide" MO [11]. Different kinds of dimensionally stable anodes have been used for the EO treatment of a large variety of organic molecules [12-21]. In the presence of Cl^- ions, the complexity of EO increases significantly due to the oxidation of this anion to active chlorine according to Reaction (2), (a process exploited in the chlor-alkali industry) [6]:

$$2\ Cl^- \rightarrow Cl_{2(aq)} + 2\ e^- \quad (2)$$

ClO_2, ClO^-/HClO, ClO_2^-, ClO_3^- and ClO_4^- can also be formed, depending on the operational conditions including exposure time, temperature, electrode materials and hydrodynamic conditions [22].

Owing to their low cost, oxide-based anodes have also found use as a counter electrode in Fenton-based EAOPs including electro-Fenton [20,23-27], electro-Fenton-like [28] and UVA or solar photoelectro-Fenton [20]. In these processes the degradation of the pollutants is mainly guided by the action of free $^{\bullet}$OH radicals generated in the bulk.

In spite of the reported superiority of BDD over other potential anodes, some exceptions have been reported. For example, Coria et al. [29] found a greater removal of total organic carbon (TOC) using an IrO_2-based anode as compared to BDD during the treatment of naproxen by EO. This result was attributed to higher adsorption of organics on the anode surface. Results like these, when combined with improved industrial success of mixed metal oxides [30] and the higher corrosion resistance and longer service life of IrO_2-based anodes as compared to RuO_2-based ones [31-33], justify the interest in the optimization of the synthesis of IrO_2-based dimensionally stable anodes. Specifically, those developed as a metal-oxide mixture, with Ta_2O_5 as the stabilizer, seem the most interesting. These mixed-oxide anodes are more electrochemically stable and exhibit enhanced service life from the coating [34] than pure IrO_2-based anodes.

In the modern world, the availability of clean water has become increasingly problematic due to both natural causes and human activity [35]. One significant problem is the presence of polycyclic aromatic hydrocarbons (PAHs), which can be produced during the incomplete combustion of organic materials including coal, oil, gas, wood, garbage, and tobacco. PAHs, due to inefficient removal processes, have been found widely in municipal wastewater and industrial effluents [36]. As a consequence of their hydrophobic nature, PAHs tend to become strongly adsorbed in sediments and aquatic organisms, as well as on the surface of particulates including micro-plastics [37], whose presence in water is also a very critical issue [38]. PAHs are included in a group of organic pollutants causing significant concern within the European Union [39], as they are suspected of being mutagens, carcinogens and endocrine disruptors [40].

Several authors have reported the electrochemical treatment of various PAHs with different types of mixed metal oxides [41-43]. Our teams have recently shown the feasibility of PAHs removal by EO with IrO_2-based anodes synthesized using different techniques [44]. Classical synthesis routes have included thermal decomposition and the sol-gel ‘Pechini’ method [28]. Reactive sputtering [45] and physical vapor deposition [46] are other existing alternatives. This

work addresses the synthesis of IrO_2-Ta_2O_5-coated Ti-electrodes by electrodeposition using four different Ir:Ta ratios, to determine the optimal composition to stimulate the maximum concentration of hydroxyl radicals to be available for treatment. All the electrodes were characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV) and accelerated life testing. During EO testing, the production of M($^{\bullet}$OH) was monitored using either UV/vis spectrophotometry or liquid chromatography with fluorescence detection. The oxidation power of these electrodes was verified by using them as anodes in the EO treatment of synthetic aqueous solutions containing naphthalene or phenanthrene, monitoring the concentration decay by high performance liquid chromatography (HPLC) and their mineralization from the analysis of TOC abatement.

2. Materials and methods

2.1. Electrode manufacture

The precursor solutions were prepared using H_2IrCl_6 [31-34] and $TaCl_5$ [47], both purchased from Strem Chemicals (≥ 99.9% purity). They were then dissolved in HCl [44] and isopropanol [34,44], respectively, under vigorous stirring. Four different test precursor solutions were further prepared to be used in the coating process by mixing the appropriate amount of prepared metal solutions to obtain Ir:Ta molar ratios of 100:0, 70:30, 30:70, and 0:100. Before electrodeposition, the Ti-plates (each 5.0 mm × 15.0 mm × 1.0 mm) that were to be used as substrates were pretreated by sandblasting [34,44], etching in a 40% oxalic acid solution for 20 min [31,44], and finally rinsed with deionized water and dried. Electrochemical deposition was performed at a constant current density of 14 mA cm^{-2} for 20 min under constant stirring at 825 rpm [44]. Once the coated Ti-electrodes were prepared, the coatings were transformed into metal oxides using a 2-step thermal decomposition procedure: heating at 523 K for 10 min, followed by heating to 723 K and holding for 1 h [34,44]. Three electrodes, at each of the four coatings compositions, were prepared.

2.2. Electrode characterization

Microstructural analysis, to study the morphology of the deposits, was performed by SEM-EDX using a Jeol JSM6500 microscope, operating at 15 kV. Surface distribution of Ir and Ta was performed in the SEM using the Oxford Inca 300 EDX analyzer.

Electrochemical characterizations were made using cyclic voltammetry in a conventional three electrode glass cell. Each of the various test IrO_2-Ta_2O_5|Ti electrodes was placed as the working electrode (0.75 cm^2), with a platinum (Pt) wire (BASi) and an Ag|AgCl (3M KCl, BASi) used as counter and reference electrodes, respectively, in the cell. All experiments were performed at 298 K with 10 mL of 0.5 M H_2SO_4 (J. T. Baker, 98%) as supporting electrolyte and employing a Bioanalytical Systems BAS-Epsilon™ potentiostat. Before the electrochemical tests, O_2 was purged from the test cell by bubbling ultrapure nitrogen (Praxair, grade 5.0) through the electrolyte for at least 20 min, and this gas continuously flowed over the solution during the measurement cycles. In all the cyclic voltammograms shown in this work, the active area of each coated Ti-electrode has been considered, as previously described [44]. For each of the different working electrode compositions the tests were performed in triplicate.

The service life of each of the various IrO_2-Ta_2O_5|Ti coated electrodes was evaluated according to the methodology reported in NACE TM0108 [48]. A two-electrode electrochemical cell was employed, placing the coated electrodes as the working electrode (0.75 cm^2) and an uncoated Ti-plate as a counter electrode (3.5 cm^2). These experiments were performed at 298 K with 70 mL of 1 M H_2SO_4 as supporting electrolyte using a constant current of 3.18 A (supplied by an EZ Digital model GP-4303DU DC power supply), and with constant stirring at 825 rpm. As required in the NACE TM0108 protocol, these tests were run until an increase of 30% was observed in the inter-electrode potential difference compared to the initial value.

The production of hydroxyl radicals was evaluated from tests monitoring the transformation of coumarin to 7-hydroxycoumarin [49]. For this, several electrolytic tests were performed using a

two-electrode electrochemical glass cell equipped with an anode, using one of each of the compositional variation IrO_2-Ta_2O_5|Ti electrodes (0.75 cm^2), and a Pt-wire as the cathode. Solutions of 10 mL of 0.3 mM coumarin (Sigma-Aldrich, 99%) in 0.5 M H_2SO_4 were electrolyzed at room temperature and 50 mA under constant stirring. Samples were withdrawn at selected time periods to monitor changes in the concentration of coumarin. Testing by UV/vis spectroscopy, on a Shimadzu UV-1800 UV-Vis spectrophotometer within the range between 200 and 800 nm, was used during these characterizations. For the same samples, the accumulation of 7-hydroxycoumarin was assessed by HPLC using a Shimadzu LC-10ADVP chromatograph equipped with a Thermo Electron Hypersil ODS (5 µm, 150 mm × 3 mm) column coupled to a Shimadzu RF-10AXL fluorescence detector. An acetonitrile:water (60:40, v/v) mixture was used as a mobile phase to elute the samples at a flow rate of 0.5 mL min^{-1}, with excitation and emission wavelengths of 325 nm and 400 nm, respectively. A 7-hydroxycoumarin analytical standard from Sigma-Aldrich was used for quantification.

2.3. Electrochemical degradation of hydrocarbons

Bulk electrolyses for the performance evaluation of the manufactured electrodes to degrade PAHs, such as phenanthrene and naphthalene, were made in a two-electrode electrochemical cell, using the various IrO_2-Ta_2O_5|Ti electrodes (0.75 cm^2) and a Pt-plate as the anode and cathode. Solutions of 50 mL containing either 2 µM phenanthrene (from Acros Organics, 97%) or 2 µM naphthalene (from Alfa Aesar, 99%) in 0.05 M Na_2SO_4 at natural pH (i.e., without pH adjustment) were treated at room temperature under a constant current of 50 mA and with constant stirring. To investigate the decay kinetics of each pollutant, samples were withdrawn at selected times for 120 min and analyzed using a Waters 600 liquid chromatograph fitted with a BDS Hypersil C18 6 µm, 250 mm × 4.6 mm, column at 35 ºC and coupled to a Waters 996 photodiode array detector set at λ of 254 nm. These measurements were made by injecting 20 µL aliquots into the chromatograph using a 60:40 (v/v) acetonitrile/water mixture at 1.3 mL min^{-1} as mobile phase. Peaks at 7.7 and

13.7 min were found for naphthalene and phenanthrene, respectively. Organic solvents and other chemicals were of HPLC or analytical grade from Sigma-Aldrich and Panreac. All the solutions were prepared using ultrapure water from a Millipore Milli-Q system (resistivity >18 MΩ cm).

To assess the mineralization ability of the anodes, the TOC content was monitored during the treatment of 50 mL of 25 $mg \cdot L^{-1}$ TOC (0.19) naphthalene in 0.05 M Na_2SO_4, at room temperature and 50 mA under constant stirring of 825 rpm (with natural pH), using the same experimental setup mentioned and employed above. Samples were measured on a Shimadzu VCSN TOC analyzer, after filtration with 0.45 µm PTFE filters (Whatman) over a 360 min test cycles. The results were obtained with ±1% accuracy. The following reaction for total mineralization of naphthalene was assumed:

$$C_{10}H_8 + 20\,H_2O \rightarrow 10\,CO_2 + 48\,H^+ + 48\,e^- \quad (3)$$

The mineralization current efficiency (MCE) values were estimated as follows [20]:

$$\%\ \mathrm{MCE} = \frac{n\,F\,V\,\triangle(\mathrm{TOC})_{\mathrm{exp}}}{4.32 \times 10^7\,m\,I\,t} \times 100 \quad (4)$$

where n = 48 is the number of electrons for the mineralization, m = 10 is the number of carbon atoms of naphthalene, and all the other parameters have been defined elsewhere [20].

3. Results and discussion

3.1. Microstructural and electrochemical characterization

Fig. 1A (at 2000x) and 1B (at 5000x) shows the surface morphologies of the four different IrO_2-Ta_2O_5 coating layers found on the Ti-substrates after electrodeposition and heat cycling. In the coatings prepared using Ir:Ta ratios of 100:0 and 70:30, it is possible to observe the cobblestone morphology that is typical from this kind of mixed metal oxides manufactured at high temperature, and please note its enhanced prominence in 70:30 coating. However, their surface appearance did not exactly match a dried-mud cracked coating (i.e., mud-like islands surrounded by cracks) usually

observed after thermal decomposition at ≥ 450 ºC [50]. The distribution of cracks (see red arrows) was not uniform over the entire surface as some areas were relatively flat and smooth. This may be attributed to the particular distribution of Ir and Ta on the surface during the electrodeposition step. Distributions using this method are clearly different from those resulting from a conventional painting process or by immersion of the Ti-plate into a precursor solution. As a result, the fast volatilization of solvents along with the high stress induced from anisotropic thermal expansion (different expansion coefficients of Ti and coating) seem to be substantially minimized with the electrochemical deposition treatment. This yields a more compact coating with no cracks connected over long distances, eventually reducing the possibility of coating peeling-off. In contrast, in the coatings prepared from predominately Ta ratios (30:70 and 0:100), whose microstructure when viewed at higher magnification is shown in Fig. 1B, the presence of aggregates with greater roughness can be identified (as indicated by green arrows). This suggests poor mixing of metal oxides during electrodeposition, which would likely be detrimental for further application. A poor distribution of Ta_2O_5 will lead to poor separation between the substrate and the IrO_2 catalytic layer, promoting the passivation of the Ti-base metal. The presence of these kinds of agglomerates has also been reported for layers formed using non-electrochemical procedures [34].

Fig. 2 shows the atomic percentages of Ti, Ir, Ta and oxygen determined by EDX for the four different IrO_2-Ta_2O_5|Ti electrodes under study. No chloride, which could have been sourced from the solutions used for the electrodeposition, was detected. The relative content of titanium and oxygen is similar for the electrodes prepared from solutions at 100:0, 70:30 and 30:70 ratios, and the proportion of Ir and Ta changes (as expected) from one to another. Importantly, the proportions are in quite good agreement with the Ir:Ta molar ratios employed in each precursor solution. The consistency of the resulting mixed metal oxide compositions suggested the absence of segregation, a very positive feature that also occurs when using sol-gel preparation methods like Pechini´s [31]. In the coating prepared using only the Ta-containing precursor, the amount of titanium measured

was higher than expected and that of Ta was too low, a result suggesting that without Ir the deposition of Ta is neither homogeneous nor quantitative, leading to a partially uncoated Ti-substrate. Therefore, this low quality electrode might well be expected to perform worse than the others.

Fig. 3 presents the cyclic voltammograms recorded from test employing the four IrO_2-Ta_2O_5|Ti electrodes in 0.5 M H_2SO_4 at room temperature and a scan rate of 50 mV s^{-1}. The response for an uncoated Ti-substrate is not included but has been reported in earlier reports [44]. In this earlier study, no current steps were noted until a steep increase appeared in the anode potential vs Ag|AgCl at 0.05-0.10 V, which can be expected due to the low oxidation power of pure Ti-anodes. On the other hand, here it is possible to observe that for the three electrodes modified with IrO_2, the O_2 gas evolution occurred at a potential close to 0.90 V. According to Reaction (1), adsorbed hydroxyl radicals (M($^{\bullet}$OH)) should be generated as a first step, prior to gas evolution, and hence, their existence is investigated below. In addition, it can be seen that the increase in IrO_2 content in the coating, upon use of a higher initial Ir:Ta molar ratio from 30:70 to 100:0, enhances the response of the dimensionally stable anode, as deduced from the gradually greater current measured at a given potential over the oxygen evolution reaction (OER) region. Conversely, the electrochemical response of the electrode prepared with only Ta in the precursor solution (0:100 ratio) was much less significant using the same analytical sensitivity threshold. Thus, it can be concluded that Ta_2O_5 does not perform well as an electrocatalytic oxide for hydroxyl radical formation, but, rather it serves as an interlayer to promote coating adhesion and corrosion resistance for long term use in anodic electrodes [34,44,47].

3.2. Production of hydroxyl radicals

The treatment of 10 mL of a 0.3 mM coumarin solution in 0.5 M H_2SO_4 by EO with an IrO_2-Ta_2O_5|Ti anode and a Pt cathode at 50 mA allowed us to study the formation of M($^{\bullet}$OH) in two complementary ways. First, the decay of the coumarin content and second the generation of 7-

hydroxycoumarin formed upon hydroxylation of coumarin. Decay of coumarin was tracked by UV/vis spectrophotometry over 180 min test cycles for the various anode materials. As observed in Fig. 4, the anode without Ir (i.e., Ir:Ta ratio of 0:100) showed no decay of the coumarin absorbance, due to a lack of electrode catalytic response (Fig. 3). In contrast, all the anodes containing Ir showed decrease in coumarin content during the tests compared with the coumarin spectrum at time zero. A greater rate of decay was observed as the Ir content in the precursor solution increased from 30% to 100%, confirming the catalytic ability of IrO_2. In particular, significant decays were found using the 70:30 and 100:0 ratios, which allows inferring a progressively larger production of M($^{\bullet}$OH), although a more direct proof of hydroxyl radical generation is needed. For this, the samples collected at the same electrolysis times were simultaneously analyzed, by HPLC coupled to fluorescence detection, aiming to confirm and quantify the 7-hydroxycoumarin formed upon hydroxylation of coumarin.

Fig. 5 presents the time variation of the 7-hydroxycoumarin concentration under each test condition. The profiles confirm that as the the Ir:Ta molar ratio in the precursor solution increased from 0:100 to 100:0, higher production of M($^{\bullet}$OH) was achieved. This is consistent with the inactivity of pure Ta_2O_5 coatings as well as with the superior electrocatalytic power of layers with a high content of IrO_2 (> 30%). Note that, as an additional proof of the formation of M($^{\bullet}$OH) in these types of electrodes, in a previous work we reported the electron paramagnetic resonance (EPR) analysis [44]. At this stage, the real performance of these IrO_2-Ta_2O_5|Ti electrodes as potential anodes in typical treatment scenarios for the electro-oxidation of organic pollutants was studied.

3.3. Electro-oxidation of aqueous solutions of PAHs

The oxidation power of the four IrO_2-Ta_2O_5|Ti electrodes for degrading toxic organic pollutants was tested in triplicate. Independent EO treatments of 50 mL of solutions containing ~ 2 µM of each hydrocarbon in 0.05 M Na_2SO_4, at natural pH and room temperature by applying 50 mA were carried out. Phenanthrene (see Fig 6A) and naphthalene (see Fig. 6B) were chosen as model PAHs,

since serious concerns have arisen about their presence in the environment. The decline in their concentration, as a function of electrolysis time, is shown in the two figures. Note, too, that the anode prepared without Ir (0:100 ratio) was able to remove 65%-70% phenanthrene (Fig. 6A) and 79%-84% naphthalene (Fig. 6B) at 120 min, despite its poor ability to produce M($^{\bullet}$OH) (Fig. 4 and 5). This suggests the occurrence of direct anodic oxidation of both hydrocarbons at the Ta_2O_5|Ti anodic surface. Direct oxidation of organic aromatic compounds upon adsorption on the anode surface has been suggested before, in phenol treatments for example [6]. Within the framework of PAHs oxidation, it is known that multiple bonds with angular arenes are particularly prone to electron loss. Phenanthrene is a typical substrate with such activated bonds [51] and thus, it can be gradually transformed into several intermediates. Anthracene, whose structure is similar to that of phenanthrene and naphthalene, has also been reported to become oxidized directly at the anode, yielding a radical carbocation that, in the presence of water, is not dimerized but hydrolyzed and further oxidized to anthraquinone [52].

As seen in Fig. 6A and 6B, all the electrode coatings containing Ir promoted a faster and greater degradation of both PAHs, in agreement with the induced formation of M($^{\bullet}$OH) in the presence of IrO_2. In the case of phenanthrene, the anode at the 70:30 ratio outperformed the others, reaching the limit of quantification (LOQ) of 0.3 μM at 120 min, which accounts for > 86% removal. For naphthalene, the anodes prepared with 100:0 and 70:30 ratios performed similarly and both reached the naphthalene LOQ, of 0.15 μM, and greater than 93% removal during testing. Taken together, the decay of contaminants with and without Ir, one can conclude that the IrO_2-Ta_2O_5|Ti anodes degrade phenanthrene and naphthalene by combined direct and M($^{\bullet}$OH)-mediated oxidation processes. None of the concentration abatements can be associated to pseudo-first-order reaction kinetics which would have been expected for reactions between the organic pollutant and a constant concentration of M($^{\bullet}$OH) [20,29]. This fact further reinforces the idea of a simultaneous action of direct and indirect oxidation processes, whose contribution is time-dependent.

The ability of the four electrodes to completely destroy solution TOC was also assessed. Fig. 7A depicts the TOC abatement over time during the EO of 50 mL of a 25 $mg \cdot L^{-1}$ (0.19 mM) naphthalene solution in 0.05 M Na_2SO_4 at natural pH by applying 50 mA. The anode with no IrO_2 exhibited a certain ability to transform the organic carbon to CO_2, reaching 56% mineralization at 360 min. The oxidation power of the anodes containing Ir was again evident as mineralization reached 74% TOC removal (i.e., final TOC content of 6.5 mg L^{-1} TOC). At times less than 2 h, the anodes prepared with only Ir and at Ir:Ta ratio 70:30 behaved better than the 30:70 material, as expected due to their greater ability to form M($^{\bullet}$OH). However, no substantial differences were observed between the three types of electrodes at the end of the electrolysis, This observation can be explained by the generation of highly refractory intermediates, like carboxylic acids, that cannot be easily degraded by M($^{\bullet}$OH) [3]. The presence of this type of stable compound was confirmed by mineralization current efficiency profiles calculated from Eq. (4). As can be observed in Fig. 7B, which charts MCE vs. time, the efficiency was highest during the early stages of the treatment tests, reaching 8-10%, but it progressively decreased, as a result of the lower organic load and its higher refractory nature, ending in values as low as ~ 3%.

3.4. Service life testing

From previous sections, it is clear that the presence of IrO_2 in the coatings is crucial to make degradation occur more rapidly, and to a greater extent. We noted that the improvement found in the performance by anodes coated with precursor solutions containing 70% and 100% Ir was minimal. A final comparison between them would be determined by coating stability for extended use. To study if any life-use differences existed between them, their service life was determined by applying the NACE TM0108 standard service life procedure (see experimental section). In these tests, a stable potential was initially observed, but a steep rise in potential was recorded once the resistance of the anode increased dramatically, causing its failure. Increasing electrical resistance can be attributed to the detachment (i.e., peeling-off) of the IrO_2, Ta_2O_5 or IrO_2-Ta_2O_5 coating from

the Ti-substrate [31]. In contrast to studies described above, a very remarkable superiority of the electrode prepared with a 70:30 ratio can be easily seen in Fig. 8. It performed for nearly 93 h before failure while each of the other three materials failed in less than 2 h. This electrode offers advantage from the differing performance characteristics of the two metal oxides. Its relatively high concentration of IrO_2 ensures significant production of M($^{\bullet}$OH), while the moderate quantity of Ta_2O_5 provides coating stability against corrosion. The absence of this oxide in the electrode prepared with 100% Ir causes a dramatic decay of its performance upon prolonged electrolysis.

Many researchers have studied the service lifetime of IrO_2-Ta_2O_5|Ti anodes under galvanostatic conditions in 1 M H_2SO_4 over the potential region corresponding to the OER. Huang, et al. [50] have recently prepared compositionally similar anodes by thermal treatment, reporting a service lifetime between 70 and 110 h. Results presented here agree with those in Comninellis et al. [9], who prepared IrO_2-Ta_2O_5|Ti electrodes by thermal decomposition at 550 ºC over a wide range of compositions from 10 to 100 mol.% Ir. They reported maximum electroactivity, along with the greatest electrode service life, for the electrodes containing 70% Ir.

4. Conclusions

IrO_2-Ta_2O_5|Ti electrodes have been successfully prepared by electrodeposition using precursor solutions containing four different Ir:Ta molar ratios, followed by a two step thermal treatment. The coated electrodes were then used as working electrodes in tests for the degradation of PAHs. The electrodes prepared with an Ir:Ta ratio of 70:30 were found to be superior during testing. This compositional ratio produced homogenous coatings showing good coverage and minimal segregation. They displayed the longest service life (about 93 as compared to all the other compositional electrodes with Ir content of 0%, 30%, and 100%. The ability of such an electrode to generate M($^{\bullet}$OH) was confirmed by the gradual transformation of coumarin into 7-hydroxycoumarin during testing. Its applicability to EO treatment of organic pollutants was tested

by treating aqueous solutions of phenanthrene and naphthalene, at natural pH and low current. Removal of more than 86% and 93% (respectively) of these contaminates was observed after 120 min. A large degree of mineralization was also attained after 360 min, although the anode was unable to degrade some highly refractory intermediates. The oxidation power of the electrodes prepared from precursor solutions with 30% and 100% Ir provided similar degradation, but their service life was found to be below 2 h. The electrode coated with only a Ta-containing precursor exhibited limited catalytic power but it did remove some of the pollutants, likely by a direct anodic oxidation of PAHs.

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References

[1] S. Bebelis, K. Bouzek, A. Cornell, M.G.S. Ferreira, G.H. Kelsall, F. Lapicque, C. Ponce de León, M.A. Rodrigo, F.C. Walsh, Highlights during the development of electrochemical engineering, Chem. Eng. Res. Design 91 (2013) 1998-2020.

[2] Y. Feng, L. Yang, J. Liu, B.E. Logan, Electrochemical technologies for wastewater treatment and resource reclamation, Environ. Sci.: Water Res. 2 (2016) 800-831.

[3] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, Environ. Sci. Pollut. Res. 21 (2014) 8336-8367.

[4] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: A critical review, Chem. Rev. 115 (2015) 13362-13407.

[5] A. Kapałka, G. Fóti, C. Comninellis, The importance of electrode material in environmental electrochemistry. Formation and reactivity of free hydroxyl radicals on boron-doped diamond electrodes, Electrochim. Acta 54 (2009) 2018-2023.

[6] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev. 109 (2009) 6541-6569.

[7] Y. Zhang, X. Xiong, Y. Han, X. Zhang, F. Shen, S. Deng, H. Xiao, X. Yang, G. Yang, H. Peng, Photoelectrocatalytic degradation of recalcitrant organic pollutants using TiO_2 film electrodes: An overview, Chemosphere 88 (2012) 145-154.

[8] W. Wu, Z.-H. Huang, T.-T. Lim, Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water, Appl. Catal. A: Gen. 480 (2014) 58-78.

[9] C. Comninellis, G.P. Vercesi, Characterization of DSA®-type oxygen evolving electrodes: Choice of a coating, J. Appl. Electrochem. 21 (1991) 335-345.

[10] D. Rosestolato, S. Neodo, S. Ferro, G. Battaglin, V. Rigato, A. De Battisti, A comparison between structural and electrochemical properties of iridium oxide-based electrocatalysts prepared by sol-gel and reactive sputtering deposition, J. Electrochem. Soc. 161 (2014) E151-E158.

[11] G. Fóti, D. Gandini, C. Comninellis, A. Perret, W. Haenni, Oxidation of organics by intermediates of water discharge on IrO_2 and synthetic diamond anodes, Electrochem. Solid State Lett. 2 (1999) 228-230.

[12] S. Aquino Neto, A.R. de Andrade, Electrooxidation of glyphosate herbicide at different DSA® compositions: pH, concentration and supporting electrolyte effect, Electrochim. Acta 54 (2009) 2039-2045.

[13] O. Scialdone, S. Randazzo, A. Galia, G. Filardo, Electrochemical oxidation of organics at metal oxide electrodes: The incineration of oxalic acid at IrO_2-Ta_2O_5 (DSA-O_2) anode, Electrochim. Acta 54 (2009) 1210-1217.

[14] O. Scialdone, A. Galia, S. Randazzo, Oxidation of carboxylic acids in water at IrO_2-Ta_2O_5 and boron doped diamond anodes, Chem. Eng. J. 174 (2011) 266-274.

[15] M. Pérez-Corona, A. Corona, E.D. Beltrán, J. Cárdenas, E. Bustos, Evaluation of IrO_2-Ta_2O_5|Ti electrodes employed during the electroremediation of hydrocarbon-contaminated soil, Sustain. Environ. Res. 23 (2013) 279-284.

[16] B. Borbón, M.T. Oropeza-Guzman, E. Brillas, I. Sirés, Sequential electrochemical treatment of dairy wastewater using aluminum and DSA-type anodes, Environ. Sci. Pollut. Res. 21 (2014) 8573-8584.

[17] E. Mousset, N. Oturan, E.D. van Hullebusch, G. Guibaud, G. Esposito, M.A. Oturan, Treatment of synthetic soil washing solutions containing phenanthrene and cyclodextrin by electro-oxidation. Influence of anode materials on toxicity removal and biodegradability enhancement, Appl. Catal. B: Environ. 160-161 (2014) 666-675.

[18] A. Galia, S. Lanzalaco, M.A. Sabatino, C. Dispenza, O. Scialdone, I. Sirés, Crosslinking of poly(vinylpyrrolidone) activated by electrogenerated hydroxyl radicals: A first step towards a simple and cheap synthetic route of nanogel vectors, Electrochem. Commun. 62 (2016) 64-68.

[19] M.J.R. Santos, M.C. Medeiros, T.M.B.F. Oliveira, C.C.O. Morais, S.E. Mazzetto, C.A. Martínez-Huitle, S.S.L. Castro, Electrooxidation of cardanol on mixed metal oxide (RuO_2-TiO_2 and IrO_2-RuO_2-TiO_2) coated titanium anodes: insights into recalcitrant phenolic compounds, Electrochim. Acta 212 (2016) 95-101.

[20] J.R. Steter, E. Brillas, I. Sirés, On the selection of the anode material for the electrochemical removal of methylparaben from different aqueous media, Electrochim. Acta 222 (2016) 1464-1474.

[21] D.T. Araújo, M.A. Gomes, R.S. Silva, C.C. de Almeida, C.A. Martínez-Huitle, K.I.B. Eguiluz, G.R. Salazar-Banda, Ternary dimensionally stable anodes composed of RuO_2 and IrO_2 with CeO_2, SnO_2, or Sb_2O_3 for efficient naphthalene and benzene electrochemical removal, J. Appl. Electrochem. 47 (2017) 547-561.

[22] S. Neodo, D. Rosestolato, S. Ferro, A. De Battisti, On the electrolysis of dilute chloride solutions: Influence of the electrode material on Faradaic efficiency for active chlorine, chlorate and perchlorate, Electrochim. Acta 80 (2012) 282-291.

[23] O. Scialdone, E. Corrado, A. Galia, I. Sirés, Electrochemical processes in macro and microfluidic cells for the abatement of chloracetic acid from water, Electrochim. Acta 132 (2014) 15-24.

[24] F. Sopaj, N. Oturan, J. Pinson, F. Podvorica, M.A. Oturan, Effect of the anode materials on the efficiency of the electro-Fenton process for the mineralization of the antibiotic sulfamethazine, Appl. Catal. B: Environ. 199 (2016) 331-341.

[25] S. Ellouze, S. Kessemtini, D. Clematis, G. Cerisola, M. Panizza, S.C. Elaoud, Application of Doehlert design to the electro-Fenton treatment of Bismarck Brown Y, J. Electroanal. Chem. 799 (2017) 34-39.

[26] S. Lanzalaco, I. Sirés, M.A. Sabatino, C. Dispenza, O. Scialdone, A. Galia, Synthesis of polymer nanogels by electro-Fenton process: investigation of the effect of main operation parameters, Electrochim. Acta 246 (2017) 812-822.

[27] Y.-U. Shin, H.-Y. Yoo, S. Kim, K.-M. Chung, Y.-G. Park, K.-H. Hwang, S.W. Hong, H. Park, K. Cho, J. Lee, Sequential combination of electro-Fenton and electrochemical chlorination processes for the treatment of anaerobically-digested food wastewater, Environ. Sci. Technol. 51 (2017) 10700-10710.

[28] Z.G. Aguilar, E. Brillas, M. Salazar, J.L. Nava, I. Sirés, Evidence of Fenton-like reaction with active chlorine during the electrocatalytic oxidation of Acid Yellow 36 azo dye with Ir-Sn-Sb oxide anode in the presence of iron ion, Appl. Catal. B: Environ. 206 (2017) 44-52.

[29] G. Coria, I. Sirés, E. Brillas, J.L. Nava, Influence of the anode material on the degradation of naproxen by Fenton-based electrochemical processes, Chem. Eng. J. 304 (2016) 817-825.

[30] S. Trasatti, Electrocatalysis: understanding the success of DSA®, Electrochim. Acta 45 (2000) 2377-2385.

[31] L. Xu, Y. Xin, J. Wang, A comparative study on IrO_2-Ta_2O_5 coated titanium electrodes prepared with different methods, Electrochim. Acta 54 (2009) 1820-1825.

[32] X. Qin, F. Gao, G. Chen, Effects of the geometry and operating temperature on the stability of Ti/IrO_2–SnO_2–Sb_2O_5 electrodes for O_2 evolution, J. Appl. Electrochem. 40 (2010) 1797-1805.

[33] S. Ferro, D. Rosestolato, C.A. Martínez-Huitle, A. De Battisti, On the oxygen evolution reaction at IrO_2-SnO_2 mixed-oxide electrodes, Electrochim. Acta 146 (2014) 257-261.

[34] J.-Y. Lee, An investigation on the electrochemical characteristics of Ta_2O_5-IrO_2 anodes for the application of electrolysis process, Mater. Sci. Appl. 2 (2011) 237-243.

[35] E. Lichtfouse, J. Schwarzbauer, D. Robert (Eds.), Environmental chemistry for a sustainable world – Vol. 2: Remediation of air and water pollution, Springer, The Netherlands, 2012.

[36] F. Fatone, S. Di Fabio, D. Bolzonella, F. Cecchi, Fate of aromatic hydrocarbons in Italian municipal wastewater systems: an overview of wastewater treatment using conventional activated-sludge processes (CASP) and membrane bioreactors (MBRs), Water Res. 45 (2011) 93-104.

[37] W. Wang, J. Wang, Different partition of polycyclic aromatic hydrocarbon on environmental particulates in wastewater: Microplastics in comparison to natural sediment, Ecotoxicol. Environ. Safety 147 (2018) 648-655.

[38] O.M. Lönnstedt, P. Eklöv, Environmentally relevant concentrations of microplastic particles influence larval fish ecology, Science 352 (2016) 1213-1216.

[39] Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy official J. L 327, 22 December 2000, pp. 0001–0073 (www.europa.eu.int.).

[40] D. Han, M.J. Currell, Persistent organic pollutants in China's surface water systems, Sci. Total Environ. 580 (2017) 602-625.

[41] J. Muff, E.G. Søgaard, Electrochemical degradation of PAH compounds in process water: a kinetic study on model solutions and a proof of concept study on runoff water from harbour sediment purification, Water Sci. Technol. 61 (2010) 2043-2051.

[42] A. Yaqub, M.H. Isa, H. Ajab, Electrochemical degradation of polycyclic aromatic hydrocarbons in synthetic solution and produced water using a Ti/SnO_2-Sb_2O_5-RuO_2 anode, J. Environ. Eng. 141 (2015) 1-8.

[43] E. Pepprah, M.V. Khire, Electroremediation of naphthalene in aqueous solution using alternating and direct currents, J. Environ. Eng. 134 (2008) 32-41.

[44] R.A. Herrada, A. Medel, F. Manríquez, I. Sirés, E. Bustos, Preparation of IrO_2-Ta_2O_5|Ti electrodes by immersion, painting and electrophoretic deposition for the electrochemical removal of hydrocarbons from water, J. Hazard. Mater. 319 (2016) 102-110.

[45] D. Rosestolato, S. Neodo, S. Ferro, G. Battaglin, V. Rigato, A. De Battisti, A comparison between structural and electrochemical properties of iridium oxide-based electrocatalysts prepared by sol-gel and reactive sputtering deposition, J. Electrochem. Soc. 161 (2014) E151-E158.

[46] G. Battaglin, D. Rosestolato, S. Ferro, A. De Battisti, Characterization of IrO_2-SnO_2 films prepared by physical vapor deposition at ambient temperature, Electrocatalysis 4 (2013) 358-366.

[47] S. Fierro, A. Kapałka, C. Comninellis, Electrochemical comparison between IrO_2 prepared by thermal treatment of iridium metal and IrO_2 prepared by thermal decomposition of H_2IrCl_6 solution, Electrochem. Commun. 12 (2010) 172-174.

[48] NACE International, Standard test method TM0108 Testing of Catalyzed Titanium Anodes for Use in Soils or Natural Waters, 2012.

[49] T. Maezono, M. Tokumura, M. Sekine, Y. Kawase, Hydroxyl radical concentration profile in photo-Fenton oxidation process: Generation and consumption of hydroxyl radicals during the discoloration of azo-dye Orange II, Chemosphere 82 (2011) 1422-1430.

[50] C.A. Huang, S.W. Yang, C.Z. Chen, F.-Y. Hsu, Electrochemical behavior of IrO_2-Ta_2O_5|Ti anodes prepared with different surface pretreatments of Ti substrate, Surf. Coat. Technol. 320 (2017) 270-278.

[51] M.R. Heinrich, A. Gansäuer (Eds.), Radicals in Synthesis III, Topics in Current Chemistry, Book 320, Springer-Verlag, Heidelberg, 2012.

[52] C.A. Paddon, C.E. Banks, I.G. Davies, R.G. Compton, Oxidation of anthracene on platinum macro- and micro-electrodes: Sonoelectrochemical, cryoelectrochemical and sonocryoelectrochemical studies, Ultrason. Sonochem. 13 (2006) 126-132.

528 **Figure captions**

529 **Figure 1**. Scanning electron micrographs of the surfaces of the IrO_2-Ta_2O_5|Ti electrodes
530 manufactured by electrodeposition, using four different Ir:Ta molar ratios, followed by thermal
531 decomposition. Magnification: (A) 2000x and (B) 5000x.

532 **Figure 2**. Atomic percentages of Ti, Ir, Ta and oxygen analyzed by EDX for the four IrO_2-Ta_2O_5|Ti
533 electrodes manufactured with different Ir:Ta molar ratios as seen on the x axis.

534 **Figure 3**. Cyclic voltammograms recorded using each of the four IrO_2-Ta_2O_5|Ti materials (0.75 cm^2
535 of exposed surface area), with different Ir:Ta molar ratios, as the working electrode in 0.5 M H_2SO_4
536 at room temperature. Counter electrode: Pt wire. Reference electrode: Ag|AgCl (3 M KCl). Scan
537 rate: 50 mV s^{-1}.

538 **Figure 4.** UV/vis spectra of 10 mL of a 0.3 mM coumarin solution in 0.5 M H_2SO_4, electrolyzed for
539 180 min at 50 mA and room temperature under constant stirring. Each single IrO_2-Ta_2O_5|Ti
540 electrode (0.75 cm^2) at a given Ir:Ta molar ratio and a Pt wire were employed as the anode and
541 cathode, respectively. The spectrum of coumarin at time zero is also shown for reference.

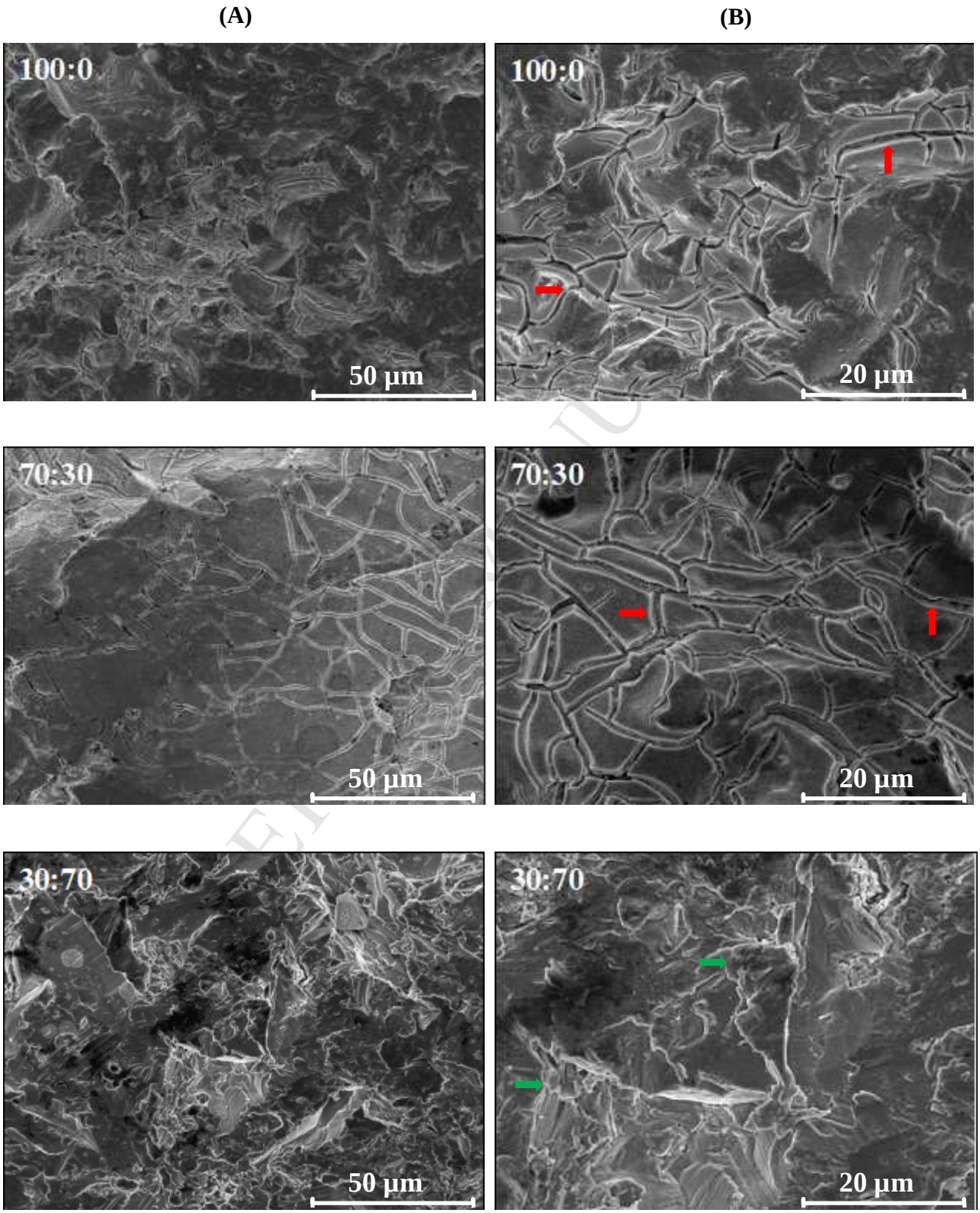
542 **Figure 5**. 7-Hydroxycoumarin concentration accumulated over time during the experiments
543 described in Fig. 4. Data were obtained from an HPLC instrument coupled to a fluorescence
544 detector.

545 **Figure 6**. (A) Decay of phenanthrene concentration with electrolysis time during the electro-
546 oxidation of 50 mL of solutions containing ~ 2 μM of the hydrocarbon in 0.05 M Na_2SO_4 at natural
547 pH and room temperature by applying 50 mA. Each IrO_2-Ta_2O_5|Ti electrode (0.75 cm^2) at given
548 Ir:Ta molar ratios and a Pt plate were employed as the anode and cathode, respectively. (B) Decay
549 of naphthalene during analogous treatments. The horizontal dashed lines represent the limit of
550 quantification for both PAHs under the selected analytical conditions.

Figure 7. (A) TOC abatement vs time during the electro-oxidation of 50 mL of a 25 $mg \cdot L^{-1}$ (0.19 mM) naphthalene solution in 0.05 M Na_2SO_4 at natural pH and room temperature by applying 50 mA. Each single IrO_2-Ta_2O_5|Ti electrode (0.75 cm^2) at a given Ir:Ta molar ratio and a Pt plate were employed as the anode and cathode, respectively. (B) Mineralization current efficiency calculated from Eq. (4) for the above trials.

Figure 8. Service life of each manufactured electrode, at a given Ir:Ta molar ratio, determined according to NACE TM0108 standard procedure.

Figure 1


(A)
(B)
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50 µm
100:0
20 µm
70:30
50 µm
70:30
20 µm
30:70
50 µm
30:70
20 µm

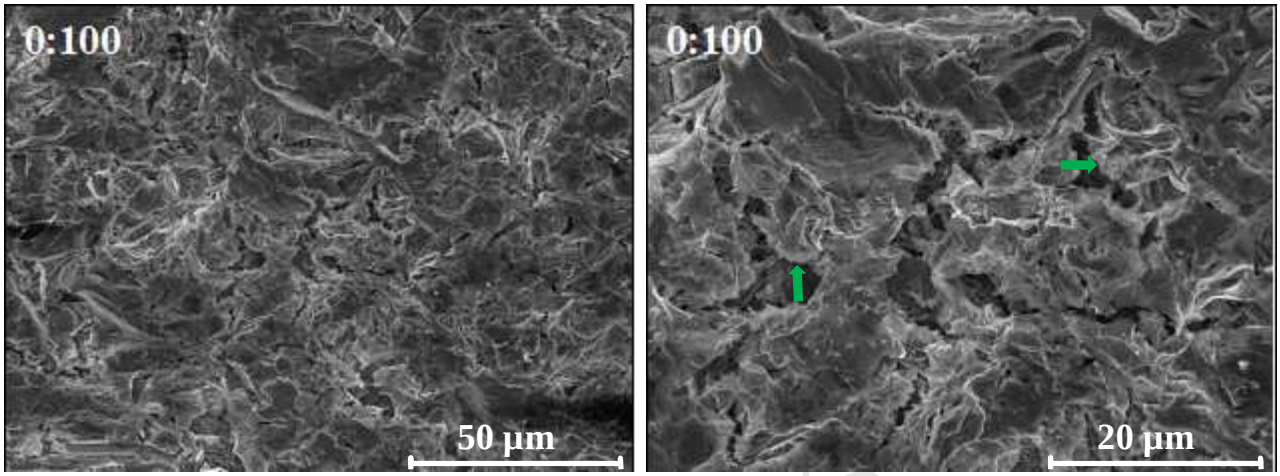


Figure 2

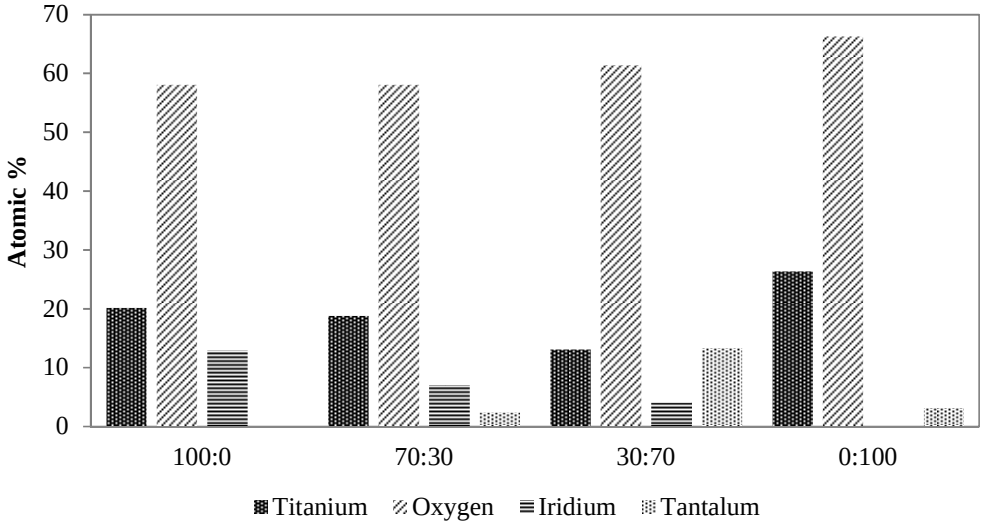


Figure 3

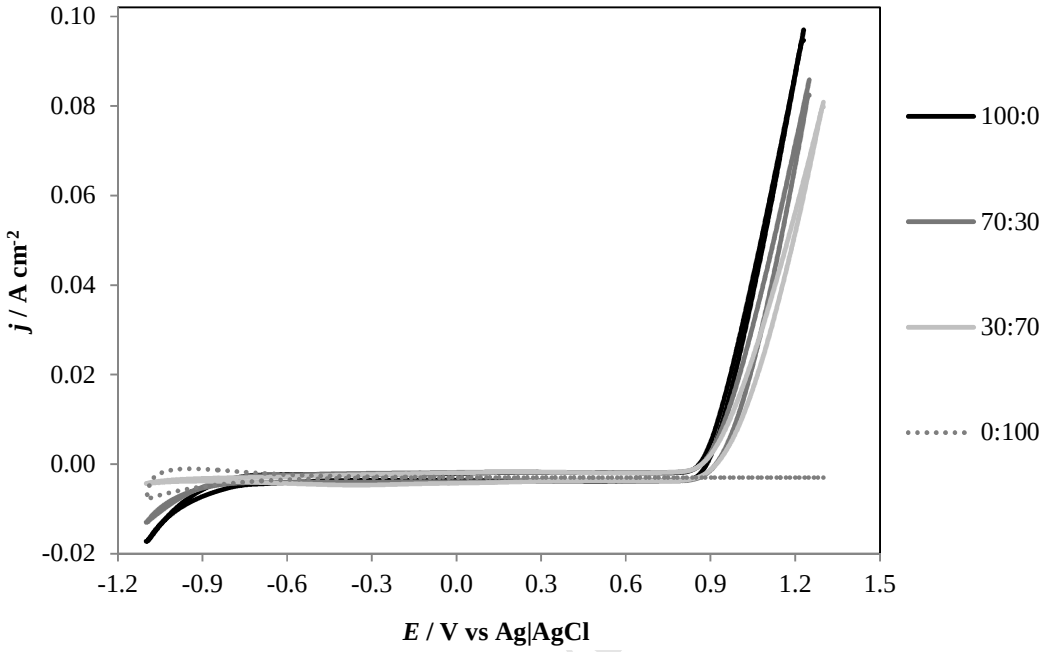


Figure 4

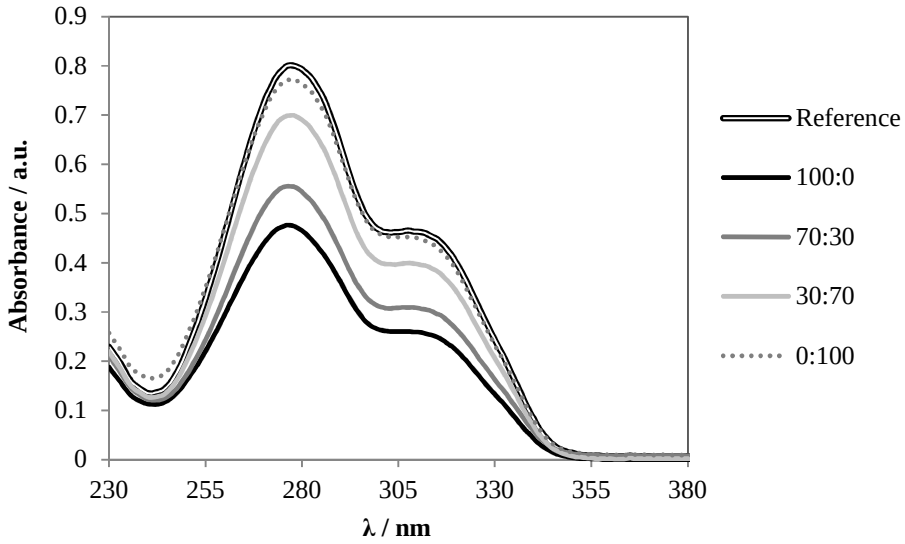


Figure 5

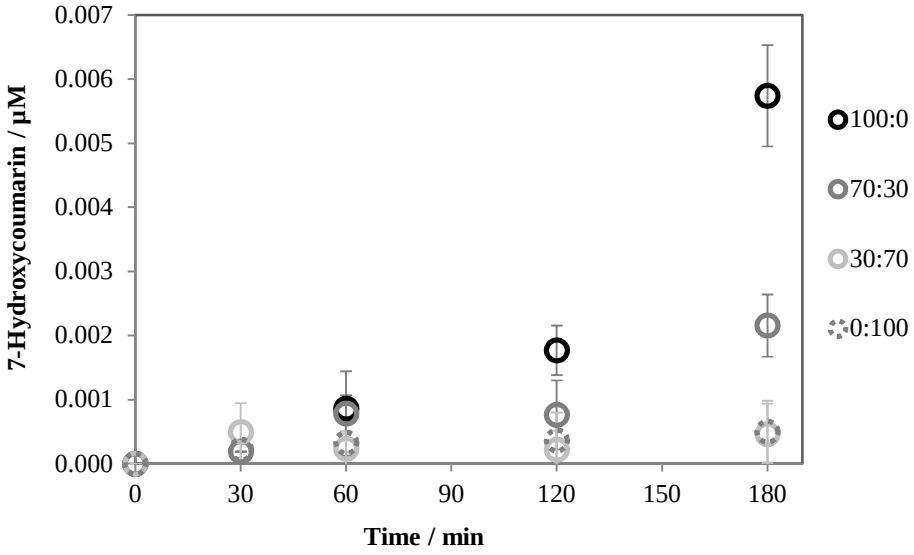
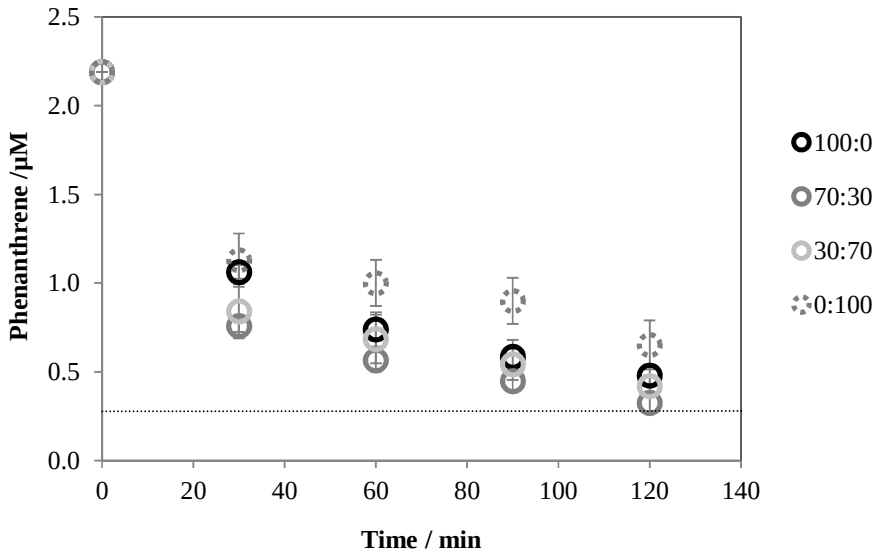


Figure 6

(A)


Phenanthrene /µM
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
Time / min
100:0
70:30
30:70
0:100

(B)

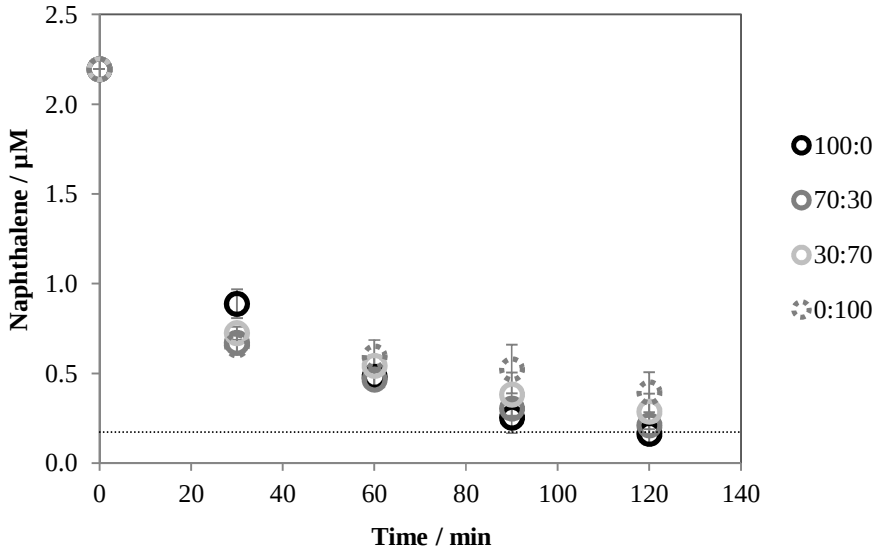
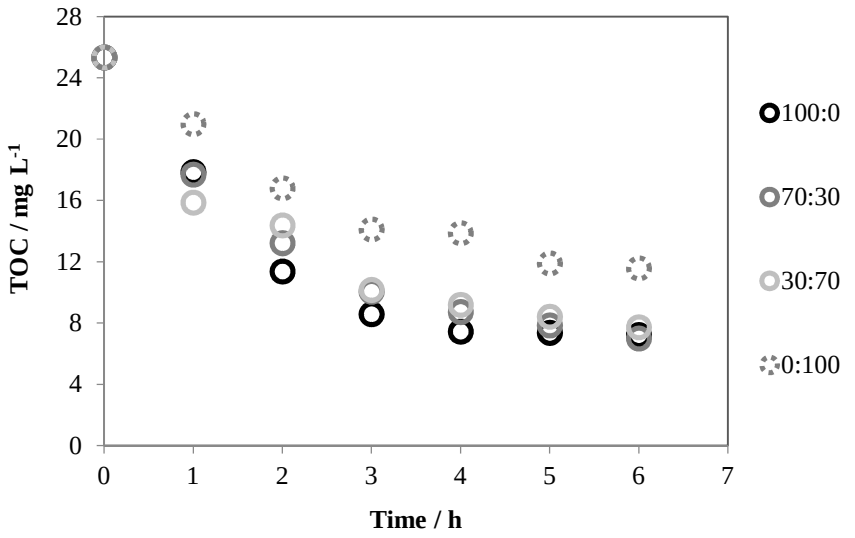
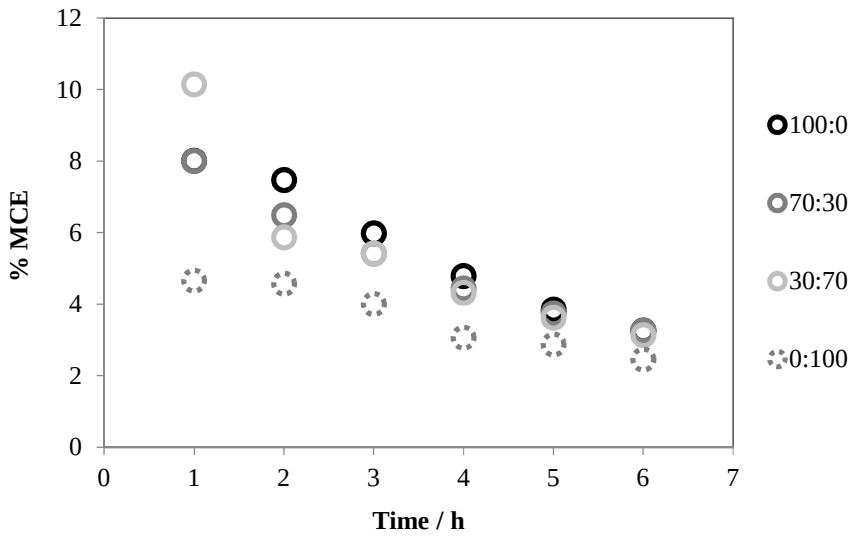

Naphthalene / µM
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100
120
140
Time / min
100:0
70:30
30:70
0:100

Figure 7

(A)


TOC / mg L-1
Time / h
100:0
70:30
30:70
0:100

(B)


% MCE
Time / h
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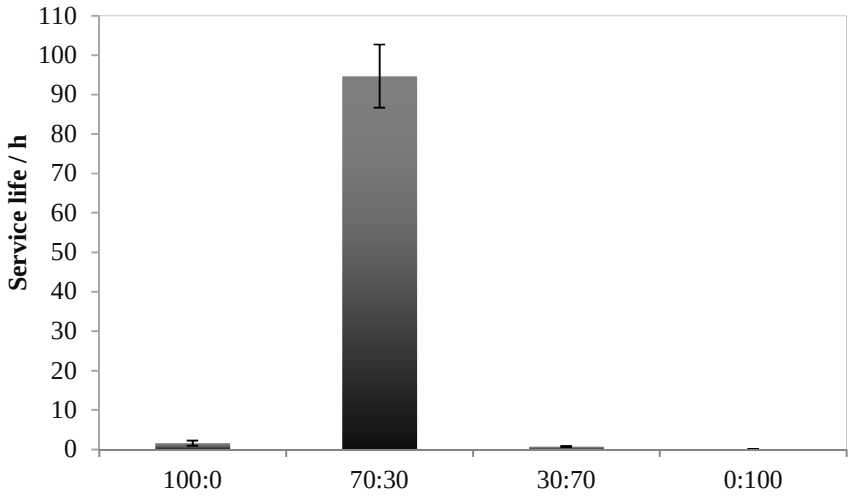
70:30
30:70
0:100

Figure 8



Highlights

- High quality coatings by electrodeposition followed by thermal treatment: 70% or 100% Ir
- Production of M($^{\bullet}$OH) clearly increased in the order (Ir:Ta): 0:100 < 30:70 < 70:30 < 100:0
- Electro-oxidation of PAHs using IrO_2-Ta_2O_5|Ti anodes: direct + M($^{\bullet}$OH)-mediated oxidation
- Up to 86% and 93% removal of phenanthrene and naphthalene, along with 74% TOC abatement
- IrO_2-Ta_2O_5|Ti electrode with Ir:Ta 70:30 showed highest electrocatalytic power and service life