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Undoped SnO₂ as Support for Ni Species to Boost the Oxygen Generation through Alkaline Water Electrolysis

*Ștefan Neațu,^{†‡} Florentina Neațu,^{†‡} Victor C. Dicuțescu,[†] Mihaela
M. Trandafir,[†] Nicoleta Petrea,[#] Simona Somacescu,^{\$} Frank
Krumeich,[|] Julian T. C. Wennmacher,^{|,||} Amy J. Knorpp,[|] Jeroen A.
van Bokhoven,^{|,||} Mihaela Florea^{*,†}*

[†]National Institute of Materials Physics, 405A Atomistilor
Street, 077125 Magurele, Romania

[#]Scientific Research Centre for CBRN Defence and Ecology, 225
Oltenitei Road, 041309 Bucharest, Romania

^{\$}"Ilie Murgulescu" Institute of Physical Chemistry, Romanian
Academy, Spl. Independentei 202, 060021 Bucharest, Romania

[|]ETH Zurich, Institute for Chemical and Bioengineering, 8093
Zurich, Switzerland

^{||}Paul Scherrer Institute, 5232 Viligen, Switzerland

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ABSTRACT: In this study, the synergistic behavior of Ni species and bimodal mesoporous undoped SnO₂ is investigated in oxygen evolution reaction (OER) under alkaline conditions without any other modification of the compositional phases or using noble metals. An efficient and environmentally friendly hydrothermal method to prepare bimodal mesoporous undoped SnO₂ with very high surface area (>130 m² g⁻¹) and a general deposition-precipitation methodology of well-dispersed Ni-species on undoped SnO₂ is reported. The powders have been characterized by adsorption-desorption isotherms, TG-DTA, XRD, SEM, TEM, Raman, TPR-H₂, and XPS. The best NiSn composite generates, under certain experimental conditions, a very high TOF value of 1.14 s⁻¹ and a mass activity higher than 370 A g⁻¹, which are remarkable results considering the low amount of Ni deposited on the electrode (3.78 ng). Moreover, in 1M NaOH electrolyte this material produces more than 24 mA cm⁻² at an overpotential value of approx. +0.33 V, with only 5 wt. % Ni species. This performance steams from the dual role of undoped SnO₂, on the one hand as support for active and well dispersed Ni species and on the other hand as an active player through oxygen vacancies generated upon Ni deposition.

1. Introduction

The increasing worldwide energetic demands in the last decades push humankind to seek for alternatives to the actual environmental unfriendly carbon-based energy production processes.¹ In this regard, alkaline water electrolysis, fuel cells and metal-air batteries are nowadays among the most studied energy conversion and storage systems.²⁻⁶ All these systems are two electrode systems, with hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) taking place at cathode, while at the anode oxygen evolution³ reaction (OER) or oxidation of chemical fuels is performing.⁷ Among these, OER, which is a complex 4 electron-transfer process, requires a higher overpotential to surpass its kinetic barrier in comparison to the more energetically favorable HER.⁸⁻¹¹ To date, there is a huge interest to find proper balanced cost/performance alternatives to the commercial RuO₂ and IrO₂, which are considered the most active OER electrocatalysts, mainly due to their low operating overpotential values.¹²⁻¹⁴ In this regard, the 3d transitional-metal oxides and oxyhydroxides and especially Ni-based materials have attracted considerable attention due to their low cost, easy availability, strong strength, better ductility, high corrosion resistance, good heat conduction, and high electrical conductivity.¹⁵⁻³² Thus, Ni-based composite electrodes, such as NiP₂, Ni chalcogenides, Ni (oxy)hydroxides or

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3 oxides and Ni-metal organic frameworks show very good activities
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5 for OER.³³⁻⁴³
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8 However, to achieve barely similar or better electrocatalytic
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10 performances to that of the benchmarked RuO₂ and IrO₂
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12 electrocatalysts, the Ni-based materials properties need to be
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14 optimized. In other words, apart from their composition, the
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16 materials must have large surface area with accessible active
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18 centres and a porous network architecture that facilitate the
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20 transport of electrons/ions within the electrode-electrolyte
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22 interface.⁴⁴⁻⁴⁸
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26 Moreover, recently modified Ni foam (NF) materials, such as
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28 Ni(OH)₂/NF,⁴⁹ MoO_x/Ni₃S₂/NF,⁵⁰ Ni₂P/Ni/NF⁵¹ or Ni₃Se₂/NF,^{31,52} gained
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30 importance due to their excellent conductivity and stability in
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32 alkaline media, which recommend them as good candidates for OER
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34 applications. For example, a composite electrode containing Ni₃S₂
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36 deposited on Ni foam presented a very good electroactivity in OER
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38 with a low onset overpotential of ~157 mV in alkaline solution, in
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40 the detriment of a high Tafel slope of 159 mV dec⁻¹.⁵³ Composites
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42 such as Ni₃Se₂ films deposited on NF revealed an overpotential of
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44 0.270 V to get 10 mA cm⁻². However, an unusual error of ±0.2 V,
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46 which represents ~75% from the observed overpotential, was
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48 reported.³¹ A more complex system Ni_xFe_{1-x}Se₂-DO achieves 10 mA cm⁻²
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50 at an overpotential of only 195 mV in alkaline solution, without
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52 elucidating the active species involved in the process.⁵⁴
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Furthermore, these Ni or NF based materials are not the most economical and viable options based on the overpriced Ni foam used in the synthesis of the anodes.

In this context, the deposition of active electrocatalytic materials in both, low amount and less costly matrices, through a preparation strategy that allows the control of the phase composition, surface segregation of different components and provide large surface areas, has become a growing topic lately.^{43,55,56} Moreover, as the OER takes place under harsh anodic conditions, then, the supports must have sufficient stability and electronic conductivity to overpass corrosion.⁵⁷ In this aspect, the use of carbonaceous materials is not recommended for this application as they usually undergo degradation under high electrical potentials applied at the oxygen electrodes, and thus, other alternative supports are required.^{58,59} Over the last decade or so, the focus has shifted towards exploring novel non-carbonaceous electrocatalyst supports that enable faster electron transfer and high electrocatalytic activity.⁶⁰ Among these, SnO₂ based materials has special features such as corrosion endurance, high electron mobility and good electric conductivity.⁶¹⁻⁶⁴ In the undoped form, SnO₂ presents n-type conductivity due to oxygen vacancies and interstitial tin atoms, which act as donors.⁵⁹ Moreover, tin oxides enhance stability and activity of an

electrocatalyst due to a strong electrocatalyst-support interaction.⁶⁶

However, although SnO₂-based materials possess these attractive electrochemical characteristics, most of its applications are focused on lithium-ions batteries^{62-64,67-73} and scarcely used for OER application.^{57,61,65,66} Meyer et al. report the use of SnO₂ doped with fluor (FTO) and surface-modified with Co(II) for OER, and underline that the FTO has a role as a conductive support for Co-catalyzed water oxidation and as sensor for O₂ as it is produced. The best results reported are a TOF of 4 s⁻¹ per Co site and a very high overpotential of 800 mV at pH 7.2.⁷⁴ There are also other studies that employ doped SnO₂ based materials for OER reaction with good results,⁷⁴⁻⁷⁶ but very few using undoped SnO₂.

Going on this research line, herein, we report a general deposition-precipitation methodology for direct synthesis of a well-dispersed Ni-based electrocatalyst on bimodal mesoporous SnO₂ support (abbreviated in this work as NiSn), which led to the formation of a highly active and stable material for OER applications. To the best of our knowledge, the use of undoped mesoporous SnO₂, with very high surface area (>130 m² g⁻¹), as support for OER electrodes, is for the first time reported in literature. The powder prepared materials containing different Ni loading (1, 5 and 15 wt. %) and thermally treated at different temperatures (80, 200 and 600 °C) were exhaustively characterized

and tested for OER. These composites can catalyze the OER under harsh alkaline conditions without any other modifications of the compositional phases or containing noble metals.

2. Experimental Section

2.1. Materials Preparation. Mesoporous SnO₂ was prepared by a hydrothermal synthesis route, as following: Tin (IV) chloride pentahydrate (SnCl₄·5H₂O) aqueous solution was added to the micellar solution formed by a very well dispersion of template -Triton X100 in Milli-Q water. The tetrabutylammonium hydroxide solution (40 wt. % in H₂O) was used to adjust the pH value at 11. After vigorous stirring, the obtained solution has been hydrothermally treated at 160 °C for 48h under autogenously pressure. The resulted precipitate was filtered and washed with Milli-Q water, dried at 100 °C and calcined at 600 °C for 8h in air. More details about the preparation procedure can be found in the Supporting Information.

The obtained SnO₂ was used as support for Ni-based electrocatalysts. For this purpose, deposition-precipitation method was employed. The preparation of NiSn materials has first involved dissolving the nickel inorganic salt (nickel (II) chloride hexahydrate) in Milli-Q water, followed by the *in-situ* reduction with hydrazine monohydrate under vigorous magnetic stirring at room temperature. Once with the formation of Ni nanoparticles, the appropriate amount of mesoporous SnO₂ (0.99 and

0.95 g, respectively) was added to each, as prepared solution containing different amounts of Ni (0.04 and 0.20 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, respectively) to finally form 1 g of material containing 1 and 5 wt. % of Ni, respectively. The slurries were left to stir for another 2h. The obtained solid materials were filtered and washed thoroughly with Milli-Q water in order to remove any unreacted reducing agent. Finally, the thermal treatment was carried out at three different temperatures (80, 200 and 600 °C) for 5h in air. The obtained samples were denoted function of Ni content and treatment temperature, as follow: 1NiSn (80, 200 or 600) and 5NiSn (80, 200 or 600), with the front number corresponding to the loading percentage and the number within the brackets representing the temperature at which the thermal treatment was made.

The same preparation and post-treatment methodology were adopted in the synthesis of Ni-based catalysts deposited on commercially available Vulcan XC-72R carbon support and 15NiSn (80, 200 or 600).

The electrodes used in the voltammetric experiments were prepared by different methods: (i) immersion of a freshly polished glassy carbon electrode ($d = 1 \text{ mm}$) in a suspension of NiSn composites with different Ni contents allowing the free adsorption to occur, and (ii) drop casting of a known amount of NiSn at the glassy carbon electrode (GCE) surface in the presence or absence of a Nafion solution. In the case of free adsorption deposition, the freshly polished GCE was immersed for different intervals

(minutely from 1 to 10 minutes) into the freshly prepared suspension of each studied NiSn composites. Before each deposition, the suspensions containing the catalysts were sonicated for at least 5 minutes to ensure a good dispersion of the solid (25 mg of material) within the solvent (10 mL of Milli-Q water). For the drop-casting deposition procedure in the presence of Nafion 117 solution (5 % in a mixture of lower aliphatic alcohols and water), 5 μL of catalyst at a concentration of 2.5 mg mL^{-1} (corresponding to a loading of 12.5×10^{-3} mg) was dropped onto the GCE surface followed by air-drying and coating with a Nafion film as a protective membrane. To drop-casting of the catalysts onto GCE surface in the absence of Nafion solution, the same procedure was followed, this time without adding the protective Nafion membrane. After each above described deposition procedure and before each electrochemical measurement, the working electrodes were rinsed thoroughly with Milli-Q water in order to remove the un-adsorbed or loosely bound catalyst and then placed into the electrochemical cell containing NaOH at different concentration where the electrochemical experiments were performed. The glassy carbon working electrode was polished using diamond (particle size 1 μm) (Kernet Int., UK) before each electrochemical experiment. After polishing, the electrode was rinsed thoroughly with Milli-Q water. Following this mechanical treatment, the electrode was placed in a buffer supporting

electrolyte and voltammograms were recorded until a steady state baseline voltammogram was obtained. This procedure ensured very reproducible experimental results.

Mili-Q water with a resistance of 18.2 M Ω at 25 °C was employed in the preparation of all electrolyte solutions used in this work. Moreover, it has to be stated that all the reagents used were highly pure and NiCl₂•6H₂O, has a purity of 99.998% (Sigma-Aldrich), with an Fe content of 2 ppm. However, for the small Ni loading used in this study, the Fe contamination and its influence over the electrochemical behavior is excluded. To highlight this, additional experiments were performed in order to prove that no Fe ions were found in the reaction media. Thus, the Fe content was investigated through ICP-MS analysis (using a Plasma Quant MS Elite equipment from Analytik Jena) that confirms that no such species were detected before/during and after performance of the OER.

2.2. Methods of Characterization

2.2.1. Thermal Characterization. The differential thermal analysis (DTA) and thermogravimetric analysis (TG) of the dried materials were carried out using a TG-DTA analyzer Shimadzu DTA-60 instrument on 4-6 mg samples in N₂ atmosphere with a heating rate of 5 °Cmin⁻¹ from room temperature to 900 °C, using alumina as reference.

2.2.2. Powder X-Ray Diffraction (XRD). The XRD analyses were carried out on a Schimadzu XRD-7000 diffractometer using Cu K α

radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA) at a scanning speed of 0.10 degrees min^{-1} in the 2θ range of 6–70 degrees with a step size of 0.02° and scan time of 2°min^{-1} .

2.2.3. Scanning Electron Microscopy (SEM). Scanning electron micrographs of the samples were taken with a scanning electron microscope model Vega II LMU from Tescan, equipped with a spectrometer of energy dispersion of X-ray (EDX) Bruker Quantax 200, at the following operational parameters: accelerating voltage 30 kV, measuring time 1200 s, working distance around 17 mm, counting rate 0.4 kcps.

2.2.4. Transmission Electron Microscopy (TEM). For the TEM investigation, the material was dispersed in ethanol and a few drops of the suspension were deposited onto a perforated carbon foil supported on a copper grid. After evaporation of the ethanol, the grid was mounted on the single tilt holder of the microscope. TEM was done on a Tecnai F30 (Thermo Fisher), operated at an acceleration potential $U_{\text{acc}} = 300 \text{ kV}$ (field emission gun (FEG)). Scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDXS) was performed on a Talos microscope (FEI; high brightness field emission gun), operated at an acceleration potential of 200 kV. Four EDX detectors are attached to this microscope allowing one to recorded EDXS maps with good signal to noise ratio in relatively short time (here 10–

20 min). STEM images were recorded with a high-angle annular dark field (HAADF) detector.

2.2.5. Textural Analyses. Porosity Analysis (BET) - Brunauer-Emmett-Teller adsorption-desorption isotherms of N₂ were investigated using a Micrometrics instrument (ASAP 2010) by N₂ adsorption at the nominal temperature of liquid nitrogen (77K) and at a wide relative pressure range from 0.01 to 0.995. Prior each analysis, the samples were degassed at 150 °C for 5h using helium.

2.2.6. Temperature Programmed Reduction Analysis (TPR-H₂). The reduction behavior was studied by TPR-H₂ on a Micromeritics Autochem 2910 equipment. About 50 mg of sample (particle size 0.25-0.42 mm) was initially flushed with Ar at room temperature (RT) for 30 min. then, the gas was switched to the reductive mixture of 10 vol. % H₂ in Ar (50 mL min⁻¹) and the temperature linearly increased from RT to 900 °C at a heating rate of 10 °C min⁻¹. Water formed in the reduction was retained in *i*-propanol/N₂(l) trap and the H₂ consumption rate was monitored with a thermal conductivity detector (TCD) previously calibrated using the reduction of CuO as reference.

2.2.7. Raman Spectroscopy. Raman spectra were obtained by using a Jobin Ivon Raman microprobe instrument, with an excited wavelength of 632 nm laser radiation. All the spectra were recorded between 200 and 1000 cm⁻¹ with a x50 objective which focuses the laser beam in a spot of 100 mm.

2.2.8. X-Ray Photoelectron Spectroscopy (XPS). Surface analysis performed by XPS was carried out on PHI Quantera equipment with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was monochromatized Al K_{α} radiation (1486.6 eV) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the Au4f_{7/2} photoelectron line (84 eV). Although the charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer, the spectra were calibrated using the C1s line (BE = 284.8 eV) of the adsorbed hydrocarbon on the sample surface (C-C or (CH)_n bondings).

2.3. Cyclic Voltammetry. The voltammetric experiments were carried out using an Ivium CompactStat running with Ivium software (Ivium Technologies, The Netherlands). A system of three electrodes was used, which consisted of an Ag/AgCl as reference electrode, a platinum wire as auxiliary and GC working electrodes prepared as described in section Electrochemical characterization. Cyclic voltammograms (CVs) were recorded in both, 0.1 M and 1 M NaOH at different scan rates using a 2 mV step potential and various scan rates.

2.4. Electrochemical Impedance Spectroscopy (EIS). EIS was carried out using a perturbation of 10 mV. The data was collected for 60 harmonic frequencies from 100 kHz to 0.1 Hz, at 10 steps/decade, and different polarization potentials. The impedance spectra were collected in 0.1 M NaOH and analyzed by fitting to a

Randles-type equivalent electrical circuit using ZView software (Scribner Associates, USA).

3. Results and Discussion

3.1. Structural, morphological and textural properties

3.1.1. Textural characterization. The N₂ adsorption-desorption isotherms for the supported and unsupported samples are presented in Figure 1 (a and c) and are characterized by a hysteresis loop at higher partial pressures. According to the IUPAC classification, this kind of isotherm corresponds to type IV and is specific to mesoporous solids. The initial part of the isotherm is attributed to monolayer-multilayer adsorption and the hysteresis loop is associated with capillary condensation taking place in mesopores.

Figure 1. Adsorption-desorption isotherms for SnO₂ (red), 1NiSn200 (blue), 5NiSn200 (green) (a) and 5NiSn treated at different temperature (80 °C- black; 200 °C green and 600 °C brown) (c) and their pore distributions (b) and (d), respectively.

The pure SnO₂ still possess a high surface area of 134 m²g⁻¹ as determined by BET formalism, even though the sample was calcined at high temperature (600 °C), while the surface area obtained using Langmuir formalism is around 187 m² g⁻¹ indicating the presence of some micropores. The pore size distribution of SnO₂ derived from

the desorption isotherms using the BJH formalism for mesopores⁷⁷ is presented in Figure 1b. The analysis revealed a bimodal pore size distribution with two kinds of pores, mainly uniform and narrow pore size distribution of about 5 nm and a low percentage of particles with pore diameter of about 12 nm. The bimodal structure can be also observed in the hysteresis loop, where different capillary condensation phenomena take place in non-uniform pores with different sizes and volumes (see Figure 1a).

It is interesting to note that by Ni deposition on the SnO₂ the surface area is almost the same for the samples post-treated at 80 and 200 °C, with surface area between 123–128 m² g⁻¹ due to a good dispersion of the Ni species on the SnO₂ surface, while for the Ni containing post-treated sample at 600 °C the surface area decreases with 20–30% (see Supporting Information, Table S1), due to the agglomeration of Ni species at the surface.

The bimodal structure observed initially in the pore distribution fade away with the increasing of the Ni loading on the SnO₂ surface (see Figure 1a, b and d) and only one narrow size distribution of pore remains for 5 wt. % Ni loading. We can assume that the pores with large diameters are easily diffused and blocked by Ni particles than pores with smaller size.

3.1.2. Powder X-Ray Diffraction. X-ray diffraction (XRD) measurements were conducted to identify the overall phase compositions of the resulting SnO₂ powders, as seen in Figure 2.

The pure SnO₂ sample calcined at 600 °C exhibited only the tetragonal phase with space group P42/mnm (JCDPS No. 77-0449) and the major diffraction lines appear at $2\theta = 26.8^\circ, 33.9^\circ, 38.6^\circ, 51.9^\circ, 62.1^\circ$ and 65.5° , respectively. It is worth noting that there is no indication of the presence of both, low temperature monoclinic or high temperature cubic phases. The peaks have a broad contour, due to the small size of particles. Indeed, the mean crystallite size of the SnO₂ nanoparticles was estimated by the Scherrer equation and was found to be approximately 4 nm (see Supporting Information, Table S1). Additionally, assuming that the particles have spherical - shape and uniform size, the average grain size was estimated from surface area using the formula $d = 6000/qA$; where q is the theoretical density of the material (theoretical density of tin dioxide nanoparticles is 6.95 mg cm^{-3}) and A is the specific surface area of the powder.^{78,79}

Figure 2. Powder X-ray diffraction patterns for 1NiSn200 (blue), 5NiSn200 (green) supported and unsupported SnO₂ (red) based materials.

The value obtained from this equation indicates also a small average grains size approximately 6 nm (see Supporting Information, Table S1). The phase structure of SnO₂ remained almost unchanged, as revealed by XRD, for the samples containing 1 wt. % Ni, and no extra peak from any impurity phase was observed (see Figure 2 and Supporting Information, Figure S1). This observation suggested that Ni did not significantly segregate on the support or is present as α -Ni(OH)₂ which has low XRD intensities owing to high general structural disorder.

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3 Additionally, with the increase of Ni loading to 5 wt. %, a new
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5 small line is observed at 44.5° for the samples 5NiSn80 and 5NiSn200
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7 (see Figure 3), which is characteristic to metallic Ni diffraction
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9 plane (111) (JCPDS, file No. 70-0989).^{80,81}
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12 The presence of metallic nickel was expected, due to the reduction
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14 with hydrazine in the preparation step. The other two
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16 characteristic peaks for metallic Ni at 51.8° and 76.8° which
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18 correspond to the (200) and (220) diffraction planes, respectively
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20 could not be excluded, since they overlap with those of SnO_2 . With
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22 the increase of the Ni post-treatment temperature, at 600°C , the
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24 diffraction line from 44.5° is shifted to a sharp new line at 43.3°
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26 characteristic to (200) diffraction plane of NiO particles (JCPDS,
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28 file No. 47-1049) and is due to the oxidation of metallic Ni
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30 particles to NiO bigger crystallite during the post-treatment at
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32 600°C in air (see Figure 3).⁸²
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Figure 3. Powder X-ray diffraction patterns for 5NiSn materials at different temperatures (80 °C, black; 200 °C green and 600 °C brown).

However, the presence of NiO on the sample 5NiSn80 and 5NiSn200 could not be excluded, because, as will be shown further from SEM and TEM analysis, Ni is very well dispersed, contrarily to the samples treated at 600 °C where agglomeration of Ni was evidenced.

3.1.3. Thermal Analysis and Temperature Programmed Reduction Characterization. The thermogravimetric and differential thermal analyses (TG-DTA) profiles of the dried SnO₂ samples are presented in Figure S2 (see Supporting Information). The TG profiles show a weight loss of 15 wt. % up to 400 °C in two steps. The first one is related to the loss of H₂O and the second one is due to the

elimination of the organic material. These losses are accompanied in DTA profiles by endothermic peaks at 100 °C and 330 °C.

Figure 4. TPR-H₂ spectra of SnO₂ (red) and NiSn samples (1 wt.% Ni, blue and 5 wt. % Ni, green).

In the literature, the transition temperature of amorphous to crystalline phase in undoped SnO₂ materials is reported to be below 300 °C.^{83,84} In this study, the transition temperature is around 330 °C, which can be related with surface chemistry of the material. Nature and high concentration of surface hydroxyls on SnO₂ together with small crystallite size might be the reason for the higher crystallization temperature.

3.1.4. The Reduction Profiles (TPR-H₂). The TPR-H₂ of tin oxide-based samples are presented in Figure 4. The thermal treatment at 600 °C of pristine tin oxide, leads to Sn species reducible at high

temperature, ~640 °C, at which the reduction profile shows one broad reduction peak.

The 1NiSn200 profile is similar with one of pure SnO₂, the difference consists in a lower reduction temperature for Sn species. The absence of any other reduction peak indicates that the Ni oxide species interact strongly with the support or they are already in the reduced state.^{85,86}

The profile of higher Ni loading containing sample (5NiSn200) consists into two regions corresponding to the reduction of the different types of Ni species as well as Sn species: i) the first peak in the low temperature range (300 to 400 °C) can be attributed to the Ni reduction of both NiO from the surface and the subsurface to metallic Ni interacting weakly with the SnO₂;^{87]} ii) the second region, in the high temperature range corresponds to the reductions of Sn⁴⁺ to Sn²⁺.⁸⁷

The absence of the very low-temperature peak, around 200 °C, which is due to the reduction of Ni³⁺ (Ni₂O₃) to Ni²⁺ (NiO)⁸⁸ indicates that in these samples no Ni³⁺ species are present. The TPR obtained results are in good agreement with the XRD results, which revealed also the existence of the Ni⁰ and Ni²⁺.

3.1.5. Raman Spectroscopy. The presence of oxygen vacancies in SnO₂ due to the thermal treatment or doping can be revealed by Raman spectroscopy.⁸⁹⁻⁹³ Theoretically, the vibration modes present

in rutile tetragonal SnO_2 are composed from 4 active Raman modes at 633, 775, 782 and 477 cm^{-1} , which are assigned to A_{1g} , B_{1g} , B_{2g} and E_g respectively, 3 forbidden modes (A_{2g} , $2B_{1u}$), and 8 IR modes, namely $3E_u$ (TO) at 244, 293 and 618 cm^{-1} , $3E_u$ (LO) 276, 366 and 770 cm^{-1} , and $2A_{2u}$ at 502 and 694 cm^{-1} corresponding to TO and LO modes respectively, which are normally silent in Raman.⁹⁴ As can be observed from Figure 5, for the pure SnO_2 and $1\text{NiSn}200$, the Raman active modes A_{1g} , B_{1g} , together with the A_{2u} (TO) IR active modes (which should be silent) and a shoulder at $440\text{--}450\text{ cm}^{-1}$ are present. The appearance of the IR modes in the spectrum was correlated to presence of a certain lattice disorder and surface defects, due to the oxygen vacancies produced during the preparation process.

Figure 5. Raman shift for SnO₂ (red), 1 NiSn200 (blue) and 5NiSn200 (green) samples.

This behavior can be translated by changes in the perfect crystal structure together with relaxation of $k = 0$ rules and activation of IR modes in Raman.⁹⁰⁻⁹³ The Raman band present at 440-450 cm⁻¹ is associated to deeper oxygen vacancies. This band significantly decreases upon post-treatment of the samples at higher temperature (see Figure 5 and Supporting Information, Figure S3) also in agreement with other studies.⁸⁹ The increase of Ni loading up to 5 wt. % produces important changes in the structure of SnO₂, as revealed in Figure 5. For instance, new IR active modes at 248 and 694 cm⁻¹, a new broad band at around 573 cm⁻¹ and a red shift of A_{1g} peak position are observed. All these changes are associated to the presence of both (sub)bridging and in-plane surface oxygen vacancies, which appear during the nickel deposition in higher loadings.⁸⁹⁻⁹¹ The increase of the calcination temperature of the Ni supported samples from 200 to 600 °C leads to the disappearance of the surface oxygen vacancies (see Supporting Information, Figure S3).⁸⁹

3.1.6. Scanning and Transmission Electron Microscopy. The morphology of the pure SnO₂ and the NiSn samples have been investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Representative SEM images

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3 accompanied with the EDX mapping of pure SnO_2 and 5NiSn200/600
4 samples are depicted in Figure S4 (see Supporting Information).
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6 For all samples, the surface morphology is relatively homogeneous,
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8 dense with a relatively rough surface and with high degree of
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10 agglomeration. The EDX spectra of the samples (see Supporting
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12 Information, Figure S5) confirm the existence of Sn, O and Ni
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14 elements. Also, the EDX mapping of the surface reveals that in the
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16 case of 5NiSn200 the Ni (coded in green color) are better
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18 dispersed on the surface of SnO_2 than for 5NiSn600, due to a
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20 sintering effect induced by the temperature and the presence of
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22 O_2 , and the Ni particles agglomerate, which is in good agreement
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24 with TEM presented further.
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30 By TEM, the SnO_2 nanoparticles were observed to have a crystallite
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32 size of approximately 5 nm (see Figure 6). This particle size
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34 remained unaltered during Ni deposition step and different thermal
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36 treatments (e.g. 80 °C, 200 °C, and 600 °C), which followed this
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38 deposition step. This is in agreement with the calculated particle
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40 sizes from X-ray diffraction.
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Figure 6. HAADF-STEM with EDX mapping of 5NiSn samples for different thermal treatments - (a, b, c) 200 °C (d, e, f) 600 °C; TEM images of 5NiSn80 (g), 5NiSn200 (h), and 5NiSn600 (i).

The NiSn samples were further characterized HAADF-STEM as well as additional EDX mapping. For 5NiSn samples, Ni was observed to be distributed homogeneously (see Figure 6) when thermally treated

at 200 °C and confirm the observation from the SEM and EDX. However due to Ni being less than Sn in atomic number, no contrast on the SnO_2 was able to be observed by STEM. As already observed by SEM, the TEM also confirms that the thermal treatment at 600 °C after Ni deposition determine the Ni agglomeration (see Figure S14-S17). The size of the Ni agglomerations covers several nm to several hundred nm and can attain various morphologies from cornered shapes to diffuse clouds shapes (see SI, Figure S14-S17).

3.2. X-Ray Photoelectron Spectroscopy Characterization

The X-ray photoelectron spectroscopy (XPS) analysis was used in order to determine the chemical states and to identify and quantify the elements present on the surface (see Figure 7 and Supporting Information, Figure S6 and Table S2). The $\text{Ni}2\text{p}_{3/2}$ high resolution spectra of all four samples display five characteristics components (denoted *c1-c5*). In the sample 5NiSn200, the component *c1* at low binding energies (BEs), 854.6 eV can be assigned to the supported Ni^{2+} oxide in octahedral arrangement,^{95,96} while the component *c2* at 856.1 eV suggests the presence of Ni^{2+} oxide with structure defect and/or the presence of the $\text{Ni}(\text{OH})_2$ species.⁹⁶⁻⁹⁹ For the sample calcined at 600 °C (5NiSn600) *c1* and *c2* are shifted to lower BEs. The component *c1* at 853.6 eV is usually associated with un-supported Ni^{2+} oxide,⁹⁶ meaning that at the surface of the catalyst NiO segregate to bigger crystallite due to the high post-

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3 treatment temperature. This phenomenon was also observed in XRD
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5 patterns and is in agreement with SEM and TEM analysis. The shift
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7 to lower BEs of *c*2 (855.7 eV) during thermal treatment is due to
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9 a change in the environment of Ni²⁺ species and a change also of
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11 the nature defects.^{96,99} The *c*2/*c*1 ratio decreases with 44% when
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13 the 5NiSn sample was heated until 600 °C (see Supporting
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15 Information, Table S2), indicating a decrease of the defect in the
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17 NiO structure and a lower amount of Ni(OH)₂ at the surface for
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19 5NiSn600 as compared with 5NiSn200, in agreement with Raman
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21 analysis. The broad loss peak (*c*3) found at 857.9 eV is a surface
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23 plasmon feature associated with Ni²⁺ species.^{95,100} The other two
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25 components (*c*4 and *c*5) at 861.4 eV and 865.4 represent the Ni²⁺
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27 energy losses due to "shake-up" process.
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Figure 7. Ni 2p_{3/2} and O1s XP spectra for the 5NiSn200 samples (a) and (b), respectively; and for the 5NiSn600 (c) and (d), respectively.

The experimental values of Ni relative concentrations are close to the nominal ones (within our experimental errors) except for the sample 1NiSn200 (see Supporting Information, Table S2), where higher Ni content was found on the surface. This behavior suggests a segregation process of Ni from the bulk to the surface, or a lower diffusion rate at this temperature.

The deconvolution of the O1s photoelectron line (see Figure 7b, d and Supporting Information, Figure S6) exhibits three features: the main lattice bound component (O²⁻), OH groups adsorbed on the

outermost surface layer and bound on Ni or in $\text{Ni}(\text{OH})_2$ as well as adsorbed water. A close examination of Figure 7b, d and Table S2 (see Supporting Information) reveals that the samples thermally treated at 200 °C show a stronger surface hydroxylation as compared to the samples treated at 600 °C. Moreover, the sample 5NiSn200 displays the highest percentage of OH groups and H_2O adsorbed, accounting for ~30% overall relative concentration. As a result of the BEs overlapping for the adsorbed OH and oxygen vacancies we cannot assess quantitatively the presence of the latter features. However, one can infer that this sizable increase of OH contribution might originate from a rise in oxygen vacancies contribution, as revealed by Raman spectroscopy.

The BEs of $\text{Sn}3d_{5/2}$ photoelectron line clearly reveals the +4 oxidation state (see Supporting Information, Figure S6 and Table S2). However, a shift to lower BEs (0.3 eV) was observed when the amount of Ni increases in the sample from 1 to 5 wt. %. This behavior can be explained by the increase of the amount of a new species formed (Ni-O-Sn) during deposition of Ni on SnO_2 , which appears at lower BEs.^{96,98,101} A small shift to lower energies (0.2 eV) was also observed during calcination, a cumulate effect owed to a higher interaction of Ni with the support and morphology modification.

3.3. Electrochemical Characterization

For each sample, cyclic voltammograms were performed in 0.1 M NaOH supporting electrolyte after free adsorption at the GCE surface during 3 min (see Figure 8a and Supporting Information, Figures S7 and S8). In general, the voltammetric profile showed on the positive-going scan, the reversible oxidation of Ni^{2+} species in the NiO/Ni(OH)_2 layer with the formation of Ni^{3+} species such as NiOOH . The oxidation peak occurred on the anodic scan at $E_{\text{pa}} \sim +0.52$ V and on the cathodic scan, the reduction at $E_{\text{pc}} \sim +0.46$ V showed the reversibility of the redox couple ($\Delta E_p \sim 60$ mV specific to 1 electron transfer) (see Figure 8a). At higher positive potential values, $E > +0.60$ V vs. Ag/AgCl, the anodic current increase is attributed to water oxidation on NiSn catalysts surface. Thus, an overpotential $\eta \sim +0.33$ V for OER on Ni/SnO_2 catalysts was estimated for all Ni containing samples based on $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 \times \text{pH}^{102}$ and $E_{\text{H}_2\text{O/O}_2}^0 = +1.23$ V for water oxidation, which is comparable to previous reports on Ni-based catalysts²⁰. Nevertheless, higher currents, related either to Ni ions redox reaction or to water oxidation, were recorded for the 5NiSn200 and 5NiSn600 samples (see Figure 8a and Supporting Information, Figure S8).

This result can be explained considering both a higher quantity of Ni loaded onto the SnO_2 support and also by the presence of NiO/Ni(OH)_2 species as evidenced by XPS and XRD, essential for the

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3 catalytic reaction, since water adsorbs favorably on the surface
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5 of the oxides or hydrated species, which is a critical step in the
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7 OER process. On the other hand, this effect is explained by a high
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9 material conductivity due to an increased carrier density induced
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11 by oxygen vacancies.^{103,104} The SnO₂ possess deeper oxygen vacancies
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13 as revealed by Raman spectroscopy. A certain lattice disorder and
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15 surface defects are evidenced after Ni deposition, and have a
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17 proportional effect with Ni loading being related to the surface
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19 oxygen vacancy. This seems to be beneficial for water oxidation
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21 process and the synergy between the SnO₂ and the Ni species increase
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23 the conductivity of this sample. However, the increase of the
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25 calcination temperature of the Ni supported samples from 200 to
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27 600 °C leads to the disappearance of the deeper oxygen vacancies,
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29 which in theory should correspond to a lower conductivity. This
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31 assumption is in good agreement with the observed electroactivity
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33 for the sample treated at 600 °C, which is less active than the
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35 one treated at 200 °C (see Figure 8a and Supporting Information,
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37 Figure S8). Other researchers also reported the synergy between
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39 the active electrocatalytic species (Ni₃S₂) and the support (Ni
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41 foam) which boost the OER performances.⁵³
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49 For comparison, the support (SnO₂), 5Ni/C treated at 200 °C and
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51 the well-established RuO₂ were evaluated in the same reaction
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53 conditions (see Supporting Information, Figure S7). The results
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showed the inactivity of SnO_2 sample, while 5Ni/C catalytic activity has a similar electrocatalytic behavior compared with that of 5NiSn200, but lower electroactivity for water oxidation. Concerning RuO_2 sample, the catalytic activity takes place for higher positive potential values, $\eta \sim +0.53$ V in our working conditions. Thus, if initially the main role of SnO_2 was as spectator, to inertly support the Ni species, it turned out that after Ni deposition, SnO_2 was transformed into an active player which intensively participates with Ni to the OER.

Tafel analysis has been also performed on 1NiSn200 and 5NiSn200 in order to estimate their efficiency for water oxidation (see Supporting Information, Table S3). The smallest Tafel slope ~ 59 mV/decade was achieved in the case of 5NiSn200 sample and the highest ~ 250 mV/decade was recorded for 1NiSn200 (see Supporting Information, Table S3). This result proves that 5NiSn200 has the highest catalytic efficiency for water oxidation and for this reason this sample has been subjected to intense electrochemical investigation. Is worth noting that higher Ni loading (15 wt.%) was also tested (see Figure S7) and increased amount of Ni is detrimental to OER.

First, the adsorption time effect was investigated for 5NiSn200 sample (see Figure 8b). By increasing the adsorption time, both currents related to Ni ions redox reaction and water oxidation

increased, in agreement with the deposition of a larger quantity of the catalyst. Taking into consideration this result, an adsorption time of 3 minutes was used for further investigation.

The effect of the scan rate on 5NiSn200 sample was also evaluated (see Supporting Information, Figure S9). By increasing the scan rate the processes corresponding to Ni ions redox reaction showed increased currents. The plots of $\log I_{pa}$ and $\log I_{pc}$ function of $\log v$ were linear with slope of approx. 0.85 (see Supporting Information, Figure S9b), in agreement with a mixed adsorption and diffusion-controlled processes of the OH^- ions necessary for the formation of the oxohydroxide film through reactions (1) and/or (2):

The electrochemical performances of the 5NiSn200 sample can be explained by the amount of OH^- ions found on the surface, which, according to the Raman and XP spectroscopic results, is much higher than for the other prepared catalysts. Also, the plot of $\delta E_p / \delta \log v = 29/\alpha n$, where n is the number of electrons involved in the rate-determining step and α the charge transfer coefficient, were linear with slopes of approx. 30 mV per decade (see Supporting Information, Figure S9c). Thus $\alpha_a \sim \alpha_c \sim 1$ as for metallic electrodes. This result confirms the metallic character of the sample and is

in agreement with the presence of the Ni metallic species, as identified in XRD for the 5NiSn200 sample.

Graphical integration of the anodic current vs. potential curve obtained at $v = 10 \text{ mV s}^{-1}$ gave the total charge $Q = (6.2 \pm 0.63) \times 10^{-6} \text{ C}$ (RSD = 7.6%, $n = 3$) transferred during NiO/Ni(OH)₂ layer oxidation (see Supporting Information, Figure S9). Supposing that, during the scan, all the adsorbed molecules are oxidized, the surface concentration of the adsorbed layer can be calculated as $\Gamma = Q(nFA)^{-1} = 8.2 \times 10^{-9} \text{ mol cm}^{-2}$, where A is the electrode area in cm^2 , F Faraday constant and n the number of electrons involved during the oxidation step. The superficial concentration allowed the determination of $64.4 \times 10^{-12} \text{ mol}$ of the adsorbed material, therefore the average loading mass $m = 3.78 \text{ ng}$ or 481.5 ng cm^{-2} Ni species (75.6 ng or $9.6 \mu\text{g cm}^{-2}$ 5NiSn material, since the sample has 5 wt. % Ni) can be estimated in this case. It is worth noting that the amount used is almost one order of magnitude lower than the amounts reported for Ni₃Se₂/NF³¹.

Consecutive cyclic voltammograms were also recorded in 0.1 M NaOH (see Figure 8c). While the NiO/Ni(OH)₂-oxidation peak was unaffected by the number of scans, a slight increase of the NiOOH reduction current was observed but reached constant values after 3 potential cycles. Nevertheless, the current related to water oxidation processes strongly increased during the first 10 scans.

This behavior is consistent with previous reports²⁰ and with the conversion of the NiO/Ni(OH)₂ phase to the NiOOH phase, catalytically active towards water oxidation. Being aware of the leaching of SnO₂ in the electrolyte solution as stannate (SnO₄²⁻) species, we have increased the number of scans up to 150 (see Supporting Information, Figure S10), and an insignificant improvement of the currents was observed, showing a good stability of the catalyst over the electrode surface. Furthermore, as evidenced by TPR-H₂ experiments, the Ni oxide species interact strongly with the support, thus enhancing the stability.

Electrochemical impedance spectroscopy was used to investigate the physical and interfacial properties of the 1NiSn200 and 5NiSn200 samples in 0.1 M NaOH. Spectra were recorded at OCP values and also at potential values corresponding to water oxidation reaction (see Figure 8d). The spectra were fitted using an electrical equivalent Randles type circuit (see Figure 8d), which consisted of a RC combination correlated to the NiO-Ni(OH)₂/electrolyte interface and a Warburg impedance, Z_w , which can be associated to a finite diffusional process inside the NiO-Ni(OH)₂ layer, depending especially on the film porosity.

The circuit contained as first element R_s , which represents the ohmic drop and resistance caused by the electrical contacts and wires. The constant phase elements, defined as:

$$\text{CPE} = -(\text{Ci}\omega)^{-n} \quad (3)$$

is modelled as a non-ideal capacitor where the capacitance C describes the charge separation at the double layer interface and the n exponent is due to the heterogeneity of the surface. The R_{ct} is the charge-transfer resistance. The definition of the Warburg element used is presented in equation (4):

$$Z_W(W_S) = R_{diff} (i\tau\omega)^{-\alpha} \tanh[(i\tau\omega)^\alpha] \quad (4)$$

where R_{diff} is a diffusion resistance of electroactive species, τ is a time constant depending on the diffusion rate ($\tau = l^2/D$, where l is the effective diffusion thickness, and D is the effective diffusion coefficient of the species), and $\alpha = 0.50$ for a perfect uniform flat interface. Values of α less than 0.50 correspond to a not uniform interface (as happens with CPE non-ideal capacitance when $n < 1$).

Data from analysis of EIS at OCP, included in Table 1, showed a typical behavior for systems with high charge transfer resistances and the spectra has the aspect of an inclined line. Indeed, the R_{ct} presented values in the $10^4 \Omega$ range and slightly decreased in agreement with the increase of conductivity upon greater incorporation of Ni into the SnO_2 matrix. The cell resistance, R_s , showed small fluctuations with an average value of $\sim 1.2 \Omega \text{ cm}^{-2}$. Also, the interfacial capacitance (C) increased with Ni percentage due to an increase of the electroactive surface area per cm^2 and

the formation of a more compact double-layer, whereas the heterogeneity parameter, n , maintained an average value of about 0.90, in agreement with SEM and TEM images that showed the relative homogeneity of the surface. Also, the diffusion impedance showed small variations with increasing Ni content. The resistance R_{diff} as well as the time constant slightly decreased with increasing Ni content. The high surface area of SnO_2 reported for this material could play an important role for such diffusional process as previously described. Moreover, the preparation method for the Ni species deposition onto SnO_2 conserves the textural properties of the support (see Supporting Information, Table S1) which represent an advantage. Additionally, 5NiSn200 presents a well dispersion of Ni species as evidenced by SEM and TEM.

EIS was also performed at +0.70 V vs. Ag/AgCl corresponding to water oxidation reactions (see inset Figure 8d and Table 1). In this case, the spectra have the aspect of a semicircle corresponding to the electron transfer process and R_{ct} greatly reduces four orders of magnitude to $2.9 \Omega \text{ cm}^2$ while the capacitance value almost doubled. The diffusion resistance slightly decreased but the diffusional time constant reduces two orders of magnitude showing higher accessibility for mass-transfer and of ions through the electrochemical double layer at this potential value.

3.4. Performance and OER Catalytic Activities

The performance and the catalytic activity of the 5NiSn200 sample were investigated in 0.1 and 1.0 M NaOH. Three deposition methods that consisted in free adsorption and drop-casting with or without Nafion, were compared. The experiments were carried out by amperometry (see Figures 8e and f, and Supporting Information, Figure S11) at $E = +0.70$ V vs. Ag/AgCl. For comparison, 5NiSn600 presents lower catalytic activity (see Supporting Information, Figure S12).

For this investigation, the electrochemically active surface area (ECSA) was also calculated from the CV profiles and it was found to be 0.052 cm^2 (see Supporting Information, Figure S13). Thus, all values for maximum current density, TOF and mass activity of the 5NiSn200 catalyst are reported to both, the geometrical area of the GCE and ECSA (see Table 2). The amperometric results were consistent with the CV studies. For free adsorption (see Figure 8e), it was observed that the current density sharply increased during the first 30 min. After this period, the slope of the current increase became smaller, reaching maximal values for $t > 3$ h, showing a good stability and high durability of the catalyst (see Table 2). Considering these values, the turnover number was calculated based on the equation (5):

$$\text{TOF} = jA (4nF)^{-1} \quad (5)$$

where j is the current density, A the geometrical area of the GCE or the ECSA, n the number of moles of metal ion at the electrode surface and F represents the Faraday constant. The TOF value calculated in the case of free adsorption deposition procedure was found to be 1.14 s^{-1} (see Table 2) which is one order of magnitude higher than previous reports on Ni based electrocatalysts (see Supporting Information, Table S4) and a remarkable value considering the low amount of Ni used in the preparation of the catalyst, which promote this composite as a cost efficient one. The TOF for the best material (5NiSn200) was calculated assuming that only the Ni species are catalytically active for OER and taking into account the material loadings for both deposition procedures employed in this study: $75.6 \times 10^{-6} \text{ mg}$ and $12.5 \times 10^{-3} \text{ mg}$ for the free adsorption and drop casting method, respectively.

Also, the mass activity of the catalyst at $E = +0.70 \text{ V vs. Ag/AgCl}$ was estimated using the equation:

$$\text{mass activity} = jA/m \quad (6)$$

where j is the current density, A the geometrical area of the GCE or the ECSA, and m the mass of the 5NiSn200 catalyst. The mass activity values calculated in these conditions (see Table 2) are similar or higher than other reports on Ni based catalysts (see Supporting Information, Table S4).

The performance of the catalyst drop-casted at the GCE surface by procedures (2) and (3) is presented in Figure 8f and Figure S11. Procedure (2) consisted in drop-casting of 5 μL of the catalyst at a concentration of 2.5 mg mL^{-1} (corresponding to a loading of $12.5 \times 10^{-3} \text{ mg}$) followed by air-drying and coating with a Nafion film as a protective membrane (see Figure S11). The amperometric measurement at $+0.70 \text{ V}$ vs. Ag/AgCl in 0.1 M NaOH solutions (see Figure S11 and Table 2) showed a maximal current value j_{geo} of 6.1 mA cm^{-2} , but degradation was observed for $t > 2.5 \text{ h}$.

In procedure (3), after drop-casting without Nafion and air drying, the performance of the catalyst was investigated in 0.1 M NaOH solution (see Figure 8f and Table 2). Contrary to the procedure (2), a very good stability of the catalyst over the time length of the experiment was achieved in 0.1 M NaOH with the maximal current j_{geo} reaching values of 12.8 mA cm^{-2} .

The stability of the catalyst deposited, as previously described, was also investigated in 1.0 M NaOH (see Figure 8f and Supporting Information, Figure S11). In these extreme conditions, maximal current j_{geo} values of 24.4 mA cm^{-2} were recorded but faster catalyst degradation after 1.5 h was observed. A similar behavior was observed in these conditions when the catalyst was coated with a Nafion film.

Moreover, regarding the stability of these materials it's worth noting that the catalyst suspension prepared for the free adsorption and drop-casting electrode deposition method is still viable even after more than 1 year with perfect reproducibility of the OER performances. It must be once again underlined that all these results were achieved with a material that contains only 5 wt. % Ni and was used as powder.

Comparing the three deposition methods, it is observed that the highest stable current densities j_{geo} of 12.8 mA cm^{-2} during 4 h are achieved by drop-casting method. Adsorption, apart from a similar good stability during 4h, showed the highest turnover number of 1.14 s^{-1} , which is a remarkable result considering the low amount of electrocatalyst used in the preparation of the composites. This can be explained by taking into account that the drop-cast deposition method involves superimposition of catalyst molecules. For this reason, a large part of the catalytic centres is inactive/hidden toward/from water molecules. This is supported by the fact that the amount of catalyst drop-casted is two orders of magnitude higher than the adsorbed one but there is only a four folds increase in the current density.

Concerning the Nafion-coated catalyst, it is generally accepted that this polymeric membrane allows movement of cations, but impedes the conduction of anions, which explains the low current

density recorded with this deposition method (impedes the transfer of OH^- to the catalytic centres).

Figure 8. Cyclic voltammograms in 0.1M NaOH of: **a.** 1NiSn200 (—) and 5NiSn200 (—), first scan at $v = 50 \text{ mVs}^{-1}$ after adsorption during 3 min; **b.** 5NiSn200, first scan at $v = 50 \text{ mVs}^{-1}$ after different adsorption time intervals (1 min, light green; 2 min brown; 10 min dark green) ; **c.** 5NiSn200, consecutive scans at $v = 50 \text{ mVs}^{-1}$ after adsorption during 3 min (1 scan, black and 10 scan, red); **d.** impedance spectra at OCP and at $E = +0.70 \text{ V vs. Ag/AgCl}$ (inset) of 1NiSn200 (■) and 5NiSn200 (●), after adsorption during 3 min; **e, f.:** chronoamperogram at $E = +0.70 \text{ V vs. Ag/AgCl}$ in 0.1 M NaOH recorded for 5NiSn200 **e.** after adsorption during 3 min and

f. drop casted at the GCE surface in 0.1 M or 1.0 M NaOH, with (yellow) and without (orange) a Nafion protective membrane. The inset in fig. 8e shows current variation upon O₂ bubble release from the electrode surface and the photograph presents the O₂ bubble formation at the surface of the GCE.

Table 1. Values of equivalent circuit elements obtained by fitting the spectra recorded for different NiSn samples at different potential values in 0.1 M NaOH; equivalent circuit in Figure 8d.

Material	E (V)	R_s (Ω cm ²)	CPE		R_{ct} (Ω cm ²)	W_s		
			C (F cm ⁻²)	n		R_{diff} (Ω cm ²)	τ (ms)	α
1NiSn200	- 0.17 [a]	1.02	1.4×10^{-4}	0.91	5.5×10^4	904	0.87 7	0.41
5NiSn200	- 0.22 [a]	1.02	2.5×10^{-4}	0.89	2.1×10^4	136	0.13 2	0.32
	+ 0.70	1.4	4.8×10^{-4}	0.89	3.2	1.0	0.00 2	0.50

[a] OCP values

Table 2. Values of turnover frequency (TOF) and mass activity of 5NiSn200 deposited at the GCE surface by different procedures in electrolytes with different concentrations.

Deposition procedure ^[a]	Electrolyte concentration (M)	Max. current density (mA cm ⁻²)		TOF (s ⁻¹)	Mass activity (A g ⁻¹)
		geometric	ECSA		
Free adsorption	0.1	3.6	0.54	1.140	374
Drop casting	0.1	6.1 ^[b]	8.3 ^[b]	0.100	35
		12.8	17.4	0.220	72
	1.0	14.8 ^[b]	20.1 ^[b]	0.255	93
		24.4	33.1	0.420	138

[a] the material loadings: 75.6×10^{-6} mg for the free adsorption and 12.5×10^{-3} mg for drop casting method; [b] with Nafion

4. Conclusion

SnO₂ support with high surface area has been prepared by a cost efficient (at least 10 folds lower than Ni foam matrix) and environmentally friendly hydrothermal method. The simple deposition-precipitation methodology of Ni species on SnO₂ allows us to obtain a very well dispersion as evidenced by TEM, and does not alter the textural properties. A synergistic behavior of Ni species and bimodal mesoporous SnO₂ was proved, enhancing the electronic properties and therefore boosting the electrocatalytic activity for water oxidation reaction. The best material for OER (5NiSn200) displays a turnover frequency value of 1.14 s⁻¹ and a mass activity of 374 A g⁻¹, which are remarkable results compared to literature data. This notable behavior is mainly due to: i) high surface area, which plays an important role for diffusional

processes (diffusional resistance and impedance) responsible for the uniformity of the interface and enhance the electron transfer; ii) high amount of defects, responsible for the increase of sample conductivity, which are associated with the surface oxygen vacancies generated by the synergy between the SnO_2 and the Ni species, as revealed by Raman and XP spectroscopy, and iii) high amounts of OH^- species on the surface, disclosed by XPS analysis, which are directly involved in the electrochemical performance of the material. Also, this behavior is in agreement with X-ray diffraction data which confirmed the presence of the Ni metallic species and therefore the metallic/conductive character of the 5NiSn200 .

The aforementioned suggested synergistic coupling effect between the Ni species and the SnO_2 support is doubtless one of the essential reasons for the considerably improved OER performances of the NiSn electrocatalyst obtained in this study. All these, alongside with the actual cost of the techniques and the materials used in the preparation of NiSn, and as well as the environmentally friendly nature of the hydrothermal procedure used for the support synthesis, stands as solid evidence for the sustainability of this material for practical applications.

Considering our results on powder NiSn material, which are similar or better than the one obtained on film coated Ni based materials (well known for their advantages on OER performance),

encourage us to continue improving the electroactivity of this composite, by finding appropriate ways to obtain film coated electrodes, without losing its textural and structural properties.

ASSOCIATED CONTENT

Supplementary characterization data are presented in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*(Mihaela Florea) E-mail: mihaela.florea@infim.ro.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

Notes

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