Electrochemical Deposition of Polyaniline Thin Films on Carbonic Substrates for the Application as Hydrogen Mediator and Self Catalyst in Fuel Cells

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Experiments regarding the electro deposition and the characterization of polyaniline (PANI) films on Toray Graphite Paper TGPH – 090 type based carbonic substrate, via Cyclic Voltammetry are presented. The CVs at different scanning rates show a complex stepped mechanism of PANI electro-polymerization. At a fixed scanning rate of 20mV/s, the deposited film weight increases proportional with number of cycles at a rate of 1mg/(cm² cycle), which is in agreement with similar results reported in case of metallic working electrode. The SEM micrograph of the electrochemical synthesized PANI film shows a disordered amorphous lump structure with a large porosity. The FTIR spectra confirm the formation of polyaniline on TGPH substrate in H₂SO₄ medium. The band at 1296 cm⁻¹, which is ascribed to the C–N stretching vibration of emeraldine salt form in bulk PANI is considerably shifted towards higher frequencies (1300-1311 cm⁻¹). The slight shift from 1296 cm⁻¹ to 1300 cm⁻¹ can be assigned to hydrophobic coating of the carbonic substrate.

Keywords: polyaniline, cyclic voltammetry, polymeric thin film, carbonic substrate

The materials with extremely high surface-to-volume ratios such as nano or mesoporous materials have significant potential as storage materials. These materials would need to be “designed” and “tailored”. There is a stronger binding of H atoms in high surface-area materials and therefore, catalysts may be needed for reversibly binding hydrogen [1].

Conducting polymers such as polyaniline and polypyrrole have been reported to exhibit storage capacities of around 8 wt% hydrogen [2]. Polyaniline is a unique type of conducting polymer in which the charge delocalization can, in principle, offer multiple active sites on the polymer backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by "spillover" adsorption of this hydrogen onto the adjacent nano-fibrous network [3]. The proof of this behavior is its antioxidant availability [4].

Polyanilines exist in a variety of forms that differ in physical and chemical properties [5-8]. The most common structure is the protonated green form, which is the emeraldine salt where counter anion comes from chlorine or sulfonic group [8]. The emeraldine salts have electrical conductivity in the semiconductor range (~1S/cm). This behavior rises with development of the oxidation and reduction centers on the macromolecular chain by the polymerization process. In such a way the ratio quinoid to aromatic groups can be accommodated in a proper way getting more or less donors (oxidative centers) or acceptors (reduction centers). Based on their intrinsic properties, polyanilines were used in large spectrum of applications such as filtration membranes [9], electrochromic devices [10], anticorrosion coating [11], sensors and electrocatalysis [12, 13].

Due to its peculiar properties, PANI can be doped with oxidative / reduction centers, either by control the quinoid to aromatic ratio in polymerization reactions or by addition of appropriate dopants, such as chloride or sulfonic anions. Due to the easier manipulation of PANI conduction properties, the particle size, the surface area and the polymer morphology of samples and by controlling its chemistry and polymerization process parameters, PANI could offer a large set of desirable properties with high potential for successful development as new material with storage capacity.

The electropolimerization of PANI from monomer solution is a common way for the polymer synthesis. During polarization, two reactions (protonation - deprotonation and oxidation - reduction) occur simultaneously but with different rates; they lead to the different PANI forms shown in figure 1, with a number of quinone rings going from 0 to 2 in the polymer basic unit formed by four rings, either phenyl or quinone. The nitrogen atoms separating the rings are therefore either amine or imine, and they can be protonated or not. When the experimental conditions turn from insulating leucoemeraldine, stable at cathodic polarization (four phenyl rings in the unit), to an insulating emeraldine base, stable at high anodic polarization (three phenyl and one quinone rings in the unit), a leucoemeraldine salt with metallic conduction properties is obtained and it behaves like a radical cation in front of the electrolyte anion [16].

Fig. 1. Different forms of polyaniline: LB-leucoemeraldine base; LS-leucoemeraldine salt (radical cation); ES-emeraldine salt (bipolaronic form); EB-emeraldine base [16]

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These aspects could recommend PANI as a proper material for hydrogen mediator in chemically adsorption/desorption processes.

Our work is focused on a peculiar study of electrochemical deposition of PANI on carbon paper as a fibrous networked support by cyclic voltammetry in acidic solution. The relationship between redox centers and the structure of the deposited films is discussed.

**Experimental part**

Aniline sulfate (purum, 65g, Aldrich) was dissolved in 0.5 M sulfuric acid in a volumetric flask of 1000 mL of solution according to previously reported papers [14, 15].

For polyaniline thin film deposition, cyclic voltammetry was performed with an “All-in-one” electrochemical combine VoltaLab 40 type on the potential range of –600 ÷ +450mV MMS at scan rate of 20 mV/s.

Unlike previous reports in this field, where Pt [14] or Au [15] was selected as working electrode, considering potential applications of PANI films deposited on conductive carboxylic support, in this work carbon paper (Toray Graphite Paper TGPH – 090) hydrophobized through impregnation with 20% Teflon was used. The working electrode (TGPH-090) was placed at 3cm distance by auxiliary electrode (Pt). The reference electrode was MMS (Hg/HgSO4) type. The distance between working and auxiliary electrode was established at 3cm with their surface ratio 1/1.28.

The temperature in the electrochemical cell was fixed at 23 °C using an U10 Thermostat with external recirculation. The number of scans performed for each experiment was 3.

The characterization of the PANI film deposited on carbon paper was realized through Fourier-Transformed-Infra-Red Spectroscopy (FTIR), using a FT-IR Jasco 6200 Spectrometer. The morphology of the PANI thin layer deposition was investigated by Scanning Electron Microscopy (SEM) with a Jeol 6300 scanning electron microscope equipped with computerized digital image software.

The quantity of deposited PANI polymer was determined by gravimetric technique by weighing initial and final support electrode after washing and 24 hours drying in the surrounding environment.

**Results and discussion**

Figure 2 demonstrates the complexity of mechanism for electro polymerization of aniline on support of TGPH-090 graphite electrode. At first sight current density and voltammograms area increase with scanning rates. This feature is a consequence of the capacity of the double layer formed at interface support – PANI – electrolyte. At a fixed scanning rate of 20mV/s the deposited film weight increases proportional with number of cycles at a rate of 1mg/(cm2 cycle) which is in agreement with similar results reported when is used metallic working electrode [17, 18].

Each voltammogram has the same characteristics at different scanning rates starting with PANI leucoemeraldine base (peak A) due to oxidative coupling of the anilinium ion in the polymerization process. A blue color of the film is observed in the first stage that is specific for the emeraldine base [17, 18]. The peaks C and E are due to doping with HSO3 - in the two positions in PANI-chains to quinoid groups. Maximum of doping is reached at 322mV on the anodic curve. On cathodic curves the peaks F, D, E correspond to quasireversible processes until PANI–emeraldine salt reaches the reduction state. The asymmetric shapes between anodic and cathodic peaks (E-F and A-B) are assigned to the conduction mechanism changes. In the doped state, PANI-emeraldine salt is an electronic conductor. Therefore it is expected the presence of sharper cathodic peak (F versus E), but, also, the reduction peak to be larger and small (B versus A).

Based on the experimental results regarding the aniline polymerization in sulfuric acid electrolyte, we can say that the kinetics of the electro polymerization of aniline on the carbon substrates like TGPH-090 graphite electrode respects three stages as follows:

\[
(aniline) \rightarrow R - e^- \Leftrightarrow Ox_1^+ \text{ (leucoemeraldine base) } \quad (1)
\]

\[
Ox_1^+ + HSO_3^- \Leftrightarrow P_1 \text{ (leucoemeraldine salt) } \quad (2)
\]

\[
P_1 - e^- \Leftrightarrow R_1^{++} \text{ (emeraldine salt) } \quad (3)
\]

The principal transmittance of synthesized PANI film observed in the FTIR spectrum, figure 3, shows a broad peak at 3442 cm⁻¹ corresponding to –NH₂ stretching. Nevertheless peaks at 2955 cm⁻¹ due to C-H stretching and C-N stretching are observed at 1300 cm⁻¹. The FTIR spectra
confirm the formation of polyaniline in H2SO4 medium. The characteristic peaks of polyaniline are found in the range of 400-2000 cm⁻¹ as shown in figure 3 which is similar with the spectra reported in other paper [19]. The most important peak assigned for emeraldine salt is the stretching vibration C–N, 1296 cm⁻¹, whose intensity is higher frequency (1300-1311 cm⁻¹) for different kinds of emeraldine salt of bulk PANI is considerably shifted to higher frequency (1300-1311 cm⁻¹) for different kinds of substrate spanning from metals to semimetals, such as carbon paper or for the intercalated system. It is believed that the frequency shift is caused by the physical interaction between PANI chains and fibrils structures of the carbon paper. The slight shift from 1296 cm⁻¹ to 1300 cm⁻¹ can be assigned to hydrophobic coating of the carbon paper with Teflon.

The micrograph of the electrochemical synthesized PANI film in H2SO4 electrolyte is shown in figure 4. It represents a disordered amorphous lump structure. It shows a large porosity which is suitable for developing multiple active sites sustaining the hydrogen adsorption/desorption processes and also for potential metallic nanoparticles immobilization. This image was recorded for 3 voltammetry cycles. The micrography is quite similar with other reported details, where electrochemical deposited PANI from H2SO4 solution was performed on metallic working electrodes (Pt, Au). There is still a slightly difference. The amorphous lump structure on the metallic working electrodes is well defined by comparison with other reported details, where electrochemical deposition processes and also for potential metallic working electrodes (Pt, Au).

Conclusions

The polyaniline form of emeraldine salt, electropolymerized on hydrophobized carbon paper with Teflon has disordered amorphous lump structure independent on scanning rate of cyclovoltammograms. FT-IR spectra show a slightly shift of the stretching band from 1296 cm⁻¹ to 1300 cm⁻¹, which could be assigned to the physical interaction between formed PANI and carbonic substrate. At a scanning rate of 20mV/s the deposition rate is in average 1mg/cm²/cycle.

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