Journal Pre-proof

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PII: S0013-4686(20)30306-6

DOI: <https://doi.org/10.1016/j.electacta.2020.135914>

Reference: EA 135914

To appear in: *Electrochimica Acta*

Received Date: 3 June 2019

Revised Date: 12 February 2020

Accepted Date: 14 February 2020

Please cite this article as: I. Sanjuán, L. García-Cruz, José. Solla-Gullón, E. Expósito, V. Montiel, Bi–Sn nanoparticles for electrochemical denitrification: Activity and selectivity towards N_2 formation, *Electrochimica Acta* (2020), doi: <https://doi.org/10.1016/j.electacta.2020.135914>.

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Graphical Abstract

Bi-Sn Nanoparticles for Electrochemical Denitrification: Activity and Selectivity towards N₂ Formation

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Submitted to: “Electrochimica Acta”

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Abstract

Electrochemical denitrification is a promising approach to remove NO_3^- towards its conversion to innocuous N_2 . In this work, the electrocatalytic performance of Bi, Sn and Bi_xSn_y carbon-supported nanoparticles (~ 10 nm) was evaluated for the selective NO_3^- electroreduction (*NER*) to N_2 . The different electrocatalysts were synthesised using a simple chemical method, physicochemically characterised by TEM-EDS and XPS and, subsequently, air-brushed onto a Toray carbon paper to build electrodes. These electrodes were characterised by SEM-EDS and cyclic voltammetry. Electrolyses were carried out in a slightly alkaline media to find the most active electrocatalyst towards the NO_3^- removal. Among them, $\text{Bi}_{60}\text{Sn}_{40}/\text{C}$ showed the best results with more than 50% of N_2 generated after exhaustive electrolyses, regardless of the cathode potential or the electric charge passed. Other detected non-desired secondary products were N_2O , NO_2^- and $\text{NH}_4^+/\text{NH}_3$. The results obtained point out that the combination of Sn and Bi gives rise to a higher *NER* activity and selectivity to N_2 than pure Bi and Sn nanoparticles. Therefore, these electrocatalysts are not only promising but also cost-effective for future practical applications like electrochemical denitrification of wastewater. Nevertheless, further investigation is still needed in order to assess the optimum operational conditions.

Keywords: Electrochemical denitrification, nitrate, bismuth, tin, nanoparticles.

1. Introduction.

Anthropogenic factors (nitrogen-based fertilisers in intensive agriculture, industrial activities...) are responsible for serious imbalances in the natural nitrogen cycle [1,2]. Consequently, nitrates (NO_3^-) concentration in surface and ground waters has considerably increased during the last decades, with negative impacts for the environment (eutrophication) [3] and human health [4]. NO_3^- can be reduced to nitrite (NO_2^-) in living organisms, which may cause methemoglobinemia, liver damage or even cancer. Accordingly, the legislation of different countries limits the allowed content of NO_3^- in drinking water. For instance, the World Health Organization (*WHO*) recommends $50 \text{ mg L}^{-1} \text{ NO}_3^-$ as a maximum [5].

According to this scenario, efficient denitrification strategies are clearly needed. Currently, the technologies available with this aim are divided into three groups: biological treatments, physical removal treatments, and (electro)catalytic processes. Biological treatments [6] cannot treat concentrated NO_3^- waste streams and, additionally, the risk of pathogenic bacterial contamination in drinking water and the sludge formation make it less competitive. Moreover, physical removal techniques such as ion-exchange [7], reverse osmosis [8], electrodialysis [9] and electrocoagulation [10] are not cost-effective due to the generation of concentrated NO_3^- brines. However, (electro)catalytic processes like heterogeneous catalysis [11] and electroreduction (*NER*) [2] may sidestep the drawbacks of the aforementioned technologies (no waste steam production). Particularly, *NER* is the most promising technique due to its advantages [12,13]: environmental compatibility, energy efficiency, safety, amenability and cost-effectiveness. The *NER* ideally pursues a complete conversion of NO_3^- to innocuous N_2 gas but, unfortunately, other non-desired secondary products such as N_xO_y , NH_2OH , NH_3 and NH_2NH_2 are also possible [14].

The *NER* activity and selectivity towards the direct reduction to N_2 depend on various parameters like the electrocatalytic material [15], the solution composition [2] and the applied potential [14], being the former the most relevant. Non-noble metals like Fe [16], Ni [17] or Cu [18] and their combinations [19–21] (CuSn , CuNi , CuZn ...) present high *NER* activity but high selectivity towards NH_3 . To the best of our knowledge, the most active and selective electrocatalysts reported for the direct *NER* to N_2 , are bi- and tri-metallic combinations containing at least Pd or Pt [22–25] (PdSn ,

PtCu, PdCu, PtSn, PtSnAu...) but they are not cost-effective for practical applications because of using noble metals. On the other hand, other cheap metals like Sn [26] and Bi [27] have also shown interesting rates of reduction and selectivity to N_2 . Sn cathodes achieve high activity and selectivity towards N_2 but at very negative cathodic potentials, where Sn can suffer from cathodic corrosion. Bi also shows good activity at lower potentials and thus less cathodic corrosion [26]. Nevertheless, its electrocatalytic activity and selectivity are lower compared to Sn. According to recent studies, the combination of Bi with Cu [28] (in a neutral electrolyte) or Bronze (CuSn) [29] seems to provide a synergistic effect among the metals to enhance their electrocatalytic performance. The development of novel electrocatalysts to improve N_2 selectivity is the principal challenge to be solved for the electrochemical denitrification process to become competitive. To our knowledge, BiSn combinations have not been studied in detail for this process but their good performance in some electrochemical applications like the electroanalysis of Cd [30,31] or the study of the CO_2 electroreduction [32] has been reported in recent works. In this last work [32], Wen et. al report that the combination of Bi and Sn presents excellent performance and durability for the CO_2 electrocatalytic reduction due to favourable orbital interactions at the Bi-Sn interface.

In this work, Bi, Sn, and BiSn nanoparticles (Bi:Sn ratios 80:20, 60:40, 40:60, and 20:80); supported on carbon black, were tested for the *NER*. The use of nanoparticles (NPs) provides higher active area per mass/volume than the bulk material and, generally, enhanced electrocatalytic properties due to electronic and geometric effects [33,34]. The interaction between the NPs and the carbon surface could also have enhancing effects on the electrocatalysis and corrosion resistance. Voltammetric studies and electrolytic experiments were performed in order to evaluate the electrocatalytic activity and the selectivity of the nanoparticulated cathodes on the *NER*.

2. Experimental

2.1. Preparation and characterisation of carbon-supported NPs.

Bi_xSn_y NPs (x : 0 – 100, y : 100 - x) were prepared at room temperature using a chemical reduction procedure. In detail, ($x/100$) mmol of anhydrous $BiCl_3$ (Sigma–Aldrich Co.), $y/100$ mmol of $SnCl_2 \cdot 2H_2O$ (Sigma–Aldrich Co.) and 2 mmol of polyvinylpyrrolidone (PVP) (molecular weight 55,000, Aldrich Chemical Co.) were dissolved in 40 ml of dimethylformamide (DMF) (Sigma–Aldrich Co.). Subsequently, 6

mmol of NaBH_4 (99.99%, Sigma–Aldrich Co.) were added to the solution under continuous magnetic stirring. The stirring was maintained for at least 30 min to ensure a complete reduction. By this method, prepared NPs are smaller than in the case of other methods reported elsewhere [30,31]. In brief, Chen et. al [30] employed ethylene glycol as solvent instead of DMF but the synthesis requires more time and the BiSn NPs are irregular and bigger, with approximately 20 nm of diameter. On the other hand, Suarez et. al [31] used Nafion and the non-ionic surfactant *Brij* as stabilisers, instead of PVP; obtaining bigger BiSn nanoparticles of more than 100 nm on a polymeric matrix. Carbon powder (Vulcan XC72R, Cabot Corp) was added to the mixture after the chemical reduction step to achieve carbon-supported NPs with a theoretical loading of NPs of 20 wt. %. Afterwards, both magnetic and ultrasonic stirring were alternatively applied for 1 h. Then, 160 mL of acetone were added. The incorporation of acetone destabilises the colloidal suspension forcing the NPs/C precipitation. The so-prepared NPs/C were filtered, washed with acetone and dried overnight under vacuum at room temperature. The so-prepared materials were characterised by Transmission Electron Microscopy (TEM) coupled to Energy Dispersive X-ray Spectroscopy (EDS) and X-ray photoelectron microscopy (XPS). The final loading in NPs of each material was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 7400DV, dual vision) after a previous digestion with nitric acid.

TEM was performed with a JEOL JEM-2010 working at 200 kV and an X-ray detector OXFORD-INCA Energy TEM-100 for microanalysis. About 200 NPs randomly distributed were used to estimate their average diameter.

XPS measurements were recorded on a K-Alpha Thermo Scientific spectrometer using AlK α (1486.6 eV) radiation, monochromatised by a twin crystal monochromator and yielding a focused X-ray spot (diameter of 400 μm), at 3 mA x 12 kV. Deconvolution of the XPS spectra was carried out using a Shirley background.

2.2. Preparation and characterisation of carbon-supported NPs cathodes.

Carbon-supported NPs (NPs/C) cathodes were prepared by spraying (air-brushing technique) the corresponding catalytic ink on a 3 cm x 3 cm Toray Paper (TP, TP-120, QuinTech, Göppingen, Germany), following a similar procedure from previous works [35,36]. TP was supported on a hot metallic plate at 90°C to facilitate solvent evaporation. The catalytic inks were alcoholic dispersions of NPs/C in ethanol. Nafion

is added as binder agent from a 5% Nafion solution (perfluorosulfonic acid-PTFE copolymer in 5% w/w isopropyl alcohol) with a NPs/C:Nafion mass ratio of 80:20. The mixture was finally diluted to 3 wt% in ethanol and homogenised applying ultrasonic agitation for 30 min. The cathodes were always prepared with the same amount of NP/C material, that is, 0.5 mg per cm⁻². The cathodes were named as follows: NPs/C/TP, where NPs stands for the NPs composition (Bi_xSn_y), C makes reference to the Carbon Black and TP indicates the Toray Paper support (i.e., Bi₁₀₀/C/TP, Bi₆₀Sn₄₀/C/TP...). A NPs-free cathode (C/TP) was also prepared, based only on carbon black + Nafion. All cathodes were topographically characterised using scanning electronic microscopy (SEM, HITACHI S-3000N microscope working at 20 kV with X-ray detector Bruker Xflash 3001 for microanalysis). Composition and element distribution (mapping) were determined by EDS on uncoated surfaces.

The electrochemical characterisation was performed on NPs/C/TP cathodes with an area of 0.5 cm x 0.5 cm by cyclic voltammetry (CV), in a standard three-electrode electrochemical glass cell. An Ebonex cylinder (5 mm of diameter) and an AgCl/Ag (3.5 M KCl) electrode were used as counter and reference electrodes, respectively. The electrode potential was controlled using a VMP-300 multichannel potentiostat (BioLogic). The samples were cycled between 0 and -2.0 V at a scan rate of 50 mV s⁻¹ to study the oxidation/reduction processes on the NPs surface and between -1.0 and -2.0 V to evaluate the *NER* activity. The supporting electrolyte was a buffer (pH ~9.65) aqueous solution of 0.4 M NaHCO₃ + 0.4 M Na₂CO₃ (Both: Fluka, Reagent grade, ≥99%). This supporting electrolyte was chosen because of its strong buffer capacity and its high ionic strength. The aim is to avoid drastic variations of pH and ionic strength, since these parameters influence the *NER* [37]. NO₃⁻-containing solutions were prepared with dehydrated KNO₃ (Sigma–Aldrich Co., ≥99%) in the supporting electrolyte with concentrations of 0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M and 0.5 M. Solutions employed in this work were prepared with doubly-distilled water with a resistivity not less of 18 MΩ cm and deaerated with Ar prior to CVs.

2.3. Electrolytic experiments.

Electrolyses were conducted using a Potentiostat/Galvanostat (AMEL Instruments Model 2049 General-Purpose Potentiometer) and an H-type electrochemical cell with compartments separated by a cation-exchange membrane (Nafion 117 DuPont, USA). A 2.5 cm x 4.0 cm polycrystalline BDD, supported on

silicon (from Adamant Technologies Switzerland) and doped with 700-800 ppm of boron, was employed as counter electrode and an AgCl/Ag (3.5 M KCl) was used as reference electrode -via Luggin probe-. Electrolyses were carried out at controlled potential and room temperature, under stirring and aerated conditions. The cathodic compartment was always filled with 60 ml of a 0.05 M KNO₃ solution in the supporting electrolyte (catholyte) and the anodic compartment with 60 ml of the supporting electrolyte. The electrical charge passed (Q) during the electrolyses was measured using a Digatron coulometer. pH was measured by a Crison Micro pH 2000 pH-meter and the electric conductivity by a 4510-JENWAY conductivity meter.

Theoretical charge (Q_t) makes reference to the electric charge which would be necessary for a complete transformation of NO₃⁻ into N₂ (5 mol_e⁻/mol NO₃⁻), assuming that no other secondary reactions are taking place. For example, for a 60 ml of a 0.05 M KNO₃ solution, 1440 C of Q would be necessary so that all the NO₃⁻ was reduced exclusively to N₂ gas, with no other processes taking place. Two different electrolytic experiments were carried out. In the first set of experiments, Q corresponded to 100% of Q_t . These electrolyses were performed at -2.0 V for the TP, C/TP and all the NPs/C/TP cathodes, with an area of 4.5 cm². In this case, only concentrations of NO₃⁻, NO₂⁻ and NH₄⁺/NH₃; and the total nitrogen in solution (TN), were measured. The difference between the initial and final TN was considered as the amount of gaseous compounds produced. In the second set, the electrolyses were performed at -1.7, -2.0 and -2.5 V and only for Bi₆₀Sn₄₀/C/TP electrode. In this case, the Q was of 100% and 250% of the Q_t and the gaseous compounds were also analysed.

2.4. Analytical determinations.

The concentrations of NO₃⁻ (C_{NO_3}), NO₂⁻ (C_{NO_2}) and NH₄⁺/NH₃ (C_{NH_3}) in solution were determined before and after the electrolyses by standard spectrophotometric methods [38]. In particular, NO₃⁻ was determined after its reduction with metallic cadmium and analysed as NO₂⁻ (the sum of NO₂⁻ from NO₃⁻ reduction + NO₂⁻ already present in solution). C_{NO_2} (only NO₂⁻ present in solution) was obtained by its reduction with ferrous sulphate yielding nitrous oxide. Both form a brownish-green coloured complex whose absorbance is measured at $\lambda = 585$ nm. The difference between the values obtained by both methods corresponds with C_{NO_3} [39]. Ammonia-nitrogen (C_{NH_3}) was analysed via the salicylate method at $\lambda = 655$ nm. For these colorimetric determinations

the Hach DR 2000 apparatus was used. TN in solution as mg N L^{-1} was measured by a Total Organic Carbon (TOC) SHIMADZU TOC-V CSH coupled to a TN module. NH_2OH and NH_2NH_2 are intermediates which can be detected during the NER [40]. Moreover, their concentrations are expected to be very low (especially in basic media [41]) and only measurable at intermediate times of the experiments. In this work, we focused on analysing the products at the end of the electrolyses, when those compounds are supposed not to be detected [26,27,37]. Besides, the comparison between the TN values and the sum of $C_{\text{NO}_3} + C_{\text{NO}_2} + C_{\text{NH}_3}$ allows to confirm the absence of other products in solution. Samples were always analysed promptly after sampling and stored at 4°C (when necessary) for no more than 2 days. All the samples were analysed at least twice to ascertain the accuracy of the determinations and the final values given are an average value. The standard deviation (SD) was calculated in all cases. The ratio between the SD and the total initial amount of nitrogen was also calculated and, in all cases, it was lower than 5% (see an example in Table ESI-1). Hence, it is considered that the selectivity does not change significantly despite the variability associated to the error of analytical determinations. C_{NO_3} was also determined in the anolyte to determine whether the crossing of the anion through the cation-exchange membrane is taking place during the experiments but less than 1% of NO_3^- was found in all cases. The C_{NH_3} in the anolyte as well as the NH_3 escaping from the cathode solution were previously verified to be negligible compared to the total amount of $\text{NH}_4^+/\text{NH}_3$ in the cathode solution and, therefore, they have not been measured in the experiments presented.

The loading of Bi and/or Sn in the NPs/C materials was calculated by the following procedure: I) NPs/C materials are dissolved in concentrated HNO_3 (65%, Sigma-Aldrich). II) The resulting solutions are diluted up to a 2wt% of HNO_3 . III) The Bi and/or Sn concentration is measured in these diluted samples by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 7400DV, dual vision).

The gaseous compounds were analysed by gas chromatography (GC, Hitachi 163 GC) coupled to a thermal conductivity detector (TCD), at a constant column temperature of 80°C and a detector temperature of 250°C . The chromatographic column was a MS-13X and a He stream was the carrier gas. The gaseous compounds were collected from the cathodic compartment (sealed) during the electrolyses and introduced in the GC-TCD with aliquots of $250\ \mu\text{L}$, taken directly from the cell by a Hamilton

syringe. A previous external calibration was carried out by pure gaseous samples of N₂, O₂, N₂O and NO₂. The quantification of the compounds cannot be conducted accurately by the system employed for the measurements (hydrogen generation during the experiment, possible leakages in the electrochemical cell and during sample collection, air contamination, etc.). By GC-TCD, however, the ratio between the products detected can be determined. Also, the amount of N released as gaseous compounds can be calculated by the difference between the *TN* in solution before and after the experiment. Knowing the amount of gaseous N and the ratio between the products detected, we can calculate the amount of each product in the sample. The amount of N₂ coming from air contamination is considered by measuring O₂ as well. Knowing the amount of O₂ in the sample, the atmospheric N₂ coming from air interference can be estimated according to the ratio O₂:N₂ in air, which is 21:78. This amount of atmospheric N₂ is subtracted from the total amount of N₂ quantified to give the amount of N₂ produced by the *NER* reaction. H₂ was not measured for any experiment.

2.5. Performance parameters.

The nitrate removal (*NR*) was calculated by:

$$NR (\%) = \frac{(n_o - n)}{n_o} \cdot 100 \quad (1)$$

where n_o is the initial moles of NO₃⁻ and n is the moles of NO₃⁻ in the final solution.

The selectivity respect to a specific compound *P* was evaluated according to the percentage of product distribution, that is, the percentage of each compound *P* produced (S_p , $P = \text{NO}_3^-$, NO₂⁻, NH₄⁺/NH₃, N₂O, N₂, NO₂...). S_p was calculated according to the equation:

$$S_p (\%) = \frac{C_p}{C_T} \cdot 100 \quad (2)$$

where C_p is the concentration of *P* in mg N L⁻¹ in the final solution; C_T is the total mg N L⁻¹ in the initial solution.

The faradaic efficiency (*FE*) for a certain product *P* is defined as the ratio between the electric charge invested in the formation of *P* and the total electric charge passed:

$$FE (P) = \frac{Q_P}{Q} = \frac{n_P \cdot F \cdot n_e}{Q} \quad (3)$$

where Q_P is the electric charge invested in the formation *P* measured in Coulombs (C), Q is the total electrical charge passed also in C, n_P is the moles of *P*, n_e is the moles of

electrons involved in the reaction of interest (mol_e) per mole of P and F is the Faraday constant ($95,485 \text{ C mol}_e^{-1}$).

The reaction of interest is the complete transformation of NO_3^- into N_2 :

3. Results and discussion.

3.1. Physicochemical characterisation of NPs/C.

Fig. 1 shows some representative TEM images for all the NPs/C synthesised. NPs showed spherical morphology with a mean particle size of about 10 nm (Fig. ESI-1) and they were well-distributed onto the Carbon Black (CB) surface. Pure NPs can be also prepared by the same methodology but without the carbon addition. However, the dispersion onto the CB surface hinders their agglomeration (Fig. ESI-2). Table 1 shows the results of EDS analyses from which we confirm that the Bi and Sn atomic ratios correspond well with the nominal ones according to the preparation. Table 1 also includes the Bi to Sn ratios estimated from XPS. According to XPS results, the catalysts contained C, O, Bi and Sn. XPS patterns of the Bi4f and the Sn3d spectra were registered (Figs. ESI 3-5). The Bi4f_{7/2} envelope was deconvoluted into two components at ~159 eV and ~157 eV, which were assigned to Bi (III) ions (as Bi₂O₃) and Bi (0), respectively [42]. On the other hand, the Sn3d_{5/2} envelope was also deconvoluted into two components; ~487 eV for Sn (II) - Sn (IV) (SnO/SnO₂/Sn(OH)₄) and ~484 eV for Sn (0) [43]. It is difficult to distinguish between Sn (II) and Sn (IV) by XPS since their binding energies are very close [44]. The peaks assigned to oxidised forms of Bi and Sn have higher area than the assigned for the reduced metal in all cases, indicating the existence of oxides on the NPs surface due to the air exposition. The formation of metastable oxidised layers on the surface of these metals may have beneficial effects on electrocatalytic reduction processes [45]. The comparison between EDS and XPS experiments suggests that NPs are Sn-rich at the surface than in the bulk. The analysis of the C1s (Figs. ESI 3-5) spectra revealed the presence of different oxygenated groups on the surface of the CB [46], which may be beneficial for the NPs support and for electronic effects towards a higher electrocatalytic performance. Finally, Table 1 also includes the loading of NPs measured by ICP-OES for all the NPs/C/TP materials after their nitric acid digestion. The loading is lower than the expected according to the

synthesis (20 wt.%) and it varies depending of the type of NPs. This issue has been taken into account for the experiments of the following section.

3.2. Physicochemical and electrochemical characterisation of NPs/C/TP cathodes.

Fig. 2 shows the representative SEM images of the different cathodes prepared with the NPs/C materials, obtained using a backscattered electron detector. The NPs/C inks rendered a uniform coverage over the substrate, that is, the TP fibers. The backscattered electron signal depends strongly on the atomic number of the sample (higher atomic number gives brighter signal) and, accordingly, it can be inferred that the NPs are well-distributed on the surface of the carbon fibers since bright nanometric spots can be observed. The good NPs distribution and the absence of important agglomerations over the TP surface were also corroborated by EDS mapping (Fig. ESI-6).

Fig. 3 displays the voltammetric profiles of the samples in the supporting electrolyte. CVs in this figure have been normalised taking into account the NPs loading for each NPs/C/TP material. In brief, the CVs showed anodic and cathodic contributions between -1.0 and -0.2 V related to the oxidation/reduction processes of Sn - SnO_x (SnO₂ and/or Sn(OH)₄) [47] and Bi - Bi_xO_y in basic media [48]. The different NPs/C/TP composition can be qualitatively confirmed according to the relative electric charge involved on those contributions. From -1.7 V to more negative potentials, an evident reduction process is observed which can be mainly attributed to the H₂ evolution. In all the experiments the back side of the Toray paper will also contribute to the electrochemical response. In addition, CVs between -1.0 and -2.0 V were registered for all the materials (TP and C/TP included) in the same buffer solution but containing various C_{NO3} (see Fig. ESI-7 and ESI-8). The reason to start at -1.0 V was to avoid the oxidation/reduction processes on the metal surfaces. In all cases, the current intensity (*I*) increased as the cathode potential (*E*_{cat}) did; from about -1.4 to -2.0 V. *I* also augmented with the C_{NO3} as well, evidencing the electrochemical activity of this cathodes towards the *NER*. TP and C/TP cathodes are also investigated (Fig. ESI-8) because it is known that carbon-based materials like graphite [15] and boron-doped diamond (BDD) [49] are electroactive towards the *NER*. Both TP and C/TP cathodes are demonstrated in this work to be electroactive for this process. NP-free carbon based cathodes showed an onset potential for *NER* and hydrogen evolution less cathodic than in the case of the

NP/C/TPs (Fig. ESI-7 vs ESI-8). The interaction of the BiSn nanoparticles with the carbon surface may involve a change in the nitrate reduction mechanism; moving the commencement of the process up to lower cathodic potentials and altering the final products obtained. This assumption can be supported by a work of Bouzek et. al [50], where it is stated that graphite exhibits different NER mechanism and selectivity than metals like Cu or Ni. The poor performance of Bi and Sn metals towards the H_2 evolution may also contribute to the shift of the process commencement to lower cathodic potentials.

Fig. 4 shows the plot I (background subtracted) vs C_{NO_3} at -1.7 and -2.0 V for all the NP/C/TP materials, from which several conclusions can be stated. In this plot, I have been normalised to the mass of NPs in each NP/C/TP material. On the other hand, Figs. ESI-8C and ESI-8D shows the plot I (background subtracted) vs C_{NO_3} at -1.7 and -2.0 V; respectively, for the TP and the C/TP. They are compared in the same figure with the most active NP/C/TP materials from Fig. 4 at each potential. First of all, it is interesting to note that $Bi_{80}Sn_{20}/C/TP$ was the most active NP/C/TP material giving rise to the highest I , followed by $Bi_{60}Sn_{40}/C/TP$. At -1.7 V, the $Sn_{100}/C/TP$ is the cathode with the lowest NER activity whereas at -2.0 V the $Bi_{100}/C/TP$ is the least active. The activity is noticeably enhanced by the mixture of Sn and Bi respect to the metals separately. This finding is in concordance with previous works by Gao et. al [28,29]. Regarding the comparison among the carbon materials and the NPs/C/TP; only C/TP shows higher I than $Bi_{80}Sn_{20}/C/TP$ at -1.7 V for C_{NO_3} higher than 0.3 M. However, this can be understood not in terms of NER activity but in terms of differences in density among the metals [ρ (Bi) = 9.780 g cm⁻³, ρ (β -Sn) = 7.265 g cm⁻³, ρ (α -Sn) = 5.769 g cm⁻³] and the carbon Black [ρ (CB XC-72) = 0.264 g cm⁻³]. Since all the cathodes evaluated present the same mass of electrocatalytic material, the density differences entail that NPs-free carbon based cathodes will present more volume per mass of material (Bi and Sn weights more than C) and inevitably higher electrochemical active surface area.

Fig. 5 compares the electrochemical behaviour of the cathodes $Bi_{60}Sn_{40}/C/TP$ and C/TP by means of CVs between -1.0 and -2.0 V; for both the buffer solution 0.4 M $NaHCO_3$ / 0.4 M Na_2CO_3 and the buffer solution with 0.5 M of KNO_3 . It can be observed that the electrochemical responses are different between them. C/TP shows higher currents than the $Bi_{60}Sn_{40}/C/TP$ at all the potentials even for the background

current without NO_3^- . The addition of NPs may alter the capacity of the material for the H_2 evolution since Bi and Sn are poorer electrocatalysts for this reaction than carbon materials. The comparison of activity between the carbon materials and the NPs-modified materials must be affected by the aforementioned higher electrochemical active surface area of the carbon-based materials. These differences can be also attributed to a higher blockage by the binder agent (Nafion) on the $\text{Bi}_{60}\text{Sn}_{40}/\text{C}/\text{TP}$ electrode. The same amount of Nafion is added to both kind of cathodes but C/TP cathode is expected to have higher active electrochemical surface area than the $\text{Bi}_{60}\text{Sn}_{40}/\text{C}/\text{TP}$. Hence, it can be inferred that the degree of Nafion blockage will be higher in the NPs/C/TP cathodes than in the case of NPs-free carbon based cathodes, thus justifying the features observed in Fig. 5.

It can be concluded that, despite the carbonaceous materials are active for the process, the incorporation of these NPs (especially $\text{Bi}_{60}\text{Sn}_{40}/\text{C}$, $\text{Bi}_{80}\text{Sn}_{20}/\text{C}$ and $\text{Bi}_{40}\text{Sn}_{60}/\text{C}$) results in a significant increase of activity, mainly at low C_{NO_3} and very negative potentials; where the *NER* takes place actively.

3.3. Electrolytic experiments. Selectivity of NPs/C/TP cathodes.

Electrolytic experiments were carried out at -2.0 V in order to evaluate the selectivity of the different cathodes. Experiments were performed in the conditions detailed in section 2.3 for 100% of Q_t (eq. 4). Fig. 6 shows the product distribution and the calculated $FE(N_2)$ after the electrolysis for all the tested materials. The remaining NO_3^- , C_{NO_2} and C_{NH_3} were controlled for the final solution. *TN* in solution was also measured to ascertain no secondary products were produced and the difference between the initial and final values was assigned to the formation of gaseous compounds. $FE(N_2)$ was calculated assuming that the only gaseous compound produced from *NER* is N_2 . In solution, apart from the remaining NO_3^- , the only products detected were NO_2^- and $\text{NH}_4^+/\text{NH}_3$ in all cases. The sum of remaining $\text{C}_{\text{NO}_3} + \text{C}_{\text{NO}_2} + \text{C}_{\text{NH}_3}$ did not differ from the measured *TN* in more than 10 – 20 mg N L^{-1} (attributed to the experimental error) and therefore we may conclude that no other products in solution were generated. In these conditions, the materials giving rise to the highest amounts of formed gaseous compounds as well as the highest *NR* and $FE(N_2)$ values were $\text{Bi}_{60}\text{Sn}_{40}/\text{C}/\text{TP}$ and $\text{Bi}_{40}\text{Sn}_{60}/\text{C}/\text{TP}$. Clearly, the *NER* competes with the H_2 evolution since *NR* values were always below 100%. $FE(\text{H}_2)$ for all the experiments are calculated in Table ESI-2. It is found that the mixture of Bi and Sn also provides a higher selectivity towards the

formation of gaseous compounds respect to the metals separately and the NP-free carbon-based supports. This enhancement in selectivity seems to be higher as the Bi:Sn ratio is closer to 1:1. This conclusion coincides with the stated by *Gao et. al* [29] in their work where is reported that a mixture between Bi and bronze (CuSn) gave improved *NER* activity and N_2 selectivity. In this work, it is also stated that the combination of Bi with CuSn provides more cathode stability. Stability has not been evaluated in this work but the materials combining Bi and Sn may be more stable than the materials with pure Bi and Sn, according to the findings of the mentioned work. This is a very interesting issue to study in future works.

3.4. Selectivity of the $Bi_{60}Sn_{40}/C/TP$ cathode.

The $Bi_{60}Sn_{40}/C/TP$ cathode was chosen for more exhaustive experiments since it showed the highest selectivity to gaseous compounds. For this cathode, two rows of experiments were conducted (section 2.3): electrolyses at -2.0 V with different Q_t (100% and 250%) and electrolyses at different E_{cat} (-1.7, -2.0 and -2.5 V) for 250% of Q_t . For these experiments, the produced gaseous compounds were analysed by GC-TCD. Fig. 7 displays a summary of the results obtained after the former set of experiments. A *NR* higher than 90% was achieved when $Q_t = 250\%$. The $FE(N_2)$ value decreased from 73% (100% Q_t) to 36% ($Q_t = 250\%$), which means than the $FE(N_2)$ decreases as the NO_3^- is being consumed. The only gaseous compounds detected were N_2O and N_2 but interestingly no harmful nitrogen oxides like NO or NO_2 were found in any case. N_2 was the main product in all cases (more than a 50% of S_{N_2} after 3500 C passed), indicating a good selectivity of the $Bi_{60}Sn_{40}/C$ material towards the formation of N_2 . N_2O is generated in much smaller amount, being the S_{N_2O} of about 10% as the most. These results are in agreement with a work of *Dortsiou et. al* [44] where they stated that N_2O and N_2 are the only gaseous products generated by Sn and Bi. In that work, current controlled electrolyses were performed at 150 mA cm^{-2} (E_{cat} between -2.3 and -2.7 V vs AgCl/Ag) passing up to 3000 C for a 0.05 M NO_3^- solution. In these conditions, $S_{N_2} = 46.7\%$ and $S_{N_2O} = 40.7\%$ were obtained for Sn while $S_{N_2} = 28.2\%$ and $S_{N_2O} = 14.5\%$ were obtained for Bi. In the case of this work, better selectivity towards the formation of N_2 is achieved with $Bi_{60}Sn_{40}/C/TP$: $S_{N_2} = 54\%$ and $S_{N_2O} = 6.5\%$ for similar conditions (-2.0 V and 3500 C passed). This comparison allows us to confirm that the Bi:Sn at a ratio 60:40 may have a positive synergistic effect. Moreover, S_{N_2} , S_{N_2O} and S_{NH_3} augmented with the Q passed but the evolution of NO_2^- was different,

characteristic of an intermediate in a consecutive reaction mechanism. C_{NO_2} reached a maximum of concentration before starting to decrease as Q passed increased, to finally give rise to more amount of the other products. This is interesting since means that this deleterious compound may be removed by passing more Q . Furthermore, Fig. 8 and Table 2 present the main results and experimental data of the second row of electrolyses. No significant differences in selectivity were observed among the three different E_{cat} being N_2 the major product in all cases. We could remark that the NR is the lowest for -1.7 V and the highest S_{N_2} is obtained for -2.0 V. The sum of S_{P} was between 94% and 101% due to the experimental error. Nevertheless, it has to be taken into account that the NER rate noticeably increased with the applied E_{cat} , deduced from the experimental time seen in Table 2. Regarding this, I measured during the experiment was decreasing with the C_{NO_3} . As well, the intense generation of OH^- was responsible of the increase of pH and conductivity. Clearly, $\text{Bi}_{60}\text{Sn}_{40}/\text{C}$ is demonstrated to be a promising electrocatalyst for the NER , showing high activity and interesting selectivity to N_2 .

4. Conclusions.

In the present work, carbon-supported nanoparticles of Bi_xSn_y ($x = 0 - 100$, $y = 100 - x$) of about 10 nm of diameter have been successfully synthesised by a fast, simple and scalable method. Cathodes prepared with these materials were evaluated for the electroreduction of NO_3^- by cyclic voltammetry and potential-controlled electrolyses. We concluded that the combination Bi-Sn in the NPs gives rise to not only higher activity but also to better selectivity for the direct reduction of NO_3^- to N_2 than each metal separately, likely due to a synergistic effect between both. Moreover, NPs-free carbon-based materials have been demonstrated to be also electroactive for the NER but their N_2 selectivity is lower than for the most of the NPs/C materials. Specifically, $\text{Bi}_{60}\text{Sn}_{40}/\text{C}/\text{TP}$ showed the best results after exhaustive electrolytic experiments, in which the main product generated was N_2 (more than 50% of S_{N_2}) regardless of the cathode potential or the electric charge passed; evidencing the good selectivity of this material. However, non-desired N_2O , NO_2^- and $\text{NH}_4^+/\text{NH}_3$ were also produced. Interestingly, harmful nitrogen oxides like NO or NO_2 were not detected. Concentration of NO_2^- and NO_3^- in the final solution could be limited if the electrolysis was continued for a longer time but NH_3 and N_2O cannot be further reduced. Nonetheless, N_2O is a

non-toxic gas generated in a small amount and NH_3 could be diminished by several strategies such as a non-divided cell (and an efficient anode for the conversion of NH_3 to N_2) or a paired electrolysis based on the coupling to electrochlorination [51]. Therefore, these NPs/C materials, specifically with a mixture between Bi and Sn in a similar ratio, are promising effective electrocatalysts to be employed in future practical applications of the electroreduction of NO_3^- such as the electrochemical denitrification of wastewaters. Nevertheless, further investigation is needed in order to achieve the cost-effectiveness of the method in terms of generation of undesired ammonia, faradaic efficiency, operational conditions and electrochemical reactor design.

Conflicts of interest.

None.

Acknowledgements.

I. Sanjuán acknowledges the Ph.D. fellowship granted and the material and human resources provided by the University of Alicante and the company Aguas de Valencia, S.A. JSG acknowledges financial support from VITC (Vicerrectorado de Investigación y Transferencia de Conocimiento) of the University of Alicante (UATALENTO16-02).

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Tables

Table 1 – Bi:Sn ratios determined by EDS and XPS and NPs loading determined by ICP-OES, for all the samples.

	Bi:Sn (EDS)	Bi:Sn (XPS)	NPs loading (wt. %)
Bi ₁₀₀ /C	100:0	100:0	14.4
Bi ₈₀ Sn ₂₀ /C	(75 ± 1):(25 ± 1)	67:33	10.5
Bi ₆₀ Sn ₄₀ /C	(58 ± 0.5):(42 ± 0.5)	53:47	12.1
Bi ₄₀ Sn ₆₀ /C	(34 ± 0.5):(66 ± 0.5)	22:78	12.2
Bi ₂₀ Sn ₈₀ /C	(16 ± 1):(84 ± 1)	11:89	9.8
Sn ₁₀₀ /C	0:100	0:100	8.3

Table 2 – Experimental data and product analysis for the electrolyses with the Bi₆₀Sn₄₀/C/TP at different cathode potentials vs AgCl/Ag (3.5 M). 3500 C of electric charge passed. Initial solution (60 ml): 0.05 M KNO₃ in the buffer 0.4 M NaHCO₃ / 0.4M Na₂CO₃. Concentrations are presented in mg l⁻¹ of compound.

E _{cat} / V	pH	σ / mS cm ⁻¹	I / A*	t / h	C _{NO3-}	C _{NO2-}	C _{NH4+}	N ₂ O / %	N ₂ / %
-	9.6	49.6	0	0	3100	0	0	0	0
-1.7	13.0	63.5	0.02 – 0.012	48	495	367	85	2	50
-2.0	13.1	62.8	0.11 – 0.082	10	318	243	157	6.5	54
-2.5	13.3	70.8	0.15- 0.18	4	294	374	114	9	50.5

* Range of variation of the current intensity during the electrolyses.

Figure captions

Fig. 1. Representative TEM images of the NPs/C. (A) Bi₁₀₀/C, (B) Bi₈₀Sn₂₀/C, (C) Bi₆₀Sn₄₀/C, (D) Bi₄₀Sn₆₀/C, (E) Bi₂₀Sn₈₀/C and (F) Sn₁₀₀/C.

Fig. 2. Representative SEM images obtained for each cathode: (A) Bi₁₀₀/C/TP, (B) Bi₈₀Sn₂₀/C/TP, (C) Bi₆₀Sn₄₀/C/TP, (D) Bi₄₀Sn₆₀/C/TP, (E) Bi₂₀Sn₈₀/C/TP and (F) Sn₁₀₀/C/TP.

Fig. 3. CVs between 0 and -2.0 V vs AgCl/Ag (3.5 M KCl) for the NPs/C. (Black) Bi₁₀₀/C/TP, (Red) Bi₈₀Sn₂₀/C/TP, (Blue) Bi₆₀Sn₄₀/C/TP, (Pink) Bi₄₀Sn₆₀/C/TP, (Green) Bi₂₀Sn₈₀/C/TP and (Dark Blue) Sn₁₀₀/C/TP. CVs have been normalised respect to the mass of nanoparticles in each case. Solution: buffer 0.4 M NaHCO₃ / 0.4 M Na₂CO₃. Cathode area: 0.25 cm². Scan rate: 50 mV s⁻¹.

Fig. 4. Plot of current intensities ($I / A \text{ mg}_{\text{NP}}^{-1}$) as a function of NO₃⁻ concentration (C_{NO3}), for the different TP/CB/NPs cathodes ($A = 0.25 \text{ cm}^2$). *I* values (background subtracted) were registered at -1.7 and -2.0 V vs AgCl/Ag from stable CVs and normalised respect to the mass of NPs in each case. CVs were performed in the buffer 0.4 M NaHCO₃ / 0.4 M Na₂CO₃ with different C_{NO3}. Different cathodes: (■) TP/CB/Bi₁₀₀, (●) TP/CB/Bi₈₀Sn₂₀, (▲) TP/CB/Bi₆₀Sn₄₀/C, (▼) TP/CB/Bi₄₀Sn₆₀/C, (◆) TP/CB/Bi₂₀Sn₈₀/C and (◀) TP/CB/Sn₁₀₀/C.

Fig. 5. CVs between -1.0 and -2.0 V vs AgCl/Ag (3.5 M KCl) for the (Black) Bi₆₀Sn₄₀/C/TP and the (Red) C/TP cathodes. CVs are measured for the buffer 0.4 M NaHCO₃ / 0.4 M Na₂CO₃ (dashed lines) and for a 0.5 M KNO₃ solution in the buffer (solid lines). Cathode area: 0.25 cm². Scan rate: 50 mV s⁻¹.

Fig. 6. (Up) Selectivities for different products ($S_p / \%$) after an electrolysis at -2.0 V vs AgCl/Ag (100 % of the theoretical charge passed) for all the cathodes. Analysed products: remaining NO₃⁻ (black), NO₂⁻ (red), NH₄⁺/NH₃ (blue). The difference between the initial and final *TN* is attributed to the formation of gaseous compounds (pink). (Down) Faradaic efficiencies for the production of N₂ ($FE \text{ N}_2$), calculated for each experiment assuming that all the gaseous compounds are N₂.

Fig. 7. Selectivities for different products ($S_p / \%$) after as a function of the electric charge passed (1440 and 3500 C) for electrolyses carried out at -2.0 V vs AgCl/Ag, for the

Bi₆₀Sn₄₀/C/TP. The products analysed are the remaining NO₃⁻ (black), NO₂⁻ (red), NH₄⁺/NH₃ (blue), N₂O (pink) and N₂ (green). Faradaic efficiencies for the production of N₂ (*FE N₂*) are indicated in each case above the corresponding bar. Initial solution (60 mL): 0.05 M KNO₃ in the buffer 0.4 M NaHCO₃ / 0.4 M Na₂CO₃.

Fig. 8. Selectivities for different products (*S_p* / %) after electrolyses carried out at different cathode potentials (-1.7, -2.0 and -2.5 V vs AgCl/Ag) for the Bi₆₀Sn₄₀/C/TP. For these experiments, 3500 C of electric charge were passed. Products analysed: the remaining NO₃⁻ (black), NO₂⁻ (red), NH₄⁺/NH₃ (blue), N₂O (pink) and N₂ (green). Faradaic efficiencies for the production of N₂ (*FE N₂*) are indicated above each corresponding bar.

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Highlights

- Carbon-supported Bi, Sn and Bi-Sn nanoparticles are easily synthesised.
- Suitable cathodes are prepared with the carbon-supported nanoparticles.
- Bi_xSn_y are promising electrocatalysts for NO_3^- electroreduction.
- $\text{Bi}_{60}\text{Sn}_{40}$ displays the best results with $\text{FE}(\text{N}_2) > 50\%$.
- Harmful NO and NO_2 are not produced by these cathodes.

Declaration of interests

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

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