



# Electrochemical and spectroelectrochemical analyses of hydrothermal carbon supported nickel electrocatalyst for ethanol electro-oxidation in alkaline medium

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## ABSTRACT

This paper presents the study of a simple and fast method to prepare an activated hydrothermal carbon supported nickel electrocatalyst (Ni/aHC) for ethanol oxidation reaction (EOR) in alkaline medium. The cyclic voltammogram obtained for the Ni/aHC sample in a 1.0 mol L<sup>-1</sup> NaOH solution shows an anodic and a cathodic peak. These redox couple reaction peaks can be related to the reversible formation of (NiO)OH. The catalytic activity of the Ni/aHC sample regarding the EOR is clearly evident from the cyclic voltammogram obtained in presence of ethanol, where a significant increase in the current density from 0.55 V vs. Hg/HgO is observed. This potential value, related with the onset potential ( $E_{\text{onset}}$ ) of the EOR, is very close to the corresponding (NiO)OH formation potential, confirming that this species is directly involved in the EOR on the Ni/aHC electrocatalyst. The *in-situ* Attenuated Total Reflectance FTIR (*in-situ* ATR-FTIRS) spectra of this sample show two intense peaks related with acetate ion formation. Based on the ATR-FTIRS and electrochemical analyses, and in the literature information, a reaction pathway of the EOR on Ni/aHC in alkaline medium is proposed.

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## 1. Introduction

In recent years, the research of alkaline fuel cells (FCs) has received a significant attention [1–6]. The most important advantages of alkaline FCs are their faster fuel oxidation and oxygen reduction reactions as compared to the acidic FCs. The inherently faster kinetics in alkaline FCs allow the use of non-noble and low-cost metal electrocatalysts such as silver and nickel, making them potentially low cost in comparison to others fuel cells types that use platinum based electrocatalysts [6]. In addition, the use of a non-Pt electrocatalyst on the cathode eliminates the oxidation of the fuel that may be transported from the anode, which makes the cathodic potential much higher than that in acidic FCs [7]. Besides, the exchange membranes used in alkaline FCs have lower fuel permeability and allow better water management. Thus that simplifies

the cell design, since the ionic current happens due to the hydroxide ions conduction [4–6].

On the other hand, the use of liquid fuels in direct alcohol fuel cells (DAFCs), such as low-molecular weight alcohols (methanol, ethanol and others) [8,9], has several further advantages compared to the use of pure hydrogen, because liquid fuels can be easily handled, stored and transported. In particular, the use of ethanol has several advantages, such as its high energy density, higher solubility in liquid electrolytes, low cost and availability. Furthermore, ethanol is a non-toxic fuel, and it can be produced in large quantities by the fermentation process of sugar-containing biomass or agricultural products. Therefore, direct ethanol fuel cells (DEFCs) have attracted considerable interest for their technological application as alternative power sources for automobile and portable consumer electronics, among others [10].

All aforementioned advantageous features highlight a strong potential for the research and development of alkaline DEFCs that present a great interest for the scientific community. In the last years, several works related to the design and performance of the alkaline DEFCs have been conducted by Li et al. [7,11,12,13–15]. In these works, particular attention was paid to investigating the

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effects of different operating parameters, including the cell operating temperature, concentrations of both ethanol and the base electrolyte solution, the design of the electrodes materials and electrodes architecture, and to the study of anion-exchange membrane durability.

One of the current challenges in the alkaline DEFCs research area is to develop an electrocatalyst that maximizes the efficiency and the ethanol oxidation reaction (EOR) rate in the cell anode, and, if possible EOR should be performed using non-noble less expensive metals as electrocatalysts [3,6]. In this context, supported bimetallic Pd-M (M=Ru, Au, Sn and Cu) catalysts [16–19], the addition of various oxides to carbon supported Pt and Pd catalysts [19–21] and Ru-Ni and Ru-Ni-Co catalysts [22–24] have been tested for EOR in alkaline media. Considering its low cost and chemical safety, in recent years, pure nickel [2] or nickel based nanocomposites [25,26] have been tested for EOR in alkaline medium. These studies have shown that nickel is an important candidate to be used as catalyst for the EOR although there is still plenty of room to improve its electrocatalytic performance and to explore simpler and a low cost synthesis routes. Moreover, some aspects of the EOR mechanism using nickel based electrocatalyst in alkaline medium warrant further exploration for its better physico-chemical understanding.

In addition to the catalyst, another important component in the electrocatalyst preparation is the catalyst support. The essentials to the catalyst supports for electro-oxidation are their high electrical conductivity, high surface area and chemical stability [27,28]. Among the different classes of electrocatalyst test in the literature, studies have attracted special attention and indicated that carbon materials are one of the most important groups of materials used as catalyst supports and different type of these materials have been investigated and employed for this application [27–35]. In recent years, the preparation of carbon materials from wood has been studied for their application as support in electrocatalysts for EOR [31] and other applications such as an active material in supercapacitors electrodes [36,37]. Hydrothermal liquefaction (HTL) is an aqueous process, in an inert atmosphere, moderate temperature (250–550 °C) and high pressure (5–20 MPa), used for producing a liquid biofuel known as bio crude. In this process a gas phase and a solid phase rich in carbon, called hydrothermal carbon (HC), are also produced [38–41]. HCs may also have interesting properties as a catalyst support [42,43].

Another issue that still needs to be addressed is the reaction mechanism and the identification of formed products associated with the EOR on different electrocatalysts in alkaline electrolytes. *In-situ* Fourier Transform Infrared Spectroscopy (*in-situ* FTIRS) is a dynamic technique that can allow the study of the physicochemical changes in a solid/liquid interface as a function of an external electric field [44,45]. *In-situ* FTIRS has been successfully used to obtain qualitative and quantitative data on electrochemical surface processes, such as electro-oxidation of small organic molecules [45]. The *in-situ* FTIRS can be carried out using different variations, one of them is the technique *in-situ* FTIRS in the Attenuated Total Reflectance mode (*in-situ* ATR-FTIRS), which is an appropriate technique to perform *in-situ* FTIRS measurements for non-reflective surfaces like the carbon supported catalysts [46]. In recent years, some authors have reported the use of *in-situ* ATR-FTIRS, following different methodologies, to study the EOR mechanism pathways in acidic [47–51] or alkaline medium [4,26] and to determine the product distributions at different potentials. So far, EOR mechanism studies for hydrothermal carbon supported nickel based electrocatalysts using alkaline base electrolyte have not been reported.

In this work, a new, simple, fast, low cost and environmental friendly route was applied for hydrothermal carbon supported nickel electrocatalyst preparation. The morphology, structure and chemical composition of the prepared electrocatalyst were determined by X-ray diffraction (XRD), transmission electron

microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). These properties were correlated to their electrocatalytic performance in EOR, and by *in-situ* ATR-FTIRS, with the EOR mechanism pathways and product distributions at different potentials, using 1.0 mol L<sup>-1</sup> ethanol + 1.0 mol L<sup>-1</sup> NaOH as solution.

## 2. Experimental

### 2.1. Samples preparation

Activated hydrothermal carbon supported Ni electrocatalyst was prepared according to the scheme of Fig. 1. The *Eucalyptus globulus* wood hydrothermal liquefaction (HTL) was carried out in a stainless steel Parr (model 4575) batch reactor with continuous agitation of 150 rpm. The reactor was purged with N<sub>2</sub> prior to reaction in order to remove the oxygen. HTL was performed using a 0.54 mol L<sup>-1</sup> Ni(NO<sub>3</sub>)<sub>2</sub> aqueous solution. The solution/wood relation was 1/6 (w/w). The HTL was carried out at 350 °C in a vapor pressure of 2500 ± 37 psi during 30 min. After the reaction the reactor was cooled and the reaction gases were released. The liquid and solid phases were separate by filtration, and the solid phase was washed with distilled water and finally dried at 100 °C until the final product reaches a constant weight. This solid phase corresponds to the hydrothermal carbon supported NiO (NiO/HC). The obtained NiO/HC was then submitted to thermal and CO<sub>2</sub> activation treatments. The treatments were carried out in a horizontal Carbolite (CTF 12/75) furnace according to the following steps: a) Heating rate of 5 °C min<sup>-1</sup> in a N<sub>2</sub> atmosphere at a constant flow of 200 mL min<sup>-1</sup>, b) once reached 800 °C, the gas flow was shifted to 200 mL min<sup>-1</sup> of CO<sub>2</sub> and it was left for 1 h and c) After activation time, the oven was cooled until ambient temperature in a flow of N<sub>2</sub>. After all the process steps have been completed an activated hydrothermal carbon supported Ni electrocatalyst (Ni/aHC) was obtained.

Another hydrothermal carbon samples were obtained only to be used in the thermogravimetric analysis (TGA) for comparative purposes. These samples were prepared in the same way and under the same conditions as above mentioned. The only difference was that for the hydrothermal carbon samples, the HTL was performed in absence of Ni(NO<sub>3</sub>)<sub>2</sub>. Thus, the hydrothermal carbon (HC) and the activated hydrothermal carbon (aHC) were obtained.

### 2.2. Structural, morphological and chemical characterization

X-Ray diffraction (XRD) analyses were made with a Rigaku model Ultima IV equipment. The wave longitude was 1.54 Å corresponding to Kα<sub>1</sub> radiation of Cu. X-Ray diffractogram allows establishing the phase and the crystal structure assumed by the Ni and NiO on the hydrothermal carbon support. Morphological information for the samples was obtained with an JEOLJEM 2010 TEM, operating at 200 kV. The interplanar spacing was determined by Digital Micrograph.

X-ray photoelectron spectroscopy (XPS) has proved to be a powerful method for the investigation of surface chemistry. XPS surface characterization method combines surface sensitivity with the ability to quantitatively obtain both elemental and chemical state information. All the XPS measurements were carried out with a Kratos Axis Ultra XPS spectrometer using a monochromated Al-Kα (1486.5 eV) X-ray radiation at a power of 15 kW at 150 W. The emitted photoelectrons were detected using a hemispherical analyser and 15 μm spatial resolution. The vacuum system was maintained at approximately 10<sup>-9</sup> Torr during all the experiments. Survey scans were collected from 0 to 1100 eV with a pass energy equal to 160 eV with step size of 1 eV, in order to identify the ele-

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