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# Influence of graphitic materials microstructure in the hydrogen evolution in aqueous solution of tetra-alkylammonium-sulfonic acid ionic liquid

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## ABSTRACT

Vitreous carbon (VC), pyrolytic carbon (PC) and moulded graphite (MG) were tested as cathodic materials in hydrogen production by water electrolysis in the presence of the ionic liquid tetrafluoroborate of 3-triethylammonium-propane sulfonic acid (TEA-PS.BF<sub>4</sub>). The physical characterization of the carbon materials indicated large differences in the microstructure of VC, PC, and MG and this significantly affected their electrochemical response. The mechanism presented for all the materials studied in the hydrogen evolution reaction (HER) was Volmer–Heyrovsky, where the H<sub>2</sub> desorption at the catalytic surface is the determining step. The MG electrode presented an unfavourable performance due to the formation of nanobubbles that coalesced without H<sub>2</sub> desorption and led to the deactivation of the catalytic sites. This behaviour is attributed to the presence of large and ordered crystallites at the material surface, with a greater number of hydrophobic domains in comparison with VC and PC material surfaces. The VC and PC electrodes presented a higher performance compared to the Pt cathode, showing lower activation energy, higher cathodic exchange current and lower charge transfer resistance. The set of results indicates VC and PC as promising alternative materials to constitute cathodes for the electrolysis of water using TEA-PS.BF<sub>4</sub> aqueous solution as electrolyte.

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## Introduction

The excessive use of fossil fuels, such as coal, oil and natural gas, is leading to the depletion of natural reserves, as well as

causing ecological and climatic problems on a planetary scale [1]. Hydrogen gas (H<sub>2</sub>) is a prominent energy vector, possessing high chemical energy per mass and high heat of combustion [2–4]. Hydrogen can be produced in many ways, can be stored and transported [5], and its combustion generates only water

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and energy, more specifically, electrical energy when it is used as the feed gas for fuel cell [1]. However, 96% of the hydrogen produced in the world comes from non-renewable resources [6,7], such as natural gas by reforming and coal, petroleum coke and heavy oils by gasification.  $H_2$  generated by fossil fuels contains impurities such as CO,  $CO_2$  and traces of S and N which are poisons for fuel cell [8]. Water electrolysis is responsible for the remaining 4% of the hydrogen produced in the world, which is a very high purity hydrogen [5,8–12]. Industrially, the production of hydrogen by water electrolysis employs KOH solution (25–30 wt%) [2,9] and Ni or carbon steel electrodes [10]. In this very aggressive medium, carbon steel and Ni, despite their resistance to corrosion properties, end up deactivating during the electrolysis [2,13]. Thus, more suitable electrolytes and electrodes need to be found for this system. In recent decades, ionic liquids (ILs) have been highlighted when used as electrolyte in electrochemical devices [2,14–20]. IL are organic salts, liquid below 100 °C, composed of organic cations and organic or inorganic anions and have interesting properties as good ionic conductors [14–16]. Recently, the ionic liquid tetrafluoroborate of 3-triethylammonium-propane sulfonic acid (TEA-PS.BF<sub>4</sub>) was used as electrolyte in water electrolysis [2]. In this study, different cathodic materials such as Pt, Ni, stainless steel (SS304) and vitreous carbon (VC) were tested in 0.1 M TEA-PS.BF<sub>4</sub> solution medium. These systems presented higher current densities than systems using electrolytes composed of KOH or 1-butyl-3-methylimidazolium tetrafluoroborate (BMI.BF<sub>4</sub>) solutions. The reaction of  $H_2$  production showed extremely low activation energy when compared to the system in KOH solution medium [2].

The TEA-PS.BF<sub>4</sub> ionic liquid catalyzes the reaction, facilitating the transport of protons to the surface of the electrode. This occurs through the zwitterionic TEA-PS<sup>+</sup> species of the ionic liquid, with opposite charges on non-adjacent atoms. The zwitterionic structure TEA-PS<sup>+</sup> can form a structure of organized channels with the cathode. The positive part of the TEA-PS<sup>+</sup>, i.e., the nitrogen atom may be directed towards the cathode surface while the negative part with the hydrophilic character is directed to the solution. The percolations of several sulfonic acid groups along the solution, near the cathode, form a perpendicular structure to the surface of the electrode channels. This channel structure contributes towards proton transport to the electrode surface. The protons are carried by the Grothuss structural mechanism, namely water molecules strongly bound to sulfonic acid groups, which promotes the movement of protons through the channels by the formation and cleavage of hydrogen bonds [2,8,21,22].

The cathodic material is very important for HER, it must have high catalytic activity, small cathodic overpotential and a high surface area, besides being resistant to a very corrosive medium in order to minimize the operation costs of the electrolytic cell [9,23]. Graphitic materials such as vitreous carbon (VC), pyrolytic graphite, carbon tissue, carbon paper, amorphous carbon and even pencil graphite, are used as both nanoparticles support and inert electrodes [2,8,13,23–26]. Graphitic materials are polycrystalline materials consisting of graphitic planes [27,28]. Moreover, these materials have many defects in their structure such as crosslinks, vacancies, interstitial planes, impurities, porosity, crystallite size differences and disordered crystallographic orientation. The presence of

these defects affects significantly the properties of graphite materials. These properties vary according to the level of the disorder of the material microstructure and are controlled by the treatment that the material received during its production [27–30]. Thus, graphitic materials, due to their characteristics described above, can be used as working electrode in water electrolysis and not only as support material for nanoparticles of the noble metals, leading to a very interesting economic alternative system for hydrogen production. Furthermore, exploring the influence of different classes of graphite materials on their electrochemical behaviour in water electrolysis should give important new complementary information which, as far as is known, has not yet been the object of investigation.

The aim of this work is to test different graphitic materials used as cathode in hydrogen production by water electrolysis employing an aqueous solution of the TEA-PS.BF<sub>4</sub> (0.1 M) ionic liquid as an electrolyte. The graphitic materials used as cathodes were characterized by Raman spectroscopy, X-ray diffraction and scanning electron microscopy and their electrochemical performance was evaluated using the techniques of chronoamperometry, linear voltammetry and electrochemical impedance spectroscopy.

## Experimental

### Materials

The TEA-PS.BF<sub>4</sub> ionic liquid was synthesized according to previously published reports [21,22]. All electrochemical measurements were realized in 0.1 M TEA-PS.BF<sub>4</sub> solution medium. The pH of this solution was measured with a pH meter (ITPH-2300 INSTRUTEMP) and found to be 0.85. The ionic conductivity of this solution was 27.1 mS cm<sup>-1</sup> (conductivity meter, Hack Sension 7).

Three plane disc electrodes were made, each with one graphitic material: vitreous carbon (VC), pyrolytic carbon (PC) and moulded graphite (MG). These electrodes consisted of a cylinder of 15 mm height and diameters of 3.1 mm (VC) and 4.0 mm (MG and PC) with the laterals encapsulated with polymer. The work electrodes were polished first with 600 and 1200 mesh sandpapers and then using an aluminium oxide suspension with 1 µm grain size (FORTEL). The electrodes were then washed using deionized water and dried under a compressed air jet. Next, the polished electrodes were submitted to 20 cycles of voltammetry between  $-2.0 V_{SCE}$  and  $+0.2 V_{SCE}$  with a scan rate of 50 mV s<sup>-1</sup>, in 0.1 M TEA-PS.BF<sub>4</sub> ionic liquid aqueous solution, to clean the material surface leading to activated electrodes.

The characterization of the graphitic materials was realized by micro Raman spectroscopy (Raman), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The order of C–C bonds in the material structure was evaluated with a micro Raman system where a He–Ne LASER ( $\lambda = 632.8$  nm and 10 mW power) was focused on the material surface. The backscattered beam was filtered and captured with a Charged Couplet Device (CCD) monochromator. The crystallinity of the graphitic materials was analysed by XRD. The X-ray powder diffraction analysis was realized in a D500

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