



XVIII International Congress of the Mexican Hydrogen Society



SYNTHESIS OF CARBON-BASED SUPPORT FOR RUTHENIUM ELECTROCATALYST FOR ORR FORMED BY GRAPHITE AND ASPHALT CARBON PYROLYZED

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ABSTRACT

The oxygen reduction reaction (ORR) that takes place in the cathode of PEM fuel cells has been an object of study of great interest in the electrocatalysis field, due to its low reaction kinetics, compared to the hydrogen oxidation reaction (HOR) that occurs at the anode of the cell. Several research groups have focused on developing economic alternatives that can approximate the intrinsic kinetic values of these two reactions. Platinum (Pt) is the most efficient electrocatalyst for ORR, followed by other transition metals (Ru, Ir, Fe). The synthesis of metallic catalysts using different kinds of supports have improved their performance and helped to reduce their cost in the past. These supports are aimed to increase the dispersion of the active phase and reduce the metal loading without affecting the catalytic activity. Carbon black is a common used support, due to its high surface area, pore size distribution, and high electrical conduction properties. This study offers an alternative carbon-based support, which is obtained by pyrolysis of asphalt/graphite at 600°C (S-AG) under a nitrogen atmosphere (N₂). Through the combination of the physical and chemical properties of the two different carbon sources (asphalt and graphite) an improvement effect on the performance of the support is expected with respect to commercial carbon Vulcan[®]. For their performance evaluation, Ruthenium (Ru) at 20% W was used as an active phase. Ruthenium(III) chloride hydrate (RuCl₃·XH₂O) was used as a precursor, which was reduced in two steps, the first one by NaHB₄ and the second in a reducing atmosphere (Ar/H₂) at 420°C for 1h. The obtained material was characterized by elemental analysis (ICP), XRD, BET Area and SEM. For the electrochemical evaluation, cyclic (CV) and linear sweep (LV) voltammetry were used. In a first stage of the study, results indicate a better electrocatalytic activity of the ruthenium (Ru) impregnated on the S-AG synthesized support.

Key words: ORR, electrocatalysis, carbon-base support, heteroatoms.

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1. Introduction

The lifestyle of our modern society has caused a constant increase in the world energy consumption [1]. The consequences of fulfilling the demand, mainly through the combustion of fossil fuels, have brought a negative impact on the environment. Fuel cells are electrochemical devices that generate an electric current from chemical reactions. These devices allow a better use of energy vectors such as hydrogen and/or methanol, for the production of electricity, since they are more efficient compared to traditional fuel-burning electric generation, as well as being environment-friendly, because water and heat are their main reaction products. For this reason, they continue to be a viable option in combination with other renewable energy sources to contribute in the reduction of the carbon footprint generated by the power electricity industry.

One of the technical barriers that have prevented the establishment of this technology is the slow kinetics of the oxygen reduction reaction (ORR) in the cathode of the cell. The effectiveness of Platinum (Pt) as a catalyst for this reaction is well documented. However, its high cost associated with its scarcity and wide field of applications, has triggered a large number of researches, seeking to obtain a material with adequate electrocatalytic properties at reasonable price. For this purpose, supported catalysts have been of special interest, since they allow a better dispersion and stability of the metallic particles, provide access to a greater amount of atoms of the active phase, thus reducing the amount of metal loading and decreasing their cost [2].

The use of different types of supports for this purpose has been widely studied [3][4][5][6]. Carbon-based supports are the most commonly used due to their chemical stability in acidic and basic environments and their ease to recover the metal by just burning the support [2]. Within ideal characteristics of an electrocatalyst support for PEM fuel cells include: must be a good electrical conductor, avoid agglomeration of the active phase, present high surface area, present adequate pore size distribution that allows interaction between the polymeric electrolyte and the catalyst, be resistant to corrosion, chemically inert and do not contain impurities that may inhibit target chemical reactions [7]. The most used carbon material support is carbon black; this material has good conductive properties, corrosion resistance and low cost [6]. However, there are alternate available materials that may contribute to the desired ideal characteristics of an electrocatalyst support such as graphite and asphalt.

Graphite is a blackish gray substance made of crystallized carbon. Carbon atoms are arranged in hexagonal ring planes stacked one on top of the other [9]. Only three of the four valence electrons of each carbon atom are involved in the formation of hybrid sp^2 bonds with three other atoms of the same plane, this means that the fourth electron forms a π bond. These last electrons are mobile, so graphite has good electrical conduction properties [2] [10]. A situation to be highlighted is that although the carbons that contain sp^2 hybridization present a large number of free electrons for their π bonds, these electrons are partially inert to be used in the ORR. In the case of nanostructures doped with heteroatoms such as nitrogen (N) and sulfur (S), the π electrons of the carbon can be activated by conjugation with the pair of free electrons of the dopants, obtaining

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better results [11][12][13][14]. Besides, according to the above mentioned ideal properties of a support, graphite has a better resistance to corrosion than amorphous carbon, which is an important feature for its application in fuel cells.

Furthermore, asphalt is classified as a set of macromolecules of polycyclic aromatic rings of carbon and hydrogen with heteroatoms such as nitrogen (N), sulfur (S) and oxygen (O) and metals (V and Ni), with chains of alkanes at their ends [15]. It is one of the main precursors of sludge and sediments in the process of extraction and treatment of crude oil. Although it has some commercial uses, it is mainly considered a waste product. In addition, asphalt is considered a rich material in carbon and heteroatoms.

Moreover, an additional consideration in the catalytic phenomena deals with the presence of active sites. Therefore, during the synthesis of a catalyst it is always sought to generate the largest possible number of these. According to the literature, within an electrocatalyst the simultaneous presence of a transition metal, carbon and heteroatoms are important components for the creation of active sites [8]. For this reason, in the present research it is proposed that the combination of graphite and asphalt, as raw materials, could provide improved physical and chemical characteristics during the synthesis of a carbon-based support than the black carbon support commonly used in today's metal electrocatalysts for the ORR of a PEM fuel cell at the cathode. Furthermore, this work presents the synthesis, characterization and electrochemical evaluation of a support material obtained by the pyrolysis of asphalt-graphite at 600°C (S-AG) and its comparison against the most used carbon support, the Vulcan XC72R (Cabot), using Ruthenium (Ru) at 20% as the electrocatalyst active phase.

2. Materials and Methods

Synthesis

For the support preparation, a commercial solid asphalt bar and graphite powder (Meyer) were used as raw materials. The graphite was subjected to a milling process in high energy ball mill Spex 8000 M in a 7:1 ratio for 8 hours. 20% W ruthenium (Ru) was used as an active phase, by employing $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich) as the metal precursor, while NaBH_4 (Sigma-Aldrich) was used as a reducing agent. For the synthesis of the support (S-AG) by pyrolysis a Barnstead-Thermolyne model 21100 tubular furnace was used in combination with a stainless steel reactor equipped with an inner quartz tube to hold the sample. The initial mass in the pyrolysis reactor contained a mixture of 70% asphalt and 30% graphite. The first stage consisted of a pretreatment in air, with a flowrate of 100 ml/min, at a heating rate of 5°C/min to reach 250°C, for 60 minutes, this with the purpose of increasing the yield of the pyrolysis product up to 4%. Subsequently, a N_2 flowrate of 100 ml/min was introduced to the reactor and this further heated using a heating rate of 5°C/min, up to a temperature of 600°C, for 120 minutes. The obtained material was manually grounded in an agate mortar. For the synthesis of the electrocatalyst, the impregnation method was used. In a 125 ml Erlenmeyer flask, 1 g of NaBH_4 and 45 ml of water were mixed and stirred until complete dissolution of the sodium borohydride at room temperature (25°C). Then a 0.1 M solution of RuCl_3 was added dropwise, with the help of a hypodermic syringe, while keeping a

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moderate stirring at a temperature between 55-60°C for one hour. Then the synthesized support (S-AG) was added to this resulting liquid and it was kept under continuous stirring for two hours at the same temperature, filtered and rinsed several times with warm water (60°C). The resulting sample was exposed to a second reduction process in the tubular furnace, under a reducing atmosphere of 95% argon (Ar) and 5% hydrogen (H₂), using a gas flowrate of 100 ml/min at a heating rate of 5°C/min up to a temperature of 420°C for 60 minutes. For the reference carbon support (Vulcan-XC72R, Cabot) the same former described impregnation procedure of Ruthenium (Ru) was employed.

Characterization

For the characterization of the synthesized electrocatalyst, a FlashSmart Elemental Analyzer of the Thermo Fisher Scientific brand was used to determine C, H, N, S, and O. For the crystal structure of the samples X-ray diffraction characterization (XRD) was achieved using a PANalytical diffractometer model XPert PRO, with X Celerator detector and a monochromatic radiation emitted by Cu K α ($\lambda = 1.5406 \text{ \AA}$). The diffraction angle 2θ was varied from 5° to 90°, with a step size of 0.05° and time of 150 seconds. The Scherrer's equation was used to determine the crystallite size. To determine the BET surface area, volume and pore distribution of the sample, a Quantachrome Instruments equipment model Autosorb-1C was used. The test was carried out in nitrogen at 77K for physisorption. Morphology characterization of the samples was made by scanning electron microscopy (SEM) using a Jeol JSM-7401F field emission microscope, the sample was prepared by adding methanol and placing it in a brass, copper, and zinc sample holder. The micrographs were taken with different working distances (WD).

Electrochemical evaluation

Cyclic (CV) and linear sweep voltammetry (LVL) were performed for the electrochemical evaluation of the catalyst. The equipment used was a Princeton brand potentiostat model VersaSTAT 3 and a rotary disc with a rotor speed regulator (PINE Instruments). An arrangement of three electrodes were employed, using a working electrode, a platinum electrode as a counter electrode (CE) and an Ag/AgCl electrode as a reference electrode (ER). The evaluation was performed in acid medium, using a solution of H₂SO₄ (JT Baker) 0.5 M as an electrolyte. Catalytic inks were prepared with 20 mg of catalyst sample, 1 ml of ethanol (JT Baker 99.6%) as a solvent and 30 μ l of Nafion[®] as an adhesive. This mixture was sonicated for 40 minutes. The inks obtained were deposited with the help of a micropipette, placing 30 μ l of ink on a glassy carbon electrode of 5 mm in diameter, they were allowed to dry at room temperature for one day. The H₂SO₄ electrolyte was bubbled with nitrogen (N₂) for 20 minutes to displace any oxygen present in the solution. The material was activated by VC with a potential window of -0.2 to 1 V at 50 mV/s during 40 cycles while keeping N₂ bubbling. After activation, the electrolyte was left bubbling with N₂ for 15 minutes. Three VC cycles were run, at 20 mV/s, with the same potential window. Under the flow of N₂, a VL, from 1 to 0.2 V was run at 5 mV/s at a rotation speed of 2000 RPM. To check material activity for the ORR, the electrolyte was bubbled with O₂ for 20 minutes. A VL was performed at 5 mV/s, at the same potential window at 5 mV/s with a rotation speed of 2000 RPM, while keeping the O₂ bubbling during the test.

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3. Results and Discussion

Characterization

Table 1 present results obtained for the composition of the raw asphalt material determined by elemental analysis. It is observed that the elements of interest (C, N, and S) are present in the sample. The compositions in which these elements are found, agree well with those of asphalt reported by S. Akmaz et al. [16].

Table 1. Elemental Analysis CHNS/O of asphalt.

	C %	N %	H %	S %	O %
Asphalt	81.088	0.443	8.899	3.788	5.782

Moreover, sample S-AG synthesized by the pyrolysis process preserves the elements of interest in the amounts shown in Table 2. Here, there is an increase of 10% of carbon with respect to the asphalt sample and this is presumably due to the integration of the graphite within the material, while keeping the heteroatoms of interest.

Table 2. Elemental analysis CHNS/O of asphalt/graphite pyrolyzed at 600 ° C (S-AG).

	C %	N %	H %	S %	O %
S-AG	91.939	0.721	1.127	2.755	3.458

Figure 1 shows the XRD diffractogram for sample S-AG RuM. The diffraction peaks at $2\theta = 38.2$, 42.0 and 43.8° are assigned to the planes (100), (002) and (101), which are characteristic signals of hexagonal ruthenium according to the literature [17]. For the signals that do not correspond to the ruthenium, a literature review of articles related to the type of expected materials was carried out. According to this review L. Liu et al [18] reported a diffraction signal observed in 2θ between 24.5 - 26° which corresponds to semicrystalline carbon. The expected signals assigned to the graphitic structure are located around $2\theta = 43^\circ$ [19] [20]. However, they are not easily distinguishable by their concurrence with ruthenium (Ru) signals, which are more intense. In order to estimate the average crystallite size, the XPowder software was used, by the method of Scherrer, resulting in an average size of 6 nm.

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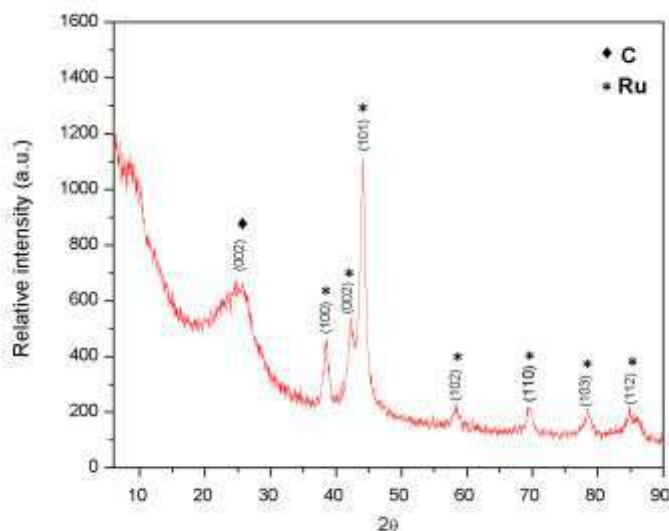


Figure 1. Diffractogram of the S-AG RuM electrocatalyst.

Figure 2 shows the adsorption/desorption N_2 isotherm obtained from the S-AG RuM sample. Here, it can be observed a type II isotherm, which is characteristic of non-porous solids or containing macropores, agreeing with results found in the literature [21]. The hysteresis loop of the isotherm does not completely close at low relative pressures ($P/P_0 < 0.4$). This effect can be explained by the desorption mechanism, which at the end of the capillary condensation, in these cases, this fall is insufficient to connect the desorption to the adsorption lines. Furthermore, the material presented a BET surface area of 403 m²/g.

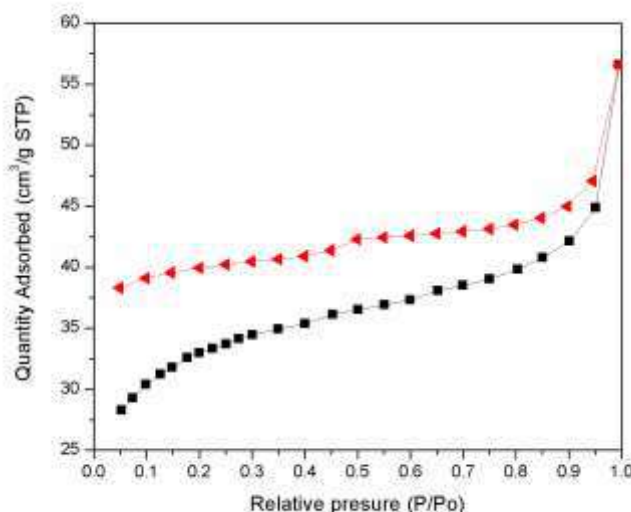


Figure 2. adsorption/desorption N_2 Isotherm for sample S-AG RuM.

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82.202	1.372	2.815	6.351	7.26
84.952	N.D.	1.377	4.73	8.941
80.883	N.D.	0.785	4.694	13.638
86.421	403	0.119	5.878	7.582



Figure 3 presents scanning electron microscope (SEM) micrographs taken at different magnifications by secondary electrons of the S-AG RuM sample. The carbon support (S-AG) exhibits irregular morphology, variable in each particle with different sizes among particles. Here in these micrographs the expected components in the electrocatalyst can be identified. The carbonaceous composition of the electrocatalyst is distinguished by presenting a dark color, and the presence of ruthenium metal active phase (Ru) can be distinguished by a lighter color. Also, ruthenium particles present agglomerations, which is undesirable for the purpose of this material.

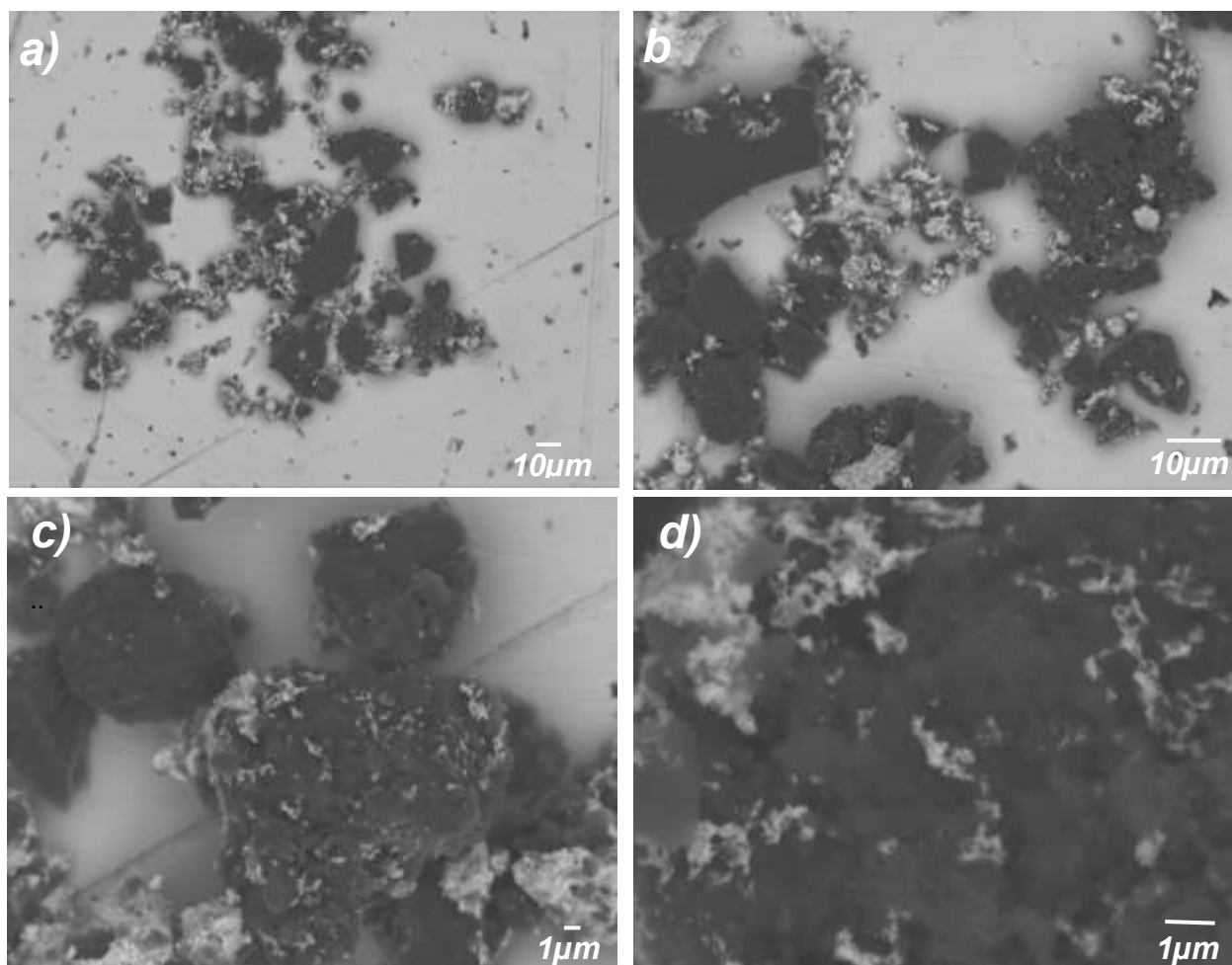


Figure 3. SEM images of S-AG RuM Electro-catalyst, taken at different magnifications: a) 500, b) 1,000 c) 3,000 and d) 10,000.

Electrochemical evaluation

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The capacitive activity of the material was evaluated by cyclic voltammetry (CV) in N_2 . Figure 4 shows the CV curves in N_2 of the materials. Both S-AG RuM and the Vulcan RuM, present good energy storage capacitance, according to the supercapacitance properties associated with carbon materials as reported in the literature [22].

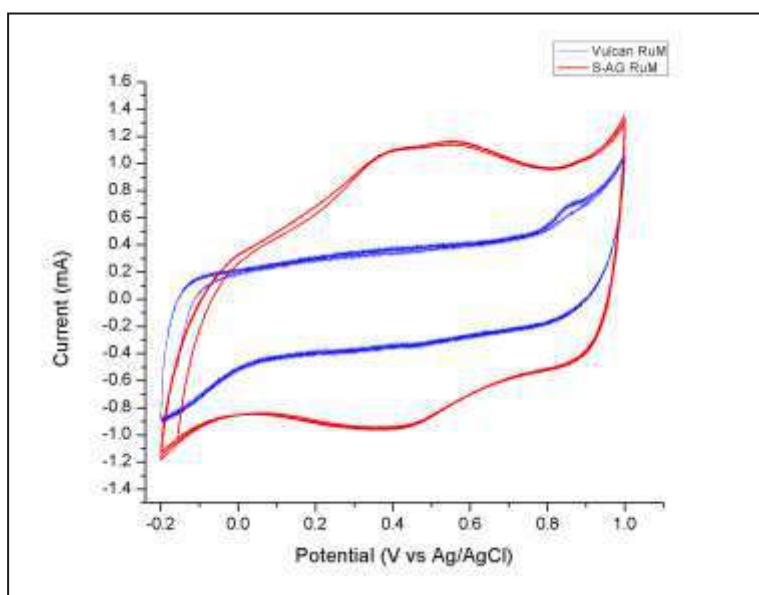
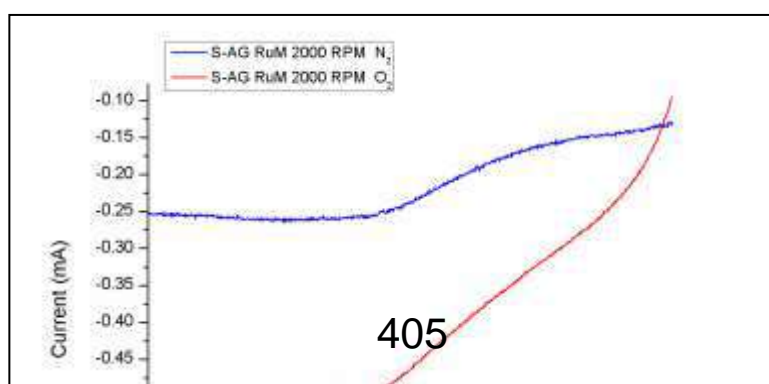


Figure 4. VC of the S-AG RuM and Vulcan RuM electrocatalyst.

Figure 5 shows the linear voltammetry of the S-AG Ru in N_2 and O_2 , which verify its electrocatalytic activity. The first significant signal occurs approximately at 0.7 V. It presents a slight-pronounced drop compared to the characteristic behavior observed in Pt/C materials under the ORR [23]. Furthermore, Figure 6 shows an electrocatalyst activity comparison of ruthenium (Ru) supported in S-AG and carbon Vulcan in O_2 at 2000 RPM based on their linear voltammetry response. It can be deduced that while being the same ruthenium material, the synthesized S-AG carbon support helps to improve the activity of the electrocatalyst, even though the difference between this and Carbon Vulcan is approximately of 30 mA, which is a significant amount.



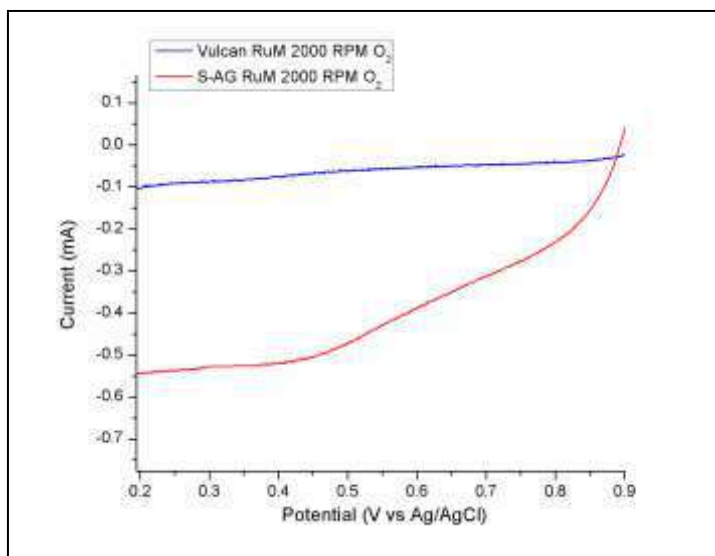


Figure 6. Linear Sweep Voltammetry of Electrocatalyst S-AG RuM Vs Vulcan RuM at 2000 RPM in O₂.

4. Conclusion

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The carbon-based support obtained by the pyrolysis of asphalt and graphite (S-AG) exhibit some important characteristics that make possible to be used as an electrocatalyst support. This S-AG combines the good conductivity and superficial area of graphite with the increase of active sites due to the presence of asphalt's heteroatoms, since this is a self-doped carbonaceous material containing elements of interest such as nitrogen (N) and sulfur (S). The free electrons of these atoms, presumably modify the electronic distribution in the material, thus helping the electron donation by the neighboring carbon. The methodology employed to synthesize the support by pyrolysis is a simple route, which does not require the use of specialized equipment, while employing easily available raw materials, doing this procedure an inexpensive process. The electrochemical evaluation showed a good performance of the S-AG support compared to the conventional Vulcan XC72R, working with ruthenium (Ru) as the active phase of the electrocatalyst, in acid medium. Results presented here, will follow with the study of this material in order to determine its functionality and corrosion resistance under specific conditions of PEM fuel cells, which are more aggressive over extended periods of time.

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