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Polyaniline rod-like structure as self-electrocatalyst for hydrogen oxidation reactions

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A chemical route for the aniline polymerization was performed in order to develop the morphology for rod-like polyaniline powder. The purpose of our research is to obtain a conductive and stable polymer, with a high surface area. The research interest is to implement the polyaniline as conducting polymers in the fuel cell technology, as self catalyst and support for noble metal deposition. The SEM micrograph shows a specific rod-like polymer morphology. The Cyclic Voltammetry test reveals that the obtained polyaniline powder in the rod like-structure is able to perform as self catalyst in the hydrogen and methanol oxidation reactions.

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1. Introduction

In the last decades the intrinsic and self doped conducting polymers (ISDCPs) became promising materials for advanced applications due to their peculiar properties which can be tunable from direct synthesis conditions [1]. Their electrical conductivity ranged from semiconductors to metals has offered large applications for the preparation of antistatic films and metallic electrodes [2], substrate for metallization [3,4] or for enzyme immobilization in biosensors [5,6]. The electro-optical properties opened up new fields for plastic electronics such as transistors [7] and LEDs on flexible display [8]. ISDCPs can be designed in various forms, where redox centers or functional groups are bonded in specific positions as results from synthesis conditions. That induce electro-optical, mechanical and chemical properties reveal their dependencies on applied voltage or stress in several specific device. The redox states distributed along on the molecular chains or on the side of the pending functional groups change the polymer properties in appropriate way: the permeability of the membranes [9], swelling-shrinking measured by ellipsometry [10] or changes from hydrophobic to hydrophilic by anion intercalation [11]. In this class of ISDPCs, polyanilines occupy a preferential position due to its high level of redox states resulted direct from polymerization which does not imply complicated routes. Beside electrochemical polymerization [12], a lot of chemical oxidative methods in protic acid aqueous solution: hydrochloric [13], sulfuric [14], perchloric [15], fluoroboric [16] can be performed. Polyanilines used as oxidant agents for material doping that induce redox states we may count some of applications: *p*-toluenesulfonic and benzenesulfonic [17], *p*-styrenesulfonic acids [18] polyamic [19], polyacrylic [20], polyvinylsulfonic acid [21], bis(2-ethylhexyl) hydrogen phosphate [22].

Materials synthesized by this procedures were predominately amorphous, intractable, and insoluble in most organic solvents [23]. Several investigators have developed various methods for improving the processability of polyaniline by a post-processing step, i.e. converting the salt to emeraldine base and reprotonating the emeraldine base with another protic acid. Polyaniline salts containing carboxyl and amino substituent are soluble in N-methylpyrrolidone and dimethylsulfoxide [24]. In addition, it may be remarked that the polyaniline salts preparation in the presence of a number of protic acids including DBSA (4-dodecylbenzenesulfonic acid) and DNNSA (dinonylnaphthalenesulfonic acid) were partial soluble in nonpolar solvents [25].

To improve the characteristics related to high specific area with redox centers placed on the polymer surface, it was engaged the emulsion polymerization where protic acid acts as dopant [26]. In the emulsions consisting of water and nonpolar solvents, the polymerization was carried out in the most cases with dodecylbenzenesulfonic (DBSA) acid, which simultaneously acts as surfactant and protonating agent [27]. The starting monomer was aniline; the products of this kind of processes were spheroid aggregated powders at micronic dimensions.

In the present work, in order to develop new shapes such as rod-like, a chemical route for the aniline polymerization was performed. The purpose of our research is to obtain a conductive and stable polymer with a high surface area. The large interest in the implementation of polyaniline as conducting polymers in the fuel cell technology, as self catalyst and support for noble metal deposition is envisaged.

It has been previously reported that modified PANI electrodes have catalytic properties for organic fuel oxidation **[**28-32**]**. It has been claimed that dispersed noble metal microparticles supported on high-area materials are of great significance to obtain effective catalysts. Our results leaded to the aspects that the obtained polyaniline powder in the rod like-structure is able to perform as self catalyst in the hydrogen and methanol oxidation reactions.

2. Experimental

Polyaniline was prepared by chemical oxidation of 0.2 M of aniline sulfate with 0.25 M ammonium peroxydisulfate according to previous papers [33,34] in addition with excess of aniline as emulsifier. Aniline sulfate (purum, 3.82 g, Aldrich) was dissolved in 50 mL of 0.2 M sulfuric acid in a volumetric flask. Ammonium peroxydisulfate (purum, 5.71g, Aldrich) was dissolved in 50 mL of 0.2 M sulfuric acid in the same glasswear. Both solutions were maintained for 1h at the room temperature. Then they were mixed in a beaker with excess of aniline (0.2 M) briefly stirred and this new solution was left at rest to polymerize for 24 h. The green precipitate was collected on a filter, washed with 300 mL 1M sulfuric acid to removes the residual monomer, the oxidant and its decomposition products. Supplementary was washed with 300 mL acetone to removes the low molecular weight organic intermediates and oligomers. The resulting polyaniline form of emeraldine salt $(C_6H_5\text{-}NH\text{-}HSO_4)_n$ was dried at the room temperature for 3h and further it was placed in a oven at 70°C for 3h.

Electrochemical activity of the obtained polyaniline powder was measured by Cyclic Voltammetry(CV) on Toray Carbon Paper (TCP) working electrode. PANI powder as emeraldine salt form, dispersed in isopropyl alcohol, was sprayed on a carbon paper of about 1cm^2 at a loading of 1mg/cm^2. The electrochemical characterization was performed with Voltalab 40 “all-in-one” equipment, at a scan rate of 5mV/s. The auxiliary electrode was Pt and the electrolyte was 0.5M sulfuric acid. Different methanol (MeOH) concentrations were added to various electrolyte environments: 0.5 M; 1 M; 1.5 M and 2 M in order to study the polymer behavior related to MeOH. The all CVs were performed in thermostatic bath at 23 ± 2^{O}C.

The PANI samples were characterized by SEM and FTIR in order to establish the polymer morphology and its chemical structure. The characterization of the PANI film deposited on carbon paper was realized by 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.

3. Results and discussion

Generally, the scientists referred the polyaniline, in its protonated state (emeraldine salt – ES), only as electrically conducting polymer. The aspect which attracted our interest is the protonated structure of polyaniline in the acidic media, whose molecular structure is presented in Fig. 1.

Polyaniline in its sulfonated form shows a close structure with the ion conducting polymers, where the inorganic anions are represented by HSO_4^- species. In the emeraldine salt (ES), the HSO_4^- species are ionically bonded with the –NH– groups that are present in the polymer chains of PANI. Actually, these kinds of bonds are very weak and can be removed very easy by changing in the pH value.

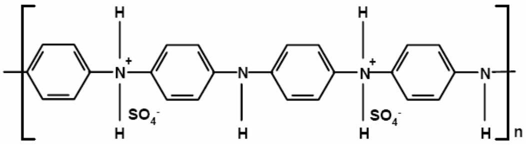

Fig. 1. Polyaniline as emeraldine salt (ES) in sulfuric acid media.

By removing the HSO_4^- dopant, this aspect involves a charge delocalization and the polymer could act like a charge carrier, and different species could bond on the polymer surface by a chemical adsorbtion process along the backbone.

The principal transmittance of synthesized PANI film recorded in the FTIR spectrum, Fig. 2, shows a broad peak at 3442 cm^{-1} corresponding to $-NH_2$ stretching, peak observed at 2995 cm^{-1} is attributed to C–H stretching and C–N stretching is observed at 1300 cm^{-1}. Thus, the FTIR spectra of this polymer confirm the formation of polyaniline in H_2SO_4 medium. The characteristic peaks of the polyaniline are found in range 400 – 2000cm^{-1} as shown in Fig. 2. Similar results were already reported [35, 36]. The most important peak assigned for emeraldine salt is stretching vibration C–N, the band at 1296 cm^{-1}, which show a sharp aspect. The band 1050 cm^{-1} assigned to sulfonic groups has half height compared with the band 1139 cm^{-1} assigned to C–H vibration from aromatic and quinoid structures in the emeraldine salt. It can be concluded that at each pair of aromatic is attached one sulfonic group and respective there is an active oxidation state.

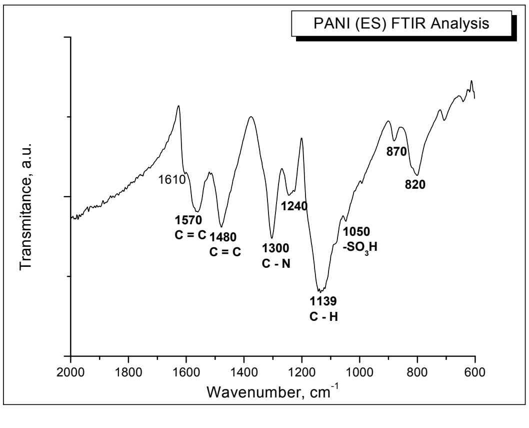

Fig. 2. FTIR spectra of a PANI obtained by self assembly polymerization.

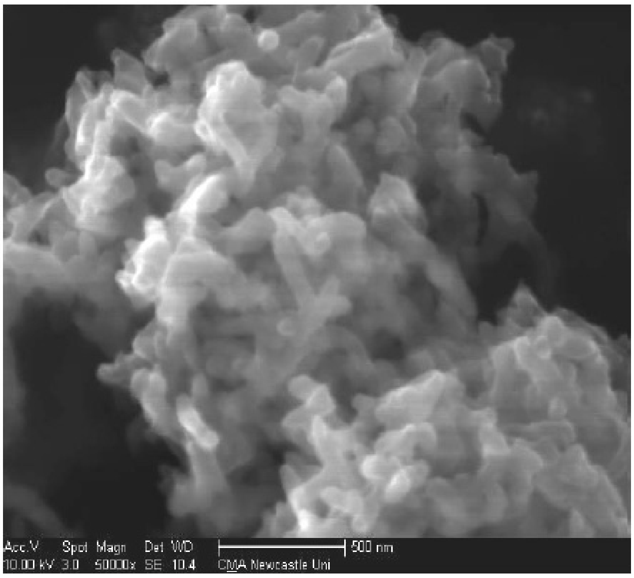

Fig. 3. SEM on a PANI sample obtained by self assembly polymerization method (magnitude x 50,000).

The scanning electron micrograph (Fig. 3) shows a specific rod-like polyaniline as emeraldine salt deposits. The obtained PANI powder was sprayed on a TCP electrode. A self assembling structure was obtained, in small aggregated nanoparticles, displaying a very large active surface (Fig. 4).

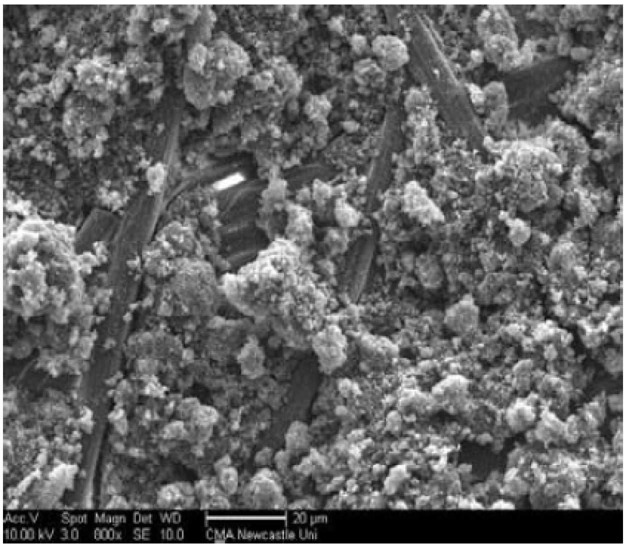

Fig. 4. SEM of PANI obtained by Self Assembly Polymerization Method sprayed on Toray paper (magnitude x 800).

The voltammogram presents the same characteristics as in literature reports [37, 38]. and starts with PANI leucoemeraldine base (peak A, Fig. 5). A blue color of the film is observed in the first stage that is specific for the emeraldine base. The peaks C and E are due to doping with HSO_3^- in the two positions in PANI-chains to quinoid groups. Maximum of doping is reached at $250mV_{MMS}$ on the anodic curve. On cathodic curves the peak F, D, E correspond to quasireversible processes until PANI–emeraldine salt reach 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 is expected as cathodic peak to be sharper (F versus E) and the reduction peak to be larger and small (B versus A).

A cyclic voltammogram for for the electrochimic behaviour of polyanilibe in the presence of methanol (MeOH) as hydrogen carrier in the electrolyte was registered at a scan rate of 5mV/s and is given in the Fig. 6. The electrocatalytic nature of the polymer toward MeOH oxydation is evident for PANI. In the presence of MeOH sollution, the peak A asociated to the leucoemeraldine base suffers a sharp depreciation and goes to a more reducing form, characterized by an associated small current density. This aspect give the indication that on the polymer surface bonded a strong reducing chemically species. The anodic peak at 0.2V vs. MMS reference is associated with CO oxidation [5]. The presence of the CO in the system coud be explained only as a consequence of methanol oxydation.

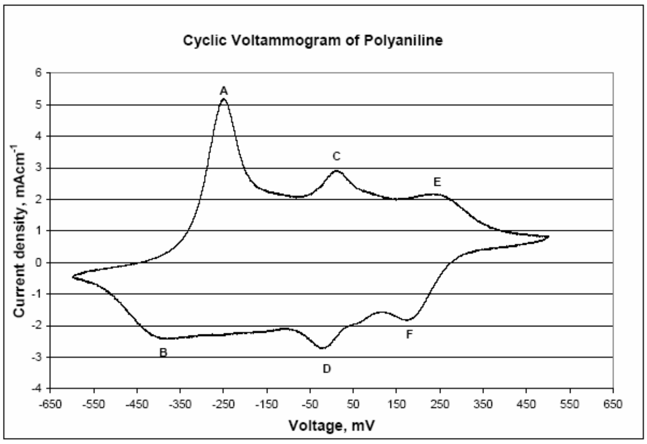

Fig.5. Cyclic voltametry on PANI electrode in 0.5M H2SO4 electrolyte.

While the peak A1 – A4 decreased severely with the concentration of methanol in the electrolyte solution, the peak C suffers a pronounced improvement to high current densities, which is associated to a strong doping process of polymer backbone. By increasing the MeOH concentration, the polymer adsorbed on its surface more and more CO, which is shown by the behavior of the peaks C1 – C4. This aspect gives the indication that the PANI is able to oxidize MeOH at a quiet high concentration.

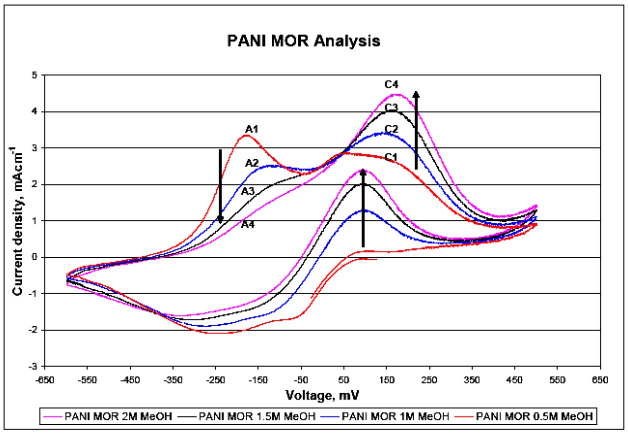

Fig. 6. Cyclic voltametry on PANI in MeOH / 0.5M H_2SO_4 electrolyte.

To the anodic behavior of the peak C corresponds the cathodic behavior of peak F, both of them performing to high current densities which are characteristics of strong oxydizing processes. The peak F shifted from cathodic current densities to anodic, which mean that supplementary oxidations take place on the polymer surface.

This reversibility of the adsorbtion/desorbtion process of CO on the polymer backbone is shown by the sharp behavior of the cathodic B peak. The shape of peak B demostrates that the reducing species on the polymer surface have been supplementary oxydized and removed, and the polymer came to the fully reducing form.

4. Conclusions

Due to easier manipulation of PANI conduction properties, the particle size, the surface area and the polymer morphology of this substrate control its chemistry and polymerization process parameters. PANI offers a large set of desirable properties with high potential for successful utilization in different technologies requiring catalytic properties.

Polyaniline could perform as selfcatalyst in hydrogen and oxidation reactions of MeOH. The polyanilite itself could be a possible competitor for combining with other catalysts like Pt, in order to enhance the catalytic activity and perform against the limiting factor in catalytic reactions like CO poisoning.

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