Study of reticulated vitreous carbon surface treated by plasma immersion ion implantation for electrodes production

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Abstract. RVC samples were treated by nitrogen plasma immersion ion implantation (N-PIII) for electrodes production. High-voltage pulses with amplitudes of ~3.0 kV or ~10.0 kV were applied to the RVC samples while the treatment time was 10, 20 and 30 min. The samples were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. The SEM images present an apparent enhancement of the surface roughness after the treatment probably due to the surface sputtering during the PIII process. This observation is in agreement with the specific electrochemical surface area (SESA) of RVC electrodes. An increase was observed of the SESA values for the PIII-treated samples compared to the untreated specimen. Some oxygen and nitrogen containing groups were introduced on the RVC surface after the PIII treatment. Both plasma-induced process: the surface roughening and the introduction of the polar species on the RVC surface are beneficial for the RVC electrodes application.

1. Introduction
The reticulated vitreous carbon (RVC) is a form of macroporous polymeric carbon, which is produced by carbonization of polymers in the expanded form or by voids generating materials. The RVC has semiconducting properties, low density (0.05 g/cm³), high corrosion resistance and low thermal expansion. The RVC is a kind of material that is frequently applied for electrodes production due to its high surface area and good electrical properties, such as high current density, low electrical resistance and chemical inertness [1]. RVC electrodes are applied in flow cells for elements detection in aqueous solutions. Additionally, it is used in the electro-analytical field for removing heavy metals (Hg, Cu, Pb) and for measuring the toxicity of water and solutions [1]. RVC has been recently applied as a stack material in thermo-acoustic devices [2], in the preparation of PbO₂ coatings for the electro-oxidation of organic pollutants [3] and in biofuel cells as an electrode [4].

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RVC electrodes can be applied as-received or modified by some kind of treatment to improve further certain desired properties. This work describes the modification of RVC by plasma ion implantation (PIII) in view of production of electrodes. The RVC samples were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), corrosion tests, cyclic voltammetry and open-circuit potential measurements.

2. Experimental
The RVC was purchased from Sanko Foams Ltda in the form of a polyurethane foam with 70 ppi (pores per inch). As-received RVC substrates were treated by PIII using nitrogen as gas precursor. A detailed description of the PIII system was given elsewhere [5]. The samples were immersed in nitrogen glow discharge plasma and pulsed at high negative voltage. Ions extracted from the plasma were implanted at normal incidence into all sides of a 3D sample. The samples were treated for 10, 20 and 30 minutes using high-voltage pulses with amplitudes of 3.0 and 10.0 kV. The other process parameters, namely, working pressure of $6.0 \times 10^{-3}$ mbar, 200 Hz pulse repetition rate and pulse width of 20 µs were kept fixed during the treatment. The morphological changes on the surface of untreated and treated samples were examined by a JEOL model JSM 5310 microscope. The chemical characterization of the surface was carried out by X-ray photoelectron spectroscopy using a Kratos XSAM 800 spectrometer, using Mg Kα radiation and fixed analyzer transmission mode. The electrochemical measurements were obtained by means of an Autolab 302N potenciostat using a conventional three-electrode glass cell.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)
The SEM technique was used to obtain information about the surface morphology of the RVC; the images obtained are presented in figure 1. Figures 1 (a-b) show the general view and the detailed view of a macroporous RVC sample. The SEM image of RVC treated at 3kV and 10 minutes shown in figure 1(c) exhibits an apparent roughening of the surface when compared to the untreated sample in figure 1(b). This effect is caused by the RVC surface sputtering during the PIII process. This observation is in agreement with the specific electrochemical surface area (SESA) values of RVC electrodes, which will be discussed later.

![Figure 1](image.png)

**Figure 1** - SEM images of untreated samples: (a) magnification of 50 x and (b) 1000X, (c) treated sample at PIII-3kV-10min - magnification of 1000 x.

3.2. X-ray photoelectron spectroscopy (XPS)
The chemical composition of surface of the RVC samples was examined by XPS analysis (table 1). For both treatments, the PIII induced surface changes on the RVCs in the form of nitrogen and oxygen containing polar groups formed on the RVC surface. The presence of oxygen groups in the as-received RVC was attributed to the furfuryl resin used in the manufacture of RVC. A gradual incorporation of nitrogen takes place upon increasing the treatment time at 3.0 kV, while at 10.0 kV an abrupt increase of the N content is observed. However, for the treatment time of 30 min, the N content tends to
saturate due to sputtering that occurs during the PIII process. Considering similar treatment times, at higher voltage (10 kV) the amount of incorporated N scales from 4% up to 11 at.% and at lower voltage (3 kV), the N content ranges from 2% up to 5 at %. This behavior can be explained by the fact that nitrogen is incorporated on the RVC surface during the N-implantation, as confirmed by PIII treatment in other materials [6]. The evolution of the O-content is not monotonic. At 3 kV after 10 min treatment, it increases from 20 to 39 at%, but at longer treatment times the increase of O-content is smaller (33 at% after 20 min and 28 at% after 30 min). A similar behavior was noted for the samples treated at 10.0 kV pulse voltage but with different O-contents. The effect can be ascribed to the presence of oxygen impurities on the PIII chamber wall, so that at lower treatments times (10 min), a higher O-content is observed. However, as the treatment time increases, the O impurities are gradually removed from the system and less O is implanted. At a higher pulse voltage (10.0 kV), a similar process takes place, with the O-content decreasing down to 18-20 at% for treatment times longer than 20 min, which is the same as for the untreated sample.

### Table 1. Surface composition of RVC samples.

| Treatment | Composition |
|-----------|-------------|
| U [kV]    | t [min] | O [at%] | N [at%] | C [at%] |
|-----------|---------|---------|---------|---------|
| 0         | 0       | 20      | 0       | 80      |
| 3         | 10      | 39      | 2       | 59      |
| 3         | 20      | 33      | 4       | 63      |
| 3         | 30      | 28      | 5       | 67      |
| 10        | 10      | 34      | 4       | 62      |
| 10        | 20      | 18      | 11      | 72      |
| 10        | 30      | 20      | 10      | 71      |

3.3. Electrochemical measurements

The open-circuit potential method consists in measuring the potential versus the time until a transition in the potential profiles is observed. Measurements of the open-circuit potential of RVC samples were performed to verify the stability of the electrodes in a NaCl 3.5% w/w and pH = 6.0 solution aiming to obtain information about the electrodes behavior in a corrosive environment. The untreated sample quickly reaches stabilization potential around 0.3 V, while the treated samples requires a longer time to achieve stabilization. The untreated sample shows a more positive potential (0.30 V) than the treated electrodes. However, the electrodes treated at 3.0 kV during 10 min and 10.0 kV during 30 min showed stabilization potential around 0.28 volts, which is closer to the untreated one indicating electrodes with higher corrosion resistance. On the other hand, the other treated electrodes exhibited a less noble behavior.

Polarization curves were investigated for analyzing the corrosion behavior of the electrodes in the NaCl 3.5% w/w solution. They were obtained immediately after the measurements of the open-circuit potential. It can be seen in figure 2 the untreated RVC samples have higher corrosion potentials ($E_{corr} = 0.23$ V) compared to the treated samples. For these samples the corrosion potential vary between 0.0 and -0.26V. The results also show that the samples treated at 10 kV and 30 minutes have corrosion current density higher by a factor of about 2.0 than the untreated sample ($3.0 \times 10^{-9}$ A/cm²), which indicates a slight decrease of the corrosion resistance after the implantation. However, this increment in the current densities is not significant because the corrosion currents still remain quite low ($10^{-9}$ A/cm²) which indicates a good corrosion resistance.

Using cyclic voltammetry it is possible to determine the specific electrochemical surface area (SESA) using the Randles-Sevcik equation [7]. These tests were performed in a solution of 1 mM K₄Fe(CN)₆·3H₂O in 0.1 M KCl using a scan rate of 5 mV/s. They are used to determine the peaks of anodic and cathodic current densities that are used in the SESA determination. It was observed that the anodic current densities peaks for treated samples increased compared to the untreated one ($2.0 \times 10^{-5}$ A/cm² up to $3.6 \times 10^{-5}$ A/cm²). The increase of these current densities results in an increase of the SESA values as can be seen in Table 2. Increasing the implantation dose (RVC electrode treated at 10 kV and 30 min) resulted in a smaller anodic current density peak. The
highest current density \((3.6 \times 10^{-5} \text{ A/cm}^2)\) was exhibited by the electrode treated at 3kV for 10 min. This current density is almost twice as high as the value of the untreated sample, which suggests an approximately twofold increase in the surface area of the RVC electrodes (table 2). The increase of the SESA values for the treated samples probably occurs due to the surface attack (sputtering) during the implantation with nitrogen, which promotes a general increase of the surface roughness [6]. However, as can be seen in table 2, as the implantation dose increases the SESA area and the anodic peak current density decrease. This is probably due to the enhanced sputtering of the RVC samples at higher implantation dose, which smoothen the material surface.

**Table 2.** SESA values for RVC samples.

| RVC Samples   | SESA \([\text{cm}^2/\text{cm}^3]\) |
|---------------|-----------------------------------|
| Untreated     | 38.0                              |
| 3kV-10 min    | 71.5                              |
| 3kV-20min     | 45.4                              |
| 3kV-30min     | 46.4                              |
| 10kV-10min    | 56.5                              |
| 10kV-20min    | 47.7                              |
| 10kV-30min    | 36.6                              |

**Conclusions**

RVC samples were treated by nitrogen plasma immersion ion implantation. The PIII treatment caused a slight decrease in the corrosion resistance of the RVC samples. However, they maintained their current densities in the same order of magnitude as the untreated sample. There was up to twofold increase of the active area (SESA) for the electrodes treated by PIII compared with the untreated sample. These results are in agreement with the SEM images, as the PIII-treated samples appear to be rougher than the untreated sample. The results of the XPS analysis for all treatments show that the N-PIII treatment introduced active oxygen and nitrogen-related polar groups on the RVC surface, thus improving their wettability. This fact, together with the increase of the surface roughness, would contribute to the RVC application as electrodes.

**References**

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