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PANi – TiO_2 nanostructures for fuel cell and sensor applications

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Composites of PANi and TiO_2 nanoparticles were investigated for applications in direct methanol fuel cell and alcohol sensors. Anilinium sulfate and TiO_2 with nanometric size were electropolymerized in 0.5M H_2SO_4 solution on carbon paper. Oxidation and response to methanol was measured by chrono amperometry and elctrochemical impedance spectroscopy.

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1. Introduction

Conductive polymers are extensive studied due to their properties and advantage to be processed from micro to nanometer scale [1,2].

The conjugated polymer polyaniline is a promising material for alcohol sensors, since its conductivity is highly sensitive to chemical vapors. Being involved oxidative mechanisms due to its redox center PAni with appropriate nanomaterials open new perspective to be used in methanol fuel cells. There are several key issues in designing of sensor array in nanofibres by interfacial electropolymerization in a template. Nanofibres of polyaniline are found to have superior performance relative to conventional materials due to their much greater exposed surface area [3-8]. The combination between emeraldine form of the polyaniline and electron-hole generator such as TiO_2 rise to advance oxidation process useful in methanol fuel cells or vapor detection. This work deal with electropolymerized polyaniline with TiO_2 nanoparticles using a solution of anilinium sulfate dissolved in 0.5M H_2SO_4. The response to methanol oxidation was measured by chromoamperometry and electrochemical impedance spectroscopy. From all the conductor polymers we guided our attention on the nanostructures of polyanilne and TiO_2, which have been investigated for applications in sensors. Nanostructures were obtained by chemical polymerization of a TiO_2 aniline sulfate mixture and electrochemical deposition on carbon paper.

2. Experimental

Aniline sulfate is obtained from aniline (monomer distilled at 184°C, then filtrated and dried) and 0.5M sulfuric acid. The active solution is stirred for 20 min, then the resulting aniline sulfate is filtered. 0.852g aniline sulphate and 0.018g TiO_2 nanopowder with 80 to 100nm in diameter is mixed with 25ml H_2SO_4 solution. Nanostructures of PANI- TiO_2 on carbon paper are obtained by electrochemical synthesis at concentration 0.5M sulphuric acid. Cyclic voltammograms, impedance spectroscopy and chronoam-perometry are obtained using a VoltaLab 4.0 Potentiostat (Radiometer Analytical) with Ag/Ag Cl electrode as reference electrode, platinum electrode as auxiliary electrode and carbon paper as working electrode. After the obtaining of polyaniline with TiO_2 films, the partial pressure of methanol vapors has been monitored, at 30^0C working temperature.

3. Results and discussion

The cyclic voltammogrames were recorded at a polarization rate of 100mV/s in range – 0.2 – 0.8V range for aniline sulfate solution in 0.5M sulfuric acid. The oxidation peak is at 440mV and reduction peak at-103mV (Fig. 1).

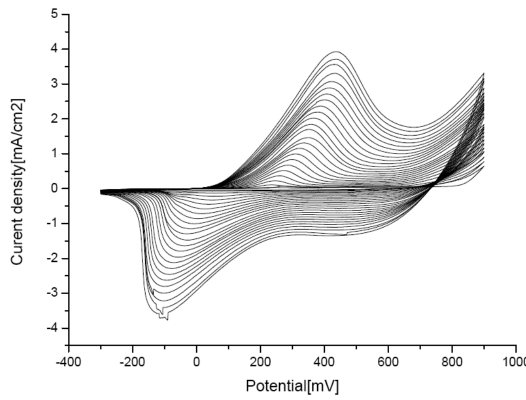
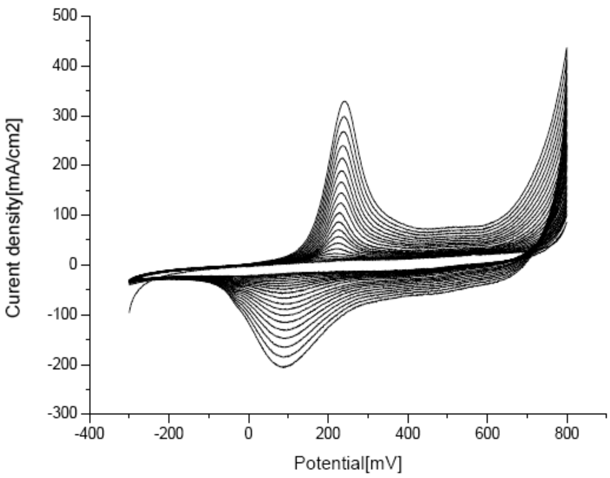


Fig. 1. Cyclic voltammogrames, electrochemical synthesis of polyaniline films in solution of 0.5M sulfuric acid on carbon paper.

The anodic peak is assigned to the formation of radical cation, indicative the oxidation of the leucoemeraldine form to emeraldine. In figure2 are shown cyclis voltammogrames with two sulfuric acid concentrations for aniline sulfate and TiO_2. The oxidation peak is dependent of sulfuric acid concentration.



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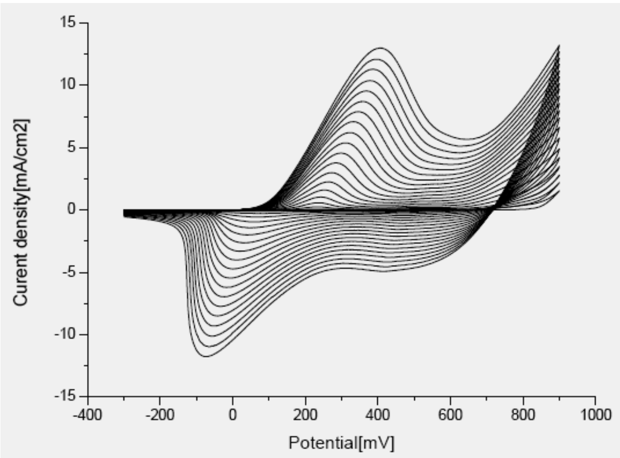

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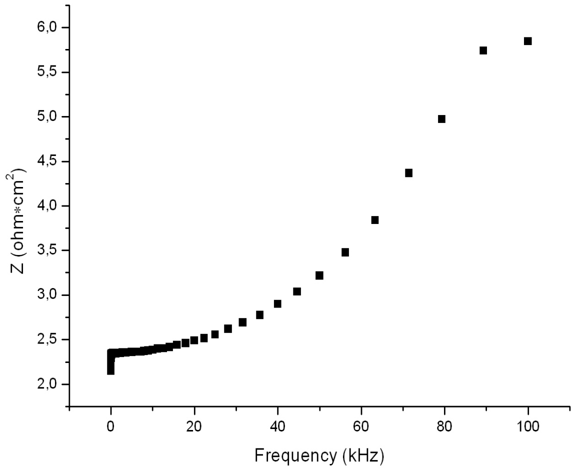
Fig. 2. a) Cyclic voltammogrames obtained at the electrochemical synthesis of PANI-TiO_2 films in solution of sulfuric acid of concentration 0.2M on carbon paper, 30cycles; b) Cyclic voltammogrames obtained at the electrochemical synthesis of PANI-TiO_2 films in solution of sulfuric acid of concentration 0.5M on carbon paper, 20 cycles.

At 0.2 M concentration oxidation peak is at 242 mV and at 05M oxidation peak is located at 405 mV. By comparing those figures we observe that redox process remains reversible.

After the poyaniline films and TiO_2 have been obtained it was followed the methanol vapor pressure at the 30C temperature, it was measured with the help of VoltaLab spectroscopy of impedance and chronoamperometry. In the case of the impedance spectroscopy it was used a potential of 5mV and the frequency was between 100 mHz and 100 kHz. In the case of the chromoamperometry there were used the following parameters: voltage of 200 mV, current range 200 and 300 mA in 3 minutes. It was noticed that the Pani-TIO_2 nanostructures have a response for the methanol concentration.



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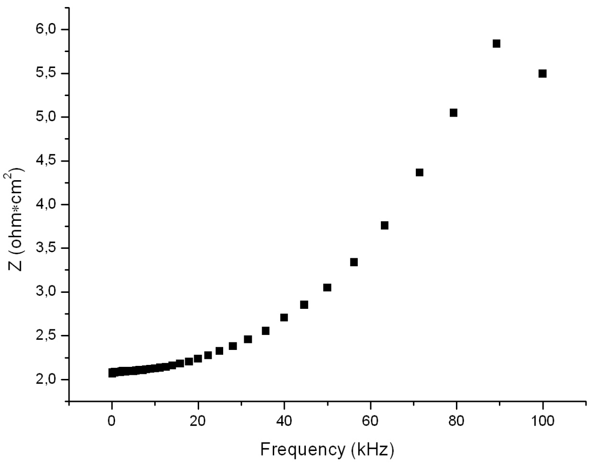

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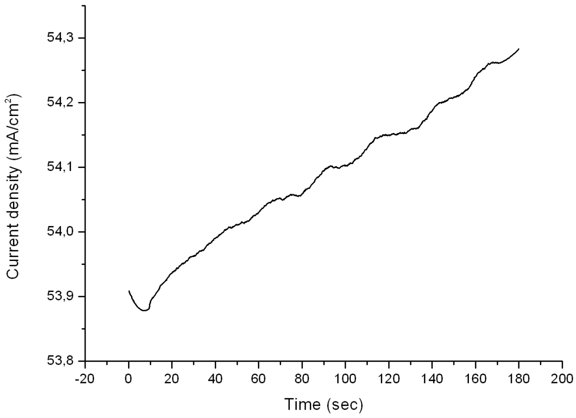
Fig. 3.a) Potential dynamic EIS obtained at the electrochemical synthesis of PANI-TiO_2 films in solution of sulfuric acid of concentration 0.5M on carbon paper in methanol 5% solution, at the frequency 100 kHz; b) Potential dynamic EIS obtained at the electrochemical synthesis of PANI-TiO_2 films in solution of sulfuric acid of concentration 0.5M on carbon paper in methanol 5% solution vapors, at the frequency 100 kHz.



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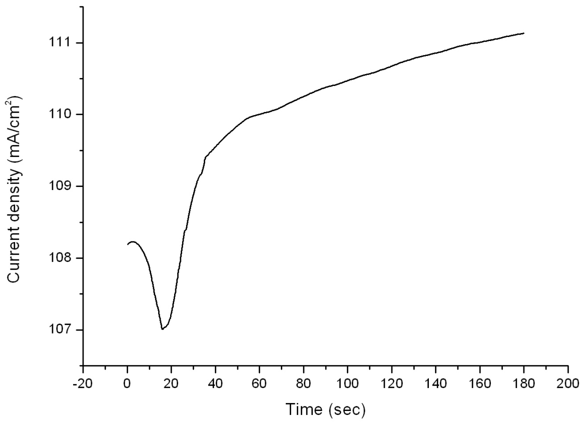

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Fig. 4. Current density dependence of time for a) electrod immersed in methanol b) methanol vapors at room temperatue. We can observe that the current density has increased when a 200mV potential was used, during 3 minutes/after that the current density has increased because of the methanol vapors

4. Conclusions

By these experiments, we intended to realize PANI-TiO_2 nanostructures using of concentration 0.5Msulfuric acid and their response at the methanol concentration to make a sensor. The PANI-TiO_2 films were prepared by aniline electrochemical polymerization in the presence of the TiO_2 nanoparticles laid on carbonic paper, it was monitored their response at the methanol concentration. Results show a linear dependence of alcohol concentration for I-V characteristics. As we can observe, the done experiments have confirmed, through the obtained results, the investigation team's expectations regarding the nanostructures applications of polyaniline –TiO_2 to realize the alcohol sensor. We can easily see that the current density increase depending on time, which mean that the obtained product is a sensor for methanol.

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