Tantalum-based electrocatalysts prepared by a microemulsion method for the oxygen reduction and evolution reactions

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Abstract

Bifunctional catalysts for oxygen electrodes, active for both the oxygen reduction and evolution reactions (ORR, OER), are highly desirable for the development of electrochemical energy conversion devices. In this work, carbon-supported tantalum based catalysts were synthesized by a microemulsion procedure from tantalum ethoxide through a fast hydrolysis reaction followed by heat treatment. The nature and composition of the different tantalates and oxides (general formula $\text{Na}_a\text{Ta}_b\text{O}_c$, with $a/b = 0 - 1$ and $c/b = 2.5 - 3$) relied on the concentration of ethanol as well as on the annealing temperature, with $\text{Na}_2\text{Ta}_8\text{O}_{21}$ as predominant crystal phase in all cases. High annealing temperatures resulted in a certain degree of oxygen substoichiometry, which creates defects responsible of electrocatalytic activity. The electrochemical response for the oxygen reduction and the oxygen evolution reactions in alkaline electrolyte (0.1M NaOH) was evaluated for the first time in this type of materials. The presence of $\text{Na}_2\text{Ta}_8\text{O}_{21}$ phase over other oxides/tantalates, a high crystallinity of such Ta-phase, and the oxygen substoichiometry are the three parameters playing a relevant role to favor ORR and OER electro-activity. The best formulations were found in a trade-off situation using 3% ethanol and annealing at 900°C.

Keywords: tantalum; sodium tantalate; oxygen reduction reaction; oxygen evolution reaction; bifunctional electrode.

1. Introduction

The design of electrocatalytic materials with high efficiency for two crucial reactions in the bifunctional oxygen electrodes, namely the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), is essential for the development of new emerging electrochemical energy storage and conversion devices, including unitized regenerative fuel cells and rechargeable metal-air batteries among others [1-3] [4-6].

Although some combinations of noble metals such as Pt and metal oxides (RuO_2 , IrO_2) possess excellent activity as bifunctional electrocatalysts, their high cost and instability hinder large-scale applications [7]. In the past few years, most research studies have focused on non-precious metal electrocatalysts using alkaline electrolytes [8], including transition metal-based and heteroatom doped carbonaceous materials [9-14].

Tantalum-based materials have demonstrated to be active and robust electrocatalysts for oxygen reduction reaction (ORR) in acidic environment due to its high corrosion resistance [15-21]. The presence of oxygen vacancies in the oxides can play a crucial role in the ORR because they may enhance the electrical conductivity as well as serve as the active sites for O_2 adsorption [22, 23] [24, 25].

Awaludin et al. [21] established that the high activity in hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) of their tantalum-based electrode was due to the formation of suboxide species, i.e. Ta^{4+} , obtained by an electrochemically reductive treatment. Furthermore, the formation of complex oxides such as $\text{Na}_2\text{Ta}_8\text{O}_{21-x}$ can change the oxidation state of metal species to form active and stable catalytic sites able to adsorb oxygen molecules and to introduce electronic levels in the energy gap [15].

The aim of this work is to synthesize tantalum-based materials as bifunctional electrocatalysts for the ORR and the OER in alkaline medium. It is known the difficulty to control group IV or V oxides on the nanoscale using conventional methods such as impregnation [26]. Primary

nanoparticles of oxide catalysts can be prepared, but these fine particles easily aggregate to form larger secondary particles during high-temperature preparation [16]. For this reason, electrodeposition methods have been commonly used to control the size and distribution of metal particles of Ta-based materials on conductive substrates [17, 19, 27, 28].

In this work, we analyze the characteristics of a procedure for fabrication of carbon-supported tantalum-based electrocatalysts by a microemulsion method [29]. The effects of the amount of ethanol and calcination temperature on the structure, as well as ORR and OER activities in alkaline medium have been investigated. To the best of our knowledge, this is the first attempt to apply tantalum-based materials as ORR and OER electrocatalysts in alkaline environment.

2. Experimental section

2.1. Synthesis of tantalum-based electrocatalysts.

Tantalum oxides (including sodium tantalates) supported on a commercial carbon black support were prepared by a microemulsion procedure [29]. The microemulsion (ME) was prepared by adding 0.25 ml of 75 mM NaOH (Alfa Aesar 99.99%) aqueous solution to an oil phase composed of 2.3 g of a surfactant (Igepal CO-520, Aldrich), 20 ml of n-heptane (Honeywell) and 6 different amounts of ethanol (Labkem 99.5%) from 0 to 1.5 ml. Afterwards, 0.05 ml of tantalum (V) ethoxide (Aldrich 99.98%) (0.3 mmol) was added to the ME at room temperature under continuous stirring. The mixture reacts producing tantalum oxide-based nanoparticles within 5 min [29]. Subsequently, 312 mg of the carbon support (commercial carbon black Vulcan XC72R) is added to the suspension and kept under stirring overnight. The material is washed with ethanol and then with water, followed by drying at 60 °C overnight. A final step consists of a heat treatment in inert atmosphere (N₂) during 90 min. Temperatures from 700 °C to 1000 °C were studied. Then the material is washed with water and dried at 60 °C overnight. The catalysts are labeled as TaO_x/C followed by the weight percentage of ethanol in the ME (0, 1, 2, 3, 4 and 6

wt.%), and the annealing temperature (700, 800, 900 and 1000°C). Table 1 shows all catalysts prepared in this work.

2.2. Solid-state characterization

Transmission electron microscopy (TEM) analyses were made with a Tecnai F30 (FEI) microscope. For the analysis, the catalysts were dispersed in ethanol and then some drops of the dispersion were deposited on a carbon film coated Cu grid. The particle size distribution of each catalyst was obtained using ImageJ software on TEM images and statistic tools of OriginLab software from the measurement of at least 50 metallic nanoparticles. The X-ray diffraction (XRD) analyses were made with a Bruker D8 Advance diffractometer with CuK α of 1600 W. The total metal oxide content in the catalysts was obtained by thermogravimetric analysis in air atmosphere with a Libra F1 Netzsch thermobalance. Energy-dispersive X-ray spectroscopy (EDX) was made with a Tecnai F30 (FEI) microscope in mode Scanning TEM-EDX at 300 kV.

2.3. Electrochemical characterization

Electrochemical studies were carried out in a three-electrode cell at room temperature controlled by an Autolab PGSTAT302 potentiostat-galvanostat, using 0.1M NaOH (Alfa Aesar, 99.99%) aqueous solution as electrolyte with ultrapure water (MilliQ, Millipore). A reversible hydrogen electrode (RHE) in the supporting electrode was used as reference and a glassy carbon rod as counter electrode. The catalysts were deposited on a rotatory disc electrode (RDE), with a disk of glassy carbon (5 mm diameter) with a catalyst loading on the disk of 500 $\mu\text{g cm}^{-2}$. The catalytic layer was obtained preparing 1 mg ml^{-1} ink by sonicating the catalyst in isopropanol/water (50:50) and Nafion® (5%, Sigma Aldrich) as binder (30 wt%). Several drops of the ink were deposited onto the glassy carbon to obtain the required mass loading.

Endurance tests were done in order to evaluate the electrode behavior with time under both ORR and OER conditions. The tests consisted of chronopotentiometric curves in which consecutive and alternative cycles of 180 s each were applied, with a current density of 1 mA cm^{-2} for the OER and -1 mA cm^{-2} for the ORR. A cut-off potential of 1.9 V vs. RHE was established for the

OER and of 0.2 V vs. RHE for the ORR. The tests were made on a RDE with same characteristics as the previous description and at a rotation rate of 400 rpm.

3. Results and discussion

3.1. Physico-chemical characterization

Transmission electron microscopy (TEM) images for carbon-supported Ta-based catalysts, synthesized with 2% and 3% of ethanol and treated at 700, 800, 900 and 1000°C, are shown in Figure 1. In all micrographs the carbon phase presents a lighter grey aspect while the metal-based nanoparticulated phase is clearly differentiated by a darker contrast. The metal oxides are not evenly distributed on the surface of carbon, but randomly mixed with the support.

Figure 1. TEM micrographs for catalysts treated at different temperatures: a-b) 700°C; c-d) 800°C; e-f) 900°C; and g-h) 1000°C. Catalysts synthesized with 2% of ethanol are shown at the left column (a, c, e, g) and those with 3% of ethanol at the right one (b, d, f, h). Scale bar: 50 nm.

The influence of the annealing temperature is depicted by comparing the images in Figure 1. The morphology of the metal oxide particles changes from a rounded shape (700°C) towards a prismatic and more ordered arrangement (1000°C) as the treatment temperature increases. At 700°C and 2% ethanol (Figure 1a), particles present a chain-like aspect formed by various series of globular particles of about 15-25 nm linked with each other. This is also the apparent morphology at the same temperature but prepared with 3% ethanol in the ME, with larger particles of about 35-45 nm (Figure 1b). This kind of morphology is derived from the use of micelles in the microemulsion. A water in oil microemulsion, like the one used in this work, allows the limitation of particle growing in the core of the nanosized droplets. Depending on the ME

composition, the nanodrops can coalesce during the reaction of Ta precursor, resulting in the chain-like aspect.

Figure 2. Particle size distribution for tantalum oxide-based nanoparticles from TEM images. (a) 2% ethanol. (b) 3% ethanol.

Particle size distributions (PSDs) of Figure 2 been obtained from TEM images. The PSD for the catalyst series synthesized with 2% of ethanol (Figure 2a) shows an increase of particle size when increasing the annealing temperature. At 700 °C, more than 70% particles present sizes between 10 and 20 nm, with a narrow distribution. The increase of annealing temperature results in an increase of average particle size and a widening of the distribution caused by the sintering of particles. In the catalyst TaOx/C-2%-1000 a bimodal distribution is observed. The effect of the treating temperature on the PSD is not so clear for the catalyst series synthesized with 3% of ethanol (Figure 2b). Relatively broad distributions were observed regardless the annealing temperature in this case.

At temperatures higher than 800°C, the morphology of the particles is mostly elongated, i.e. with a preferential growth direction, and characterized by a higher crystallinity, as envisaged from the presence of planes in comparison to the catalysts obtained at the lowest temperature (700°C) with amorphous aspect. Particles are sized in the range 40-80 nm (shorter dimension) and 80-150 nm (longer dimension) when treated at 1000°C, indicating a significant growth of the oxides with temperature.

Figure 3. TEM micrographs for catalysts synthesized (a) without ethanol; (b) with 6% ethanol. Thermal annealing at 900°C. Scale bar: 50 nm.

The effect of ethanol concentration is also very relevant to the morphology and size of the Ta-based particles. Figure 2 depicts TEM micrographs for catalysts treated at 900 °C both without ethanol (Figure 3a) and with 6% ethanol (Figure 3b). It is observed a dramatic effect of ethanol concentration on the particle size for Ta-based phase. Without ethanol, a bimodal distribution of sizes is obtained, mostly populated by small spherical particles with average diameter of 9.5 nm, and a few larger particles with elongated shape and dimensions between 20 and 40 nm. Whereas, the utilization of 6% ethanol results in the agglomeration of Ta-based particles, with rounded morphology and connected with each other. Intermediate concentrations of ethanol result in average diameters in between the latter two situations, as we can see in Figures 1(e) and 1(f), with samples treated at 900 °C with 2% and 3% ethanol, respectively.

The X-ray diffraction (XRD) patterns for the catalysts obtained using different amounts of ethanol during the synthesis is shown in Figure 4 for samples thermally treated at 900 °C. Several species of tantalum oxide and sodium tantalates were identified. These are, in increasing order of relative oxygen-to-tantalum and sodium-to-tantalum contents: Ta_2O_5 (JCPDS #25-0922, orthorhombic), $\text{Na}_2\text{Ta}_8\text{O}_{21}$ (JCPDS #28-1137), $\text{Na}_2\text{Ta}_4\text{O}_{11}$ (JCPDS #84-0810), and NaTaO_3 (JCPDS #74-2477). The Miller indexes for each of these reference patterns can be consulted in the Supplementary Information (Figures S1 to S4). The formation of the different oxides/tantalates results from the hydrolysis reaction of tantalum ethoxide with water (Eq. 1) in the presence of sodium hydroxide. Ethanol is obtained as a reaction product together with the metallic oxide phase. In the absence

of sodium hydroxide, tantalum is deposited only as Ta₂O₅. Whereas, the presence of sodium cations in the solution gives place to the precipitation of sodium tantalates with different stoichiometries. Interestingly, the nature of the tantalate can be tuned with an appropriate selection of ethanol in the solution.

Figure 4. The effect of ethanol (EtOH) concentration on the crystallinity (XRD patterns) for catalysts annealed at 900°C. Within the reference patterns (symbols), only the most intense reflections are included for the sake of clarity.

In the analysis of the nature of tantalates/oxides, some reflections are coincident in similar intervals of Bragg angles, like the one appearing at $2\theta = 22.6\text{--}22.9^\circ$, which can be related to planes (0 0 1) of Ta₂O₅, or (1 1 0) of NaTaO₃, or (3 3 0)/(0 0 1) of Na₂Ta₈O₂₁; or the reflection appearing at $2\theta = 32.2\text{--}32.6^\circ$, which can be ascribed to planes (0 1 1)/(1 0 1) of NaTaO₃, (3 3 1) of Na₂Ta₈O₂₁ or (1 1 6) of Na₂Ta₄O₁₁. For the sake of clarity, the following discussion will focus on the intense reflections that can be ascribed to only one of the phases.

All materials exhibit the reflections attributed to the Na₂Ta₈O₂₁ phase, as most clearly seen by the signals at $2\theta = 25.826^\circ$ and 34.715° , related to (3 6 0) and (3 6 1) planes of the orthorhombic structure of sodium tantalate. The catalyst prepared without ethanol presents also the reflections from orthorhombic Ta₂O₅, with peaks at $2\theta = 28.291^\circ$, 28.795° , 36.666° and 37.073° as the most

differing ones compared to the other structures, related to (1 1 1 0), (2 0 0), (1 1 1 1) and (2 0 1) planes of Ta_2O_5 .

The catalysts prepared with 1% and 2% ethanol exhibit similar profiles with each other, including $\text{Na}_2\text{Ta}_8\text{O}_{21}$ and $\text{Na}_2\text{Ta}_4\text{O}_{11}$ as main crystallographic phases, while Ta_2O_5 is no longer detected, differing from the sample prepared with 0% ethanol. Indeed, the different reflections that are more clearly visible are those appearing at $2\theta = 14.502^\circ$ and 17.173° from $\text{Na}_2\text{Ta}_4\text{O}_{11}$ (0 0 6) and (0 1 2) planes, respectively. The catalyst prepared with 3% ethanol exhibits mainly the reflections related to the phase $\text{Na}_2\text{Ta}_8\text{O}_{21}$, with small contributions from $\text{Na}_2\text{Ta}_4\text{O}_{11}$. Whereas, the catalyst prepared with 6% ethanol clearly shows reflections related to NaTaO_3 , together with the diffraction peaks of $\text{Na}_2\text{Ta}_8\text{O}_{21}$.

All these results indicate that, the selection of ethanol concentration in the microemulsion synthesis for the hydrolysis of Ta ethoxide is relevant to favor the formation of certain Ta-based crystallographic species, all of them containing $\text{Na}_2\text{Ta}_8\text{O}_{21}$, with variable contents of the other three tantalum species.

Figure 5 shows the influence of the annealing temperature on the XRD patterns for the catalysts prepared with 2% and 3% ethanol. It is clear that the treatment temperature also affects the chemical composition of the catalysts. The samples prepared with 2% and 3% ethanol contain both $\text{Na}_2\text{Ta}_8\text{O}_{21}$ and $\text{Na}_2\text{Ta}_4\text{O}_{11}$, but the relative content of these two species varies with the annealing treatment, as envisaged from the variation of the intensities of the corresponding reflections. The predominance of $\text{Na}_2\text{Ta}_8\text{O}_{21}$ is favored by annealing at 800°C for the 2% series, and over 900°C for the 3% series. In any case, 700°C appears as not sufficient temperature to result in crystalline particles, in accordance with TEM observations of globular shaped particles.

Figure 5. XRD patterns of the catalysts obtained at different temperatures synthesized with (a) 2% of ethanol and (b) 3% of ethanol.

Table 1 summarizes the crystalline species and the crystallite size of the catalysts according to the amount of ethanol used during the synthesis and the treatment temperature. The main crystals obtained for almost any synthesis condition are $\text{Na}_2\text{Ta}_8\text{O}_{21}$ and $\text{Na}_2\text{Ta}_4\text{O}_{11}$. In general terms, the average crystallite size increases with the annealing temperature.

Table 1. Crystallite size (nm) for catalysts from XRD analyses. $\text{TaO}_x/\text{C-X-Y}$ (X: percentage of ethanol used in the synthesis; Y= annealing temperature in °C).

Catalyst	Crystallite size (nm)			
	$\text{Na}_2\text{Ta}_8\text{O}_{21}$	$\text{Na}_2\text{Ta}_4\text{O}_{11}$	NaTaO_3	Ta_2O_5

TaOx/C-0%-900	35.3	-	-	21.3
TaOx/C-1%-900	45.3	57.9	-	-
TaOx/C-2%-700	16	33	-	-
TaOx/C-2%-800	37.1	33	-	-
TaOx/C-2%-900	46.4	52	-	-
TaOx/C-2%-1000	46.8	60.3	-	-
TaOx/C-3%-700	21	34	-	-
TaOx/C-3%-800	-	57	-	-
TaOx/C-3%-900	33.9	42	-	-
TaOx/C-3%-1000	43.9	34	-	-
TaOx/C-4%-900	25.6	52.7	-	-
TaOx/C-6%-900	18	31	34	-

-: not detected or weak signal

EDX analysis of the metal oxide nanoparticles in STEM mode was used to determine the composition of the tantalates, minimizing the occurrence of carbon and oxygen signals from the carbonaceous support. The calculated ratios of oxygen and sodium with respect to tantalum are summarized in Table 2, together with those corresponding to the tantalum species identified in XRD analyses. The ratio between sodium and tantalum was found between 0.05 and 0.26, indicating stoichiometries between $\text{Na}_2\text{Ta}_8\text{O}_{21}$ and Ta_2O_5 . Whereas, the O/Ta ratio is close to stoichiometric Ta_2O_5 for three of the samples and much lower (0.75 – 1.28) especially for samples treated at high temperature and prepared with 3% ethanol. According to the literature, oxygen vacancies in the oxides of metals from groups IV and V of the periodic table are responsible of oxygen adsorption and electrocatalytic activity [30].

Table 2. Atomic ratio of oxygen/tantalum and sodium/tantalum obtained by EDX.

	O/Ta	Na/Ta
TaOx/C -2%-700	2.46	0.09
TaOx/C -2%-800	4.49	0.26
TaOx/C -2%-900	2.54	0.15
TaOx/C -2%-1000	0.75	0.12
TaOx/C -3%-700	2.59	0.10
TaOx/C -3%-800	1.28	0.11
TaOx/C -3%-900	1.12	0.07
TaOx/C -3%-1000	1.24	0.04
TaOx/C -4%-900	0.87	0.27
Ta_2O_5	2.5	0
$\text{Na}_2\text{Ta}_8\text{O}_{21}$	2.625	0.25
$\text{Na}_2\text{Ta}_4\text{O}_{11}$	2.75	0.5
NaTaO_3	3	1

3.2. Electrochemical characterization

The tantalate-based catalysts were studied for the ORR and the OER in a three-electrode half-cell configuration by using a rotating disc electrode (RDE). The electrolyte was in all studies 0.1M NaOH aqueous solution, saturated with O₂ for ORR tests, and the experiments were carried out at room temperature.

3.2.1. ORR activities of Ta-based catalysts synthesized with different ethanol concentrations

The electrochemical activity for the catalysts treated at 900 °C with different ethanol concentrations (0, 1, 2, 3, 4 and 6%) towards the ORR is shown in Figure 6. The curves present the typical sigmoidal wave form for the oxygen electroreduction, with an onset potential of 0.70-0.72 V vs. RHE (at -0.1 mA cm⁻²) and approaching a limiting current with the potential scan towards more negative values ascribed to oxygen diffusion limitation.

Figure 6. Effect of the amount of ethanol on the ORR polarization curves catalyst with the same annealing treatment (900 °C). Linear sweep voltammetry at 5 mV s⁻¹, 1600 rpm, 0.1 M NaOH, 45 µg cm⁻² of Ta.

The activity of these catalysts is lower if compared to other bifunctional catalysts published in the literature [9]. Only slight differences in terms of ORR activity were found by varying the amount of ethanol in the preparation of catalysts. Table 3 summarizes some ORR parameters of interest, including the kinetic current density ($j_{k,ORR}$) at 0.65 V vs. RHE, the Tafel slope and the exchange

current density ($j_{0,ORR}$). Kinetic current densities were calculated considering the contribution of the diffusion limiting current density (j_d) to the measured current ($j^{-1} = j_k^{-1} + j_d^{-1}$). The capacitance for each catalyst in the deaerated supporting electrolyte was also determined from cyclic voltammograms (see Supplementary Information, Figures S5 to S7 and Table S1). The most active catalysts in terms of kinetic current density were those prepared with intermediate amounts of ethanol (2-3%), characterized by intermediate nanoparticle size and the absence of Ta₂O₅ and NaTaO₃ species according to XRD results. In general terms, both the Tafel slope and the exchange current density increase with the concentration of ethanol. According to the recent literature, Tafel slopes close to 60 mV dec⁻¹ denote that the hydrolysis of adsorbed oxygen is the rate determining step for the associative mechanism of ORR in alkaline medium, whereas values closer to 120 mV dec⁻¹ might indicate that the first electron transference to adsorbed oxygen contributes also to the overall reaction rate [31]. Although catalysts prepared with 4% and 6% ethanol present much larger exchange current densities than the rest of the catalysts, the also larger Tafel slope of about 90 mV dec⁻¹ leads to overall process with slower reaction compared to catalysts with Tafel slopes closer to 60 mV dec⁻¹.

Table 3. Summary of ORR electrokinetic parameters for catalysts synthesized by varying the ethanol concentration. $j_{k,ORR}$ is the kinetic part of the current density at 0.65 V vs. RHE, and $j_{0,ORR}$ is the exchange current density ($E^0 = 1.23$ V vs. RHE).

Electrocatalyst	$j_{k,ORR}$ (mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	$j_{0,ORR}$ (mA cm ⁻²)
TaOx/C-0%-900	-0.89	66	$1.1 \cdot 10^{-9}$
TaOx/C-1%-900	-0.71	65	$1.1 \cdot 10^{-9}$
TaOx/C-2%-900	-1.24	72	$3.3 \cdot 10^{-9}$
TaOx/C-3%-900	-1.24	70	$6.7 \cdot 10^{-9}$
TaOx/C-4%-900	-0.83	94	$2.4 \cdot 10^{-7}$
TaOx/C-6%-900	-0.78	90	$3.2 \cdot 10^{-7}$

The best ORR formulations within this set of electrocatalysts are the ones obtained with intermediate ethanol concentration (2-3%), in which the formation of Na₂Ta₈O₂₁ is favored over other Ta-based species. This might be responsible of sufficiently high exchange current density with a relatively low Tafel slope, resulting in the best kinetic current density among this set of catalysts.

3.2.2. OER activities of Ta-based catalysts synthesized with different ethanol concentrations

The effect of ethanol concentration in the preparation of catalysts treated at 900 °C on their OER electrocatalytic activity is reported in Figure 7. The rotating speed for the electrode was maintained at 1600 rpm to remove the produced O₂ bubbles. There is not iR-corrected OER data. For this reaction, the differences encountered for catalysts prepared with different ethanol concentrations in OER is much more pronounced than those found in the case of ORR.

Figure 7. Effect of the amount of ethanol on the OER polarization curves catalyst with the same annealing treatment (900 °C). Linear sweep voltammetry at 5 mVs⁻¹, 1600 rpm, 0.1 M NaOH, 45 μg cm⁻² of Ta.

The OER electrochemical activity increases as the amount of ethanol used increases up to 3% (TaOx/C-3%-900 catalyst), showing the highest activity of this series. However, higher ethanol concentration to 6 % leads to a progressive decrease in activity, similar to TaOx/C-1%-900 catalyst. The XRD analysis of TaOx/C-3%-900 catalyst exhibited that Na₂Ta₈O₂₁ was prevalent among the different crystalline species detected. This may indicate this phase is responsible for OH⁻ oxidation towards oxygen, since the other catalysts in the series exhibited much lower OER activity.

Table 4. Summary of OER electrokinetic parameters for catalysts synthesized by varying the ethanol concentration. j_{OER} is the current density at 1.65 V vs. RHE, and $j_{0,\text{OER}}$ is the exchange current density (1.23 V vs. RHE).

Electrocatalyst	j_{OER} (mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	$j_{0,\text{OER}}$ (mA cm ⁻²)
TaOx/C-0%-900	0.31	362	$2.2 \cdot 10^{-2}$
TaOx/C-1%-900	0.55	323	$2.6 \cdot 10^{-2}$
TaOx/C-2%-900	1.13	306	$4.9 \cdot 10^{-2}$
TaOx/C-3%-900	1.37	304	$6.2 \cdot 10^{-2}$
TaOx/C-4%-900	0.65	265	$1.6 \cdot 10^{-2}$
TaOx/C-6%-900	0.45	245	$0.8 \cdot 10^{-2}$

Table 4 summarizes some important parameters related to OER for this series of catalysts, including the current density at 1.65 V vs. RHE (j_{OER}). The highest exchange current density ($j_{0,\text{OER}}$) was observed for the catalyst prepared with 3% ethanol, whereas the Tafel slope progressively decreases from 362 to 245 mV dec⁻¹ when increasing the concentration of ethanol in the synthesis. A lower Tafel slope represents enhanced kinetics [32], but as the exchange current density also decreases in the same direction with ethanol concentration over 3%, a compromise situation is found to maximize overall activity for the catalyst TaOx/C-3%-900.

For the OER, a trade-off situation is found for intermediate ethanol concentration (3%) to maximize the electro-catalytic activity, a similar behavior than in ORR investigation. This might be an indication of similar active sites acting for both reactions.

3.2.3. ORR activities of Ta-based catalysts synthesized with different annealing temperatures

The effect of the annealing temperature has been investigated on the catalysts synthesized with 2% (Figure 8) and 3% (Figure 9) of ethanol. Table 5 summarizes the most important parameters regarding the ORR electro-activity. Within both series of catalysts, the increase of the annealing temperature improves the activity for the ORR as shown in the figures and also from the values of kinetic current density ($j_{k,\text{ORR}}$). The largest difference was observed between catalysts treated at 700°C, with low activity, and catalysts annealed at 800°C or higher, with more than 100 mV improvement at the same current density. Additionally, the Tafel slope decreases also with annealing temperature approaching 60 mV dec⁻¹, indicating faster kinetics, while the exchange current density ($j_{0,\text{ORR}}$) exhibits the largest values for the samples treated at 800°C (Table 5). This

observed pattern of activity with temperature occurs for samples prepared with both 2% and 3% ethanol concentration. Taking into account these two series of catalysts, the one exhibiting the largest activity in terms of kinetic current density is TaOx/C-3%-1000.

Figure 8. Effect of the temperature on ORR polarization curves for the catalysts synthesized with 2% of ethanol. Linear sweep voltammetry at 5 mV s⁻¹, 1600 rpm, 0.1 M NaOH, 45 μg cm⁻² of Ta.

As discussed above, the catalysts treated at 700°C showed small XRD reflections, indicating a small population of crystalline particles within the metal oxide phase. This is in agreement with TEM observation, where the catalysts treated at the lowest temperature exhibited globular and amorphous structure. Upon annealing at larger temperature, the catalysts become much more active. Therefore, it appears that the crystallinity of metal oxide particles is a key parameter to obtain ORR catalytic active sites. Much smaller differences were found for catalysts treated in the interval 800-1000°C.

Figure 9. Effect of the temperature on ORR polarization curves for the catalysts synthesized with 3% of ethanol. Linear sweep voltammetry at 5 mV s⁻¹, 1600 rpm, 0.1 M NaOH, 45 μg cm⁻² of Ta.

Table 5. Summary of ORR electrokinetic parameters for catalysts synthesized by varying the annealing temperature. $j_{k,ORR}$ is the kinetic part of the current density at 0.65 V vs. RHE, and $j_{0,ORR}$ is the exchange current density (1.23 V vs. RHE).

Electrocatalyst	$j_{k,ORR}$ (mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	$j_{0,ORR}$ (mA cm ⁻²)
TaOx/C-2%-700	-0.14	83	$1.0 \cdot 10^{-8}$
TaOx/C-2%-800	-1.08	82	$2.4 \cdot 10^{-8}$
TaOx/C-2%-900	-1.24	72	$7.4 \cdot 10^{-9}$
TaOx/C-2%-1000	-1.15	66	$1.7 \cdot 10^{-9}$
TaOx/C-3%-700	-0.14	81	$8.9 \cdot 10^{-9}$
TaOx/C-3%-800	-0.72	76	$9.9 \cdot 10^{-9}$
TaOx/C-3%-900	-1.24	72	$6.6 \cdot 10^{-9}$
TaOx/C-3%-1000	-1.54	65	$2.3 \cdot 10^{-9}$

3.2.4. OER activities of Ta-based catalysts synthesized with different annealing temperatures

The effect of the annealing temperature on OER activity is shown in Figures 10 and 11. Similarly to ORR results, the catalysts treated at the lowest temperature (700°C) show the lowest activity, with a significant increase upon annealing at higher temperature. The better OER catalytic activities for TaOx/C-900 catalysts were reflected by its more negative onset potentials and higher current densities than those of TaOx/C-700, TaOx/C-800 and TaOx/C-1000.

Figure 10. Effect of the annealing temperature on the OER polarization curves for the 2% ethanol catalyst. Linear sweep voltammetry at 5 mV s⁻¹, 1600 rpm, 0.1 M NaOH, 45 μg cm⁻² of Ta.

While at this stage the mechanism of OER catalysis remains unclear for the TaOx/C catalysts, both the geometric and electronic factors can be mainly responsible for the improvement of catalytic activity at 900 °C. The exchange current density ($j_{0,OER}$) increases progressively with the annealing temperature. The most active OER catalysts are TaOx/C-900, with a Tafel slope approaching 300 mV dec⁻¹. This is not enough information to determine the rate determining step [31], not to mention the possible contribution from side reactions (e.g. carbon electro-oxidation), but clearly indicates faster kinetics in any case. The presence of Na₂Ta₈O₂₁ crystal phase with higher crystallinity and preferential growth direction seems to favor the OH⁻ oxidation towards oxygen. A further question involves conductivity, as the annealing temperature could affect the conductivity of the composites. It is reasonable to assume that the increased contact between crystals due to a collapse of the pores, upon high-temperature sintering, such as 900 and 1000°C, can lead to an increase of the conductivity of the TaOx/C catalysts. The lower activity of the catalysts annealed at 1000 °C compared to that at 900 °C is due to a decreasing dispersion of the active phase. Therefore, the TaOx/C-2% and TaOx/C-3% treated at 900°C catalysts exhibit a potential bifunctional electrochemical performance benefit from the synergistic catalytic effects towards ORR and OER processes.

Figure 11. Effect of the annealing temperature on the OER polarization curves for the 3% ethanol catalyst. Linear sweep voltammetry at 5 mV s⁻¹, 1600 rpm, 0.1 M NaOH, 45 µg cm⁻² of Ta.

Table 6. Summary of OER electrokinetic parameters for catalysts synthesized by varying the ethanol concentration. j_{OER} is the current density at 1.65 V vs. RHE, and $j_{0,\text{OER}}$ is the exchange current density (1.23 V vs. RHE).

Electrocatalyst	j_{OER} (mA cm ⁻²)	Tafel slope (mV dec ⁻¹)	$j_{0,\text{OER}}$ (mA cm ⁻²)
TaOx/C-2%-700	0.15	361	$2.1 \cdot 10^{-2}$
TaOx/C-2%-800	0.43	328	$1.4 \cdot 10^{-2}$
TaOx/C-2%-900	1.14	306	$4.9 \cdot 10^{-2}$
TaOx/C-2%-1000	0.86	341	$5.0 \cdot 10^{-2}$
TaOx/C-3%-700	0.17	290	$1.9 \cdot 10^{-2}$
TaOx/C-3%-800	0.65	329	$3.5 \cdot 10^{-2}$
TaOx/C-3%-900	1.37	304	$6.2 \cdot 10^{-2}$
TaOx/C-3%-1000	1.14	345	$6.9 \cdot 10^{-2}$

3.2.5. Endurance tests

Endurance tests were carried out in order to evaluate the electrode behavior with time under both ORR and OER conditions. Chronopotentiometric curves are shown in Figure 12 for the four tested catalysts (TaOx/C-2%-900, TaOx/C-2%-1000, TaOx/C-3%-900 and TaOx/C-3%-1000), selected as they exhibited the most performing behavior. Cut-off values of 1.9 V vs. RHE for the OER and of 0.2 V vs. RHE for the ORR were established. The number of cycles before reaching the OER cut-off potential was 15, 13, 16 and 18 cycles for the catalysts TaOx/C-2%-900, TaOx/C-2%-1000, TaOx/C-3%-900 and TaOx/C-3%-1000, respectively. The pseudo steady-state potential

barely changes during the first 60 min of test for all the catalysts and for both oxygen evolution and reduction reactions. After a certain duration, there is a decrease of activity in both OER and ORR sides indicated by the variation of potential towards more positive values in OER and more negative values in ORR in the plot. The more pronounced variation of potential derives in reaching the upper cut-off value, and consequently the test is stopped. In view of the number of cycles, the catalyst prepared with 3% ethanol and annealed at 1000°C is the most resistant one. Interestingly, when the catalysts start losing activity with a higher degradation rate, the decay in performance in terms of larger overpotential is observed for both OER and ORR parts of the curves. This might indicate a similar nature for the active sites acting as catalytic centers for these two reactions (bifunctional sites).

Figure 12. Chronopotentiometric cycles obtained for a) TaOx/C-2%-900; b) TaOx/C-2%-1000; c) TaOx/C-3%-900; and d) TaOx/C-3%-1000. 180 s/cycle at $\pm 1 \text{ mA cm}^{-2}$, O_2 -saturated 0.1 M NaOH, 400 rpm.

ORR and OER polarization curves were recorded after the endurance tests. Table 7 shows the values of current density at the beginning and at the end of tests (BoT and EoT, respectively), together with the relative variation in percentage.

Table 7. Current density for the ORR (0.65 V vs. RHE) and the OER (1.65 V vs. RHE) by linear sweep voltammetry (5 mV s^{-1} , 1600 rpm, 0.1 M NaOH, $45 \text{ } \mu\text{g cm}^{-2}$ of Ta) at the beginning of test (BoT) and at the end of test (EoT) regarding the endurance experiments.

Electrocatalyst	ORR			OER		
	$j_{k,BoT}$ (mA/cm ²)	$j_{k,EoT}$ (mA/cm ²)	$\frac{j_{k,EoT} - j_{k,BoT}}{j_{k,BoT}}$	j_{BoT} (mA/cm ²)	j_{EoT} (mA/cm ²)	$\frac{j_{k,EoT} - j_{k,BoT}}{j_{k,BoT}}$
TaOx/C-2%-900	-1.243	-0.525	-58%	1.135	1.023	-10%
TaOx/C-2%-1000	-1.148	-0.851	-26%	0.857	0.442	-48%
TaOx/C-3%-900	-1.239	-1.230	-1%	1.368	1.020	-25%
TaOx/C-3%-1000	-1.535	-1.397	-9%	1.139	0.140	-88%

Figure 13 shows a comparison of the OER and ORR voltammetric curves for the two catalysts with the largest activity, those annealed at 900°C, including the curves after the endurance test (dashed lines). The end of test occurred for all the catalysts when reaching 1.9 V vs. RHE (overpotential of $0.67 \text{ V} = 1.9 \text{ V} - 1.23 \text{ V}$, vs. RHE) at a demand of 1 mA cm^{-2} . Table 7 indicates absolute current density values over 1 mA cm^{-2} at a lower overpotential for both OER ($0.42 \text{ V} = 1.65 \text{ V} - 1.23 \text{ V}$, vs. RHE) and ORR ($0.58 \text{ V} = 1.23 \text{ V} - 0.65 \text{ V}$, vs. RHE) for some of the composites upon the endurance test. This points to a certain recovery of catalyst activity between the behavior exhibited in the endurance tests (chronopotentiometries of Figure 12) and the activity tests (linear sweep voltammetries of Figure 13). Further work is needed to individuate the causes for degradation in order to design synthesis strategies aimed to ameliorate these phenomena.

Figure 13. ORR and OER activity before (continuous line) and after (discontinuous line) the chronopotentiometric tests for the catalysts with the best electrocatalytic activity.

4. Conclusions

Carbon-supported tantalum-based catalysts were prepared by a microemulsion methodology from tantalum ethoxide precursor. The influence of ethanol concentration in the microemulsion (0-6 %) and the annealing temperature of the catalyst (700-1000°C) were investigated. Metal oxide nanoparticles were formed by a mix of $\text{Na}_2\text{Ta}_8\text{O}_{21}$ with other tantalum oxides and sodium tantalates. The specific composition relies mainly on ethanol concentration, as it influences the hydrolysis reaction. The thermal treatment at high temperature of these materials in the presence of carbon support (carbon black) conducts to oxygen contents below stoichiometric values, which is known to favor the electrochemical activity.

The activity of the catalysts towards ORR and OER in alkaline environment is favored by high crystallinity and the presence of sodium tantalate rather than tantalum oxide. Using intermediate ethanol concentration in the microemulsion and high annealing temperatures results in the best electroactivity for both ORR and OER, despite obtaining bigger crystallite sizes of Ta-based nanoparticles (40-50 nm) with lower surface area. Endurance tests based on chronopotentiometric analysis were performed to investigate the behavior at ORR and OER with time, suggesting that

a part of the loss of activity observed during the endurance test can be recovered. Catalysts annealed at 900°C exhibited the most promising bifunctional behavior in terms of activity and durability. Further research is necessary to investigate the reaction mechanisms on the various Ta species, to individuate the nature of active sites and to determine the effect of the carbon support.

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