



# Synthesis and characterization of nanostructured electrocatalysts based on nickel and tin for hydrogen peroxide electrogeneration



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## ABSTRACT

This work describes both the preparation and the characterization of nanostructured materials based on tin and nickel. Composite materials of SnNi/C were prepared by the polymeric precursor method and were supported on Vulcan XC-72R, which is a high surface area carbon, for a comparative study. Three proportions on carbon were evaluated: 6%, 9% and 13%. Binary materials were prepared varying the atomic ratios of Sn and Ni at 6:1, 3:1, 1:1, 1:3 and 1:6 for each percentage composition tested. The materials were characterized by X-ray diffraction to determine the mean crystallites sizes of the important phases for the catalytic process, such as Ni<sub>3</sub>Sn, Ni<sub>3</sub>Sn<sub>2</sub> and Ni<sub>3</sub>Sn<sub>4</sub>, and by energy dispersive spectroscopy (EDS) measurements to determine the percentage composition of the material with highest catalytic activity. The results showed that the binary material prepared with 9% metal load at a ratio of 6:1 Sn:Ni was the best material for H<sub>2</sub>O<sub>2</sub> electrogeneration. This material showed the highest ring current, which was a consequence of the highest amount of H<sub>2</sub>O<sub>2</sub> production having a ring current higher than that obtained for the ORR for Vulcan carbon. The best electrocatalyst transferred 2.2 electrons in the ORR with an 88% yield of H<sub>2</sub>O<sub>2</sub>, while the Vulcan carbon, which is the reference material for the 2-electron transfer reaction, produced just a 63% yield of H<sub>2</sub>O<sub>2</sub>. Thus, based on these results, 9% Sn:Ni (6:1) is a promising material to be used in H<sub>2</sub>O<sub>2</sub> electrogeneration and in AOPs. This result is likely due to the presence of acid oxygen-containing species on carbon and to the large defect concentration in Ni<sub>3</sub>Sn<sub>4</sub> lattice parameters, which increase oxygen diffusion and promote H<sub>2</sub>O<sub>2</sub> production.

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## 1. Introduction

Over the past decade, a large variety of powerful oxidation methods known as advanced oxidation processes (AOPs) have been proposed for the degradation of hazardous pollutants found in groundwater, surface water and industrial wastewater [1–7]. AOPs are technologies based on the in situ generation of the hydroxyl radical ( $\bullet\text{OH}$ ); this species is the second strongest oxidant known after fluorine and has such a high standard reduction potential ( $E^\circ(\bullet\text{OH}/\text{H}_2\text{O})=2.80\text{ V/SHE}$ ) that it is a very powerful and non-selective oxidizing agent, reacting with organic species to give hydroxylated or dehydrogenated derivatives until their complete mineralization (until their transformation into CO<sub>2</sub>, water and inorganic ions).

The AOPs use oxidizing agents, such as O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, and/or catalysts, including Fe<sup>2+</sup> and TiO<sub>2</sub>, sometimes involving an additional

irradiation source, commonly UVA light [8–12]. Recently, there has been great interest in the remediation of wastewaters containing aromatic organics by electrochemical techniques, such as indirect electro-oxidation methods, based on H<sub>2</sub>O<sub>2</sub> electrogeneration. Hydrogen peroxide is considered an environmentally friendly chemical because the end products of its decomposition are harmless. Currently, it is commercially produced by a chemical route, the anthraquinone process, which involves multiple reaction steps [13,14]. However, the electrogeneration of H<sub>2</sub>O<sub>2</sub> has been of great interest because it can efficiently promote subsequent oxidation reactions and considerably reduce the costs associated with hydrogen peroxide transportation [15].

Electrochemical synthesis is the most common alternative method for production of H<sub>2</sub>O<sub>2</sub> on a small scale via the oxygen reduction reaction (ORR) [15–17]. This reaction can be performed at the cathode via two different pathways, which yield different products: (A) the four electron pathway, which forms water or hydroxyl groups, and (B) the two electron pathway, which forms hydrogen peroxide in acid medium [18–20] whereas hydrogen peroxide is also usually electrogenerated in alkaline media, where its

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conjugated base, the hydroperoxide ion  $\text{HO}_2^-$ , is obtained via the two electrons reduction of supplied oxygen gas [21–24].

A. Alkaline solutions.



Acid solutions.



B. Alkaline solutions.



Acid solutions.



The reduction pathway is strongly determined by the electrode materials [21]. It is well-known that carbon electrodes are electrocatalytically active for oxygen reduction in alkaline media [25,26]. To maximize carbon utilization as a catalyst for hydrogen peroxide synthesis, the production of carbon powder materials with high surface area is necessary. Certain metals and metal oxides are already used to bias the activity of the oxygen reduction reaction toward the two-electron transfer pathway in the ORR. Xu et al. [27] and Assumpção et al. [28] studied the effect of different proportions of  $\text{CeO}_2$  on surface of carbon substrate for hydrogen peroxide generation. Other authors introduced  $\text{TiO}$ ,  $\text{Pt/TiO}_2$ ,  $\text{WO}_3/\text{TiO}_2$  catalysts [29] and  $\text{WO}_3$  films [30] to improve the efficiency of AOPs and to degrade organic pollutants.

Such materials can be easily converted into gas diffusion electrodes (GDEs), which are very attractive for industrial and practical applications [12]. GDEs are particularly attractive for the purposes of this study because they generate hydrogen peroxide at a much higher rate than plate electrodes [31]. Additionally, GDEs can overcome the problem of low oxygen solubility, which causes mass transfer limitations at the cathode surface because GDEs consist of a conductive porous structure through which gas percolates from one face to the other while in contact with the electrolyte. These electrodes have a hydrophobic structure with hydrophilic channels in which the reaction occurs [32,33].

Problems such as electrode stability and cost are still associated with using a GDE [15]. Addition of Sn to Raney Ni catalysts improves their stability [34]. This behavior is consistent with the fact that Sn can be added to Ni surfaces to improve corrosion resistance [35]. The electronic industry also used electrodeposited Ni–Sn alloys in printed circuit boards as protective and etch-resistant coatings [36]. Electrodeposited Ni–Sn alloy films have also found applications in the fabrication of the anode for Li–ion batteries [37–39]. The importance of the above mentioned aspects has prompted us to study the performance of SnNi/C catalysts in the ORR to electrogenerate  $\text{H}_2\text{O}_2$  and subsequently apply them in AOPs to degrade organic pollutants.

The Ni–Sn phase diagram contains three known phases:  $\text{Ni}_3\text{Sn}_4$ ,  $\text{Ni}_3\text{Sn}_2$  and  $\text{Ni}_3\text{Sn}$  [40]. Several investigators have explored the reaction of different Sn-based alloys with nickel because the sequence of phase formation and the resulting morphology have pronounced effects on the electrical and mechanical properties [41–44]. In most of these studies,  $\text{Ni}_3\text{Sn}_4$  was determined to be the first phase to form at the interface between Ni and Sn.  $\text{Ni}_3\text{Sn}_2$  and  $\text{Ni}_3\text{Sn}$  were generally found to grow by subsequent diffusion of Ni through the  $\text{Ni}_3\text{Sn}_4$  layer.

The aim of this study is to improve hydrogen peroxide electrogeneration using SnNi-based catalysts and to assess the performance of these catalysts relative to that of Vulcan carbon XC-72R catalysts in the oxygen reduction reaction for hydrogen peroxide electrogeneration in alkaline media. This paper describes a comparative study of three compositions of NiSn-nanoparticles supported

on carbon (6%, 9% and 13% w/w SnNi/C). All of these materials were prepared via the polymeric precursor method.

## 2. Materials and methods

### 2.1. SnNi/C electrocatalyst preparation

Electrocatalysts consisting of SnNi (6%, 9% and 13% w/w) on Vulcan carbon XC-72R (Cabot Corporation) were prepared using the polymeric precursor method (PPM) as described by De Souza et al. [45,46]. A mass ratio of 1:50:400 (metallic precursor: citric acid (CA): ethylene glycol (EG)) was used to prepare the polymeric resin. Tin chloride ( $\text{SnCl}_2$ , Fluka) and nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , Synth) were used as the metallic precursors. The catalysts were prepared by placing a pre-determined volume of resin in a 0.5 g of carbon followed by the addition of enough EG to cover the carbon powder, thereby producing a viscous resin. The pre-determined volume of resin was chosen to yield a final product containing Sn and Ni in atomic ratios of 6:1, 3:1, 1:1, 1:3 and 1:6, which corresponded to atomic percentages of 85:15, 75:25, 50:50, 25:75 and 15:85, respectively, to find the best composition for  $\text{H}_2\text{O}_2$  electrogeneration. The mixture was homogenized in an ultrasonic bath for over 60 min and was then thermally treated at  $400^\circ\text{C}$  for 4 h in an  $\text{N}_2$  atmosphere after evaporation of excess solvent.

### 2.2. Characterization of SnNi/C materials

#### 2.2.1. X-ray diffraction analysis

The SnNi-based materials were physically characterized by X-ray diffraction (XRD) using a D8 Focus diffractometer, Bruker AXS, with a  $\text{CuK}\alpha$  radiation source, operating in continuous scan mode ( $2^\circ \text{min}^{-1}$ ) from  $20^\circ$  to  $80^\circ$ .

#### 2.2.2. Scanning electron microscopy and energy dispersive spectroscopy analysis

The SnNi/C material that exhibited the highest catalytic efficiency was investigated by scanning electron microscopy (SEM) using a JEOL JSM-6010LA instrument, with additional semi-quantitative information obtained using large area standard less energy dispersive spectroscopy (EDS) analysis.

#### 2.2.3. Electrochemical characterization

For the electrochemical measurements described in this study, we used the rotating ring-disk technique with a commercial electrode (Pine Instruments), consisting of a central glassy carbon disk (area =  $0.2475 \text{ cm}^2$ ), as a support for the working electrodes and an Au ring (area =  $0.1866 \text{ cm}^2$ ), with a collection efficiency of  $N = 0.37$ . A platinum wire and Hg/HgO were used as the counter and reference electrodes, respectively. A  $1 \text{ mol L}^{-1}$  NaOH solution was employed as the supporting electrolyte, which was prepared from super-pure grade reagent purchased from Merck.

For all electrochemical analysis, the electrolyte was first saturated with oxygen for approximately 40 min. The oxygen flow was maintained over the electrolyte during the measurements, which were performed at a fixed scan rate of  $5 \text{ mV s}^{-1}$  at room temperature.

The disk of the commercial electrode served as the substrate for the catalysts, and the working electrodes were constructed using the configuration proposed by Assumpção et al. [47,48] and Paulus et al. [49]. All experiments were conducted using an Autolab PGSTAT 302 N potentiostat/galvanostat. The electrode rotation rate was varied from 100 to 3600 rpm, and the experiments were controlled by General Purpose Electrochemical System (GPES) software. The following flowing accessories were also employed: an ED1101 rotator and a CTV101 speed control unit.

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