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Study of biocarbon supported Fe_2P particles for HER with energy applications

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Abstract. Hydrogen gas (H_2) is a molecule with several applications that can be used as clean and renewable fuel to produce electrical energy through its use in fuel cells. Although H_2 can be found rarely in its pure form on earth, is possible to obtain it in large quantities from the water electrolysis. In this process, the electrochemical hydrogen evolution reaction (HER) occurs on the surface of a suitable electrocatalyst. Pt is one of the most studied and applied catalyst for HER but its low abundance and high cost discourage it application at large scale. This has stimulated the study of other types of catalysts based on non-noble metals with low cost and available in large ammount. In the present work, a Fe_2P/activated biocarbon composite sample was prepared from a porous carbon obtained by chemical activation of a lignocellulosic precursor. The prepared electrocatalyst presents good physicochemical and electrochemical properties for its application in HER, showing low overpotential for the hydrogen evolution (54 mV *vs.* reversible hydrogen electrode) and high Tafel slope of 120 mV dec^{-1}. Future work should aim to improve the electrocatalytic stability of the material and to perform other experiments to elucidate the mechanism by which HER occurs on the electrocatalyst.

Key words

Water electrolysis, Hydrogen evolution reaction, electrocatalyst, Fe_2P nanoparticles, Porous carbon materials

1. Introduction

The increasing of energy consumption and the population awareness of environmental protection, have been promote the research on alternative and renewable energy sources. In this context, in the last years, the hydrogen gas has been considered as an alternative and environmental friendly fuel [1, 2]. In what has to do with energy applications, hydrogen gas can be used to produce electrical energy in a clean way through its use in fuel cells or it can be used to produce thermal energy by it direct combustion. Furthermore, although hydrogen gas is not directly available in the nature, there are many organic and inorganic compounds containing hydrogen element, which can be precursors for hydrogen gas production. One of the most convenient and clean methods for the hydrogen gas production is the water electrolysis. Thus, the use of electrical energy produced with a sustainable way (e.g. through wind turbines, solar cells or other clean production methods), ensures a clean and efficient hydrogen production cycle. During water electrolysis, a hydrogen evolution reaction (HER) occurs on the surface of a suitable cathode catalyst [3, 4]. Platinum (Pt) is one of the most studied and applied catalyst for HER. Although this noble metal has excellent electrocatalytic performance, with low onset potential (E_{onset}) and high efficiency, its low abundance and high cost has promoted the research to develop noble metal free catalysts [5, 6, 4, 7]. Currently, several metal alloys and metal compounds such as Ni–Co, Ni–Mo, Ni–Mn, FeP, MoS_2, have been studied [8, 9]. Some works published in the literature indicate that iron phosphide compounds have very good properties for it use as catalyst in HER [8, 10]. Besides, this type of material can be prepared by simple synthesis and from abundant and low cost precursors

On the other hand, carbon materials (CMs) including biomass derived activated carbon materials have been used as catalyst support [11, 12, 13]. CMs have also been studied as HER catalyst with interesting results [14]. Owing to their abundant sources, tunable compositions and versatile structures, heteroatom-doped carbon materials have generated tremendous research interests [3]. For example, it can be seen that co-doping N and P atoms into graphene can largely enhance the electrocatalytic activity giving much lower HER overpotential and higher current density than those of the single-doped graphene samples [15].

In this work, we study the application of Fe/P enriched biocarbon nanocomposite as catalyst for HER. The material was prepared from a porous carbon obtained by chemical activation of a lignocellulosic precursor with phosphoric acid and then heat treated in inert atmosphere. The material was structural and textural characterized and their electroctalytic behavior as HER catalyst was investigated by electrochemical analysis.

2. Materials and methods

A. Synthesis of Fe/P- enriched carbon nanocomposite

The activated biocarbon (aBC) used as support of the Fe/P compound was obtained by chemical activation of the endocarp of babassu coconut, using H_3PO_4 as activating agent [16]. The nanocomposite were prepared by a simple precipitation method [17, 18], using iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$). Then, the obtained nanocomposite was heat-treated under N_2 gas flow, using a tubular furnace at a heating-rate of 5 °C min^{-1} up to 1000 ºC (Fe_2P/aBC) with a residence time of 2 h at each final temperature.

B. Structural and textural characterization

X-ray diffraction (XRD) patterns were recorded at room temperature in a Shimadzu XRD-6000 powder diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å); the diffraction angle (2θ) was varied from 10 to 90° at steps of 0.02°. Textural analysis was conducted by recording N_2 adsorption/desorption isotherms at 77 K, using a Quantachrome Autosorb-1 instrument. Prior to each analysis, the powdered samples (with ca. 0.5 g) were purged under vacuum at 80 ºC for ca. 24 h. The specific surface area (SSA) values were determined by the Brunauer, Emmett and Teller (BET) method [19]

C. Electrochemical measurements

HER on the prepared samples was investigated at 25 ºC, in a three electrode cell using a 0.5 M H_2SO_4 solution as electrolyte. As working electrode, a suspension of 2.1 mg of the analyzed sample in Nafion® (5 wt%) was coated onto a graphite disk with geometric area of 0.496 cm^2. Platinum wire and Ag/AgCl (satured in KCl) were used as counter and potential reference electrodes, respectively. Prior to each measurement, the solution was purged with N_2 gas for 10 min to remove the dissolved oxygen. The linear sweep voltammetry (LSV) curves of each sample was recorded at the scan rate of 5 $mV \cdot s^{-1}$. In all electrochemical measurement, the Ag/AgCl was calibrated to a reversible hydrogen electrode (RHE) according to $E_{vs.RHE} = E_{vs.Ag} + 0.198\ V + 0.0591\ pH$. All the data were obtained with iR compensation. For the Fe_2P/aBC sample, a chronoamperometric experiment was also performed at -54 mV *vs.* RHE for 12 hs. All the experiments were performed with a potentiostat/galvanostat/FRA Vertex.On equipment from Ivium Technologies.

3. Results and discussion

Fig. 1 shows the DRX diffractograms obtained for the both samples. The Fe_2P/aBC sample present a well-defined set of diffraction peaks, assigned to the dominant crystalline phase of the Fe_2P compound [20]. A more detailed analysis of this XRD pattern, complemented by results of Mössbauer spectroscopy and magnetic measurements (not showed in this work), show that this sample is actually composed of a mixture of Fe_2P (major) and FeP (minor) phases, with crystallite sizes around 80 nm [18]. The textural analysis showed that the Fe_2P/aBC sample has a higher BET surface area, 1964 $m^2\ g^{-1}$, with a predomination of pore in the micropore and mesopore size ranges. Thus, it can be concluded that the used synthesis route is suitable to produce a nanostructured Fe_2P particles dispersed throughout a high porous carbon support.

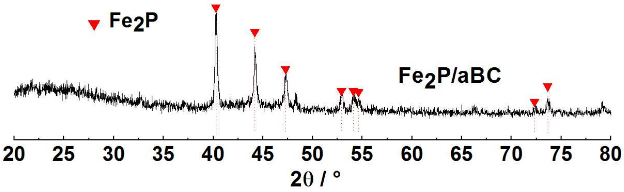

Figure 1. XRD pattern at room temperature for the Fe_2P/aBC.

The HER activity of Fe_2P/aBC was studied in a 0.5 M H_2SO_4 solution. For comparison purposes, aBC were also examined. Fig. 2 displays the LSV curves of electrodes in the potential window range of 0.1 to – 0.3 V *vs.* RHE. The best HER activity is obtained for Fe_2P/aBC, which has a much lower overpotential. For this sample, the HER E_{onset} is -54 mV *vs.* RHE beyond which, a steep increase in the cathodic current is observed. Such performance is better or similar than other reported non-noble metal HER catalysts in acidic solutions [9, 21, 22]. Further, the overpotential required for the benchmark of 50 mA cm^{-2} and 100 mA cm^{-2} current densities are 124 and 207 mV respectively. These results are good if we compared with a conventional Pt/C electrocatalyst, which exhibits the better already reported behavior (E_{onset} near zero and higher current densities) [6, 8].

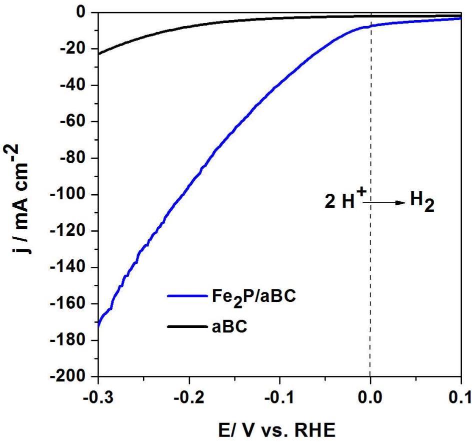

Figure 2. Linear sweep voltammetry (LSV) curves at scan rate of 5 mV·s^{-1} in the potential range of 0.1 to – 0.3 V *vs.* RHE.

The Tafel plot, representing the overpotential (η) vs. logarithm of the current density (j), for the Fe_2P/aBC catalyst is shown in Fig. 3. The Tafel line is also represented according to the equation (η = b log(j) + a) where **j** (mA cm^{-2}) is the current density, **b** (mV/dec) is the Tafel slope and **a** is the intercept which is related to exchange current density. The Tafel slope determined for the sample Fe_2P/aBC is 121 mV dec^{-1}. This value is higher than the values reported in the literature for Pt based electrocatalyst (commonly b ≈ 30 mVdec^{-1}) [8] and some previously reported works related with the application of Fe_2P based materials in HER (≈ 55 – 80 mV dec^{-1}) [8, 23]. This result may suggest that the Volmer step determining the rate of the HER. On the other hand, the mechanism of how the reaction occurs cannot be elucidated from these experiments. Some authors propose that the higher b values obtained for phosphide metal based materials, may be attributed to the abundant porous and tube structure in the materials, which result in the special absorption states [24]. This last is in accordance with the high porosity of the Fe_2P sample.

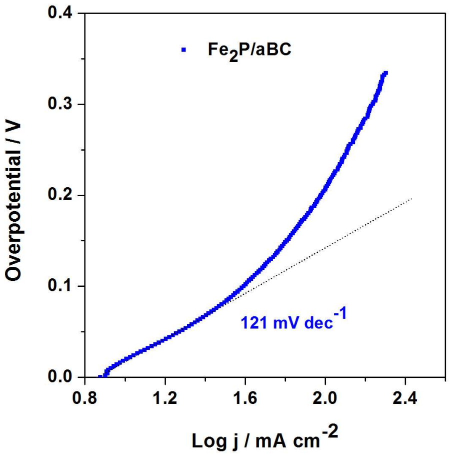

Figure 3. Tafel plot (blue curve) and the Tafel line (black line) for the Fe_2P/aBC sample.

Fig. 4 shows the time-dependent current density curve of Fe_2P/aBC under a static potential of -54 mV *vs.* RHE. After 12 hs, around 30% of the initial current density it is maintained. This stability is higher than was reported for other Fe_2P materials but is lower than Pt and graphene supported Fe_2P nanoparticles [23].

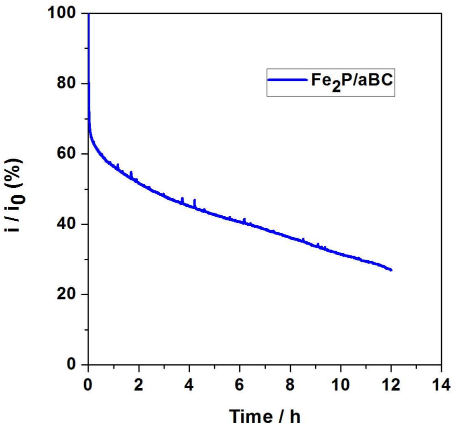

Figure 4. Time-dependent curve of current density for Fe_2P/aBC under static potential of -54 mV *vs.* RHE.

4. Conclusion

The Fe_2P/aBC sample has interesting physicochemical and electrochemical characteristics for its application as electrocatalyst in the HER. The sample showed low E_{onset} (-54 mV *vs.* RHE) and reaching 100 mA cm^{-2} at η = 207 mV. The Tafel slope determined for the sample was about 120 mV dec-1 suggesting that the Volmer step is the rate determining in the HER. The sample present acceptable stability measured for 12 hs at η = 207 mV with a retention of 30 % of the initial current. Future work should aim to improve the electrocatalytic stability of the material and perform other experiments in order to elucidate the HER mechanism on the studied catalyst.

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