The morphology control of polyaniline as conducting polymer in fuel cell technology

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Electrically conducting polymers described as a new class of '*synthetic metals*' reached a high interest in the last years, confirmed by the 2000 Nobel Prize in chemistry for the discovery and development of conductive polymers (Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa). The most commonly studied classes of conducting polymer were: polyacetylene, polytiophene, polypyrole, polyaniline and derivates, being investigated as conducting matrices for electrocatalytic applications. Among them, polyaniline (PANI) is one of the most studied materials because of its high conductivity upon doping with acids (10^{-1}-10^2 S/cm), well behaved electrochemistry, and easy preparation under reproducible conditions by both electro - polymerization and chemically oxidation of aniline, chemical and electrical stability and good environmental stability. The purpose of our research is to obtain a conductive and stable polymer, with a high surface area, by variation of different preparation techniques and parameters, in sense of polymer morphology control. The research interest is to implement the conducting polymers in fuel cell technology, as Membrane Electrode Assembly (MEA) components or conducting supports for noble metal deposition.

1. Introduction

Electrically conducting polymers described as a new class of '*synthetic metals*' reached a high interest in the last years, confirmed by the 2000 Nobel Prize in chemistry for the discovery and development of conductive polymers (Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa) [1].

The most commonly studied classes of conducting polymer were: polyacetylene, polytiophene, polypyrole, polyaniline and derivates, being investigated as conducting matrices for electrocatalytic applications [2]. Among them, polyaniline is one of the most studied material because of its high conductivity upon doping with acids, well behaved electrochemistry, and easy preparation under reproducible conditions by both electro polymerization and chemically oxidation of aniline, chemical and electrical stability and good environmental stability [2-10].

A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized "sigma" (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "pi" (π) bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition – and this is what the dopant does – charge carriers in the form of extra electrons or "holes" have to be injected into the material. A hole is a position where an electron is missing. When such a hole is filled by an electron jumping in from a neighboring position, a new hole is created and so on, allowing charge to migrate a long distance.

If for the other members of this class (e.g. polytiophene, polypyrole, and polyacetylene) the conducting mechanisms are well understood by considering their conjugated carbon backbones, the conducting mechanism in the polyaniline forms is more complex and not very well established. Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. It can changes the electronic conductivity about 10 orders of magnitude, passing from insulator state (e.g. emeraldine base with $\sigma < 10^{-10}$ S/cm) to metallic conduction (e.g. emeraldine salt with $\sigma \sim 10^{-1}$-10^2 S/cm), depending upon the protonation degree [11-13].

Is known that the electrical conductivity and mechanical properties of polyaniline increase by running the polymerization at low temperatures of $0 - 4$ °C. These properties are optimal at stoechimetrical ratio between the oxidant, hydrochloric / sulfuric acid and aniline [14,15].

Controlling the pH, doping level and polyaniline's polymerization conditions, we assume that is possible to change the morphology and thus the physic-chemical properties of polymer.

2. Experimental

2.1. Polyaniline synthesis by self assembly polymerization method

Polyaniline was prepared by chemical oxidation of 0.2 M of aniline sulfate with 0.25 M ammonium peroxydisulfate according to literature procedure [14,15]. Aniline sulfate (purum, 3.82 g, Aldrich) was dissolved in 0.2 M sulfuric acid in a volumetric flask to 50 mL of solution. Ammonium peroxydisulfate (purum, 5.71g, Aldrich) was dissolved in 0.2 M sulfuric acid to 50 mL as well. Both solution were kept for 1h at the room temperature, then mixed in a beaker, briefly stirred and left at rest to polymerize for 24h. 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 salt $(C_6H_5\text{-}NH\text{-}HSO_4)_n$ was dried at the room temperature for 3h and further in a oven at 70^oC for 3h.

2.2. Polyaniline synthesis by cyclic voltammetry Method

0.2 M of aniline sulfate was dissolved in 0.5 M sulfuric acid according to literature procedure [3]. Aniline sulfate (purum, 8.52 g, Aldrich) was dissolved in 0.5 M sulfuric acid in a volumetric flask to 150 mL of solution. The polyaniline films were formed on the working electrode by cyclic voltammetry in a three electrodes cell at 50 mVs^{-1} between – 600 to 450 mV vs. mercury/mercurous sulfate electrode (MMS). A Ti mesh was used as counter electrode.

Unlike literature reports using a platinum [3] or a gold [7] sheet as working electrode for polyaniline electro deposition, in our work the polyaniline films were electrodeposited on a graphite paper electrode (Toray Graphite Paper TGPH – 090, 20% wet proofing), having a surface area of 14 cm^2. The amount of electrodeposited polyaniline, varied by changing the number of potential cycles, was estimated by weighing the graphite electrodes before and after electro deposition. Have been obtained different loadings of 1, 2, 3 and 4 mg/cm^2, corresponding of 2, 3, 4 and 5 cycles.

2.3. Polyaniline synthesis by galvanostatic method

The polyaniline films were synthesized by Galvanostatic Method from 0.2 M of aniline sulfate dissolved in 0.5 M sulfuric acid. The working electrode was a graphite paper electrode (Toray Graphite Paper TGPH – 090, 20% wet proofing), having a surface area of 14 cm^2. A Ti mesh was used as counter electrode. The working current density was 1 mA/cm^2. The amount of electrodeposited polyaniline was estimated by weighing the working electrodes before and after electro deposition. Have been obtained different loadings of 0.5, and 1 mg/cm^2, corresponding of 15 and 30 minutes of deposition time.

2.4. Polyaniline synthesis by pulse galvanostatic method

The polyaniline films were synthesized by Pulse Galvanostatic Method using a two-electrode cell from 0.2 M of aniline sulfate dissolved in 0.5 M sulfuric acid [16]. Unlike literature report using stainless steel as working electrode for polyaniline electro deposition, in our work the polyaniline films were electrodeposited on a graphite paper electrode (Toray Graphite Paper TGPH – 090, 20% wet proofing), having a surface area of 14 cm^2. A Ti mesh was used as counter electrode. The parameters of electro deposition were: the ratio of 'on' pulse period and 'of' pulse period $(t_{on}:t_{of})$ = 50 ms : 50 ms; the working current density was 1 mA/cm^2. The amount of electrodeposited polyaniline was estimated by weighing the working electrodes before and after electro deposition. Have been obtained different loadings of 0.5, and 1 mg/cm^2, corresponding of 30 and 60 minutes of deposition time.

2.5. Polyanilines characterization

SEM and FTIR characterization have been performed on polyaniline in order to establish the polymer morphology and chemical changes in its structure. The FTIR obtained spectra and SEM images and are given in Fig. 3 – 4 and Fig. 5 – 8 respectively.

Electrical conductivity of PANI compared with a specific nanocarbon used in fuel cell technology (e.g. Ketjen Black EC 300J), was measured in a two-points probe equipment, in a range of temperatures between 25 ^oC and 120 ^oC, Fig. 9. The measured conductivities of PANI vs. Ketjen Black are given in Fig. 10.

3. Results and discussion

The ion conducting polymers used in the Polymer Electrolyte Membrane Fuel Cells (PEMFC) and Direct Methanol Fuel Cells (DMFC) are characterized by a hydrophobic back-bone grafted with hydrophilic side groups represented by some inorganic anions like: SO_3^-, $H_2PO_4^-$, HSO_4^-, responsible for the ionic transfer through the polymer.

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, 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 presented in the polymer chain. Actually, these kinds of bonds are very weak and can be removed very easy by changing the system's pH.
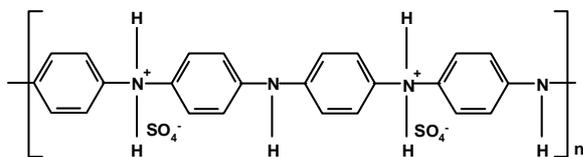
Fig. 1. Polyaniline as Emeraldine Salt (ES), in sulfuric acid media.

There are different works trying to control the conducting properties of polyaniline by a sulfonic acid ring-substitution, creating thus a protonic acid self-doped conducting polymer. In our study, we used the literature method to synthesize the -SO_3 doped polyaniline (SPANI) [17,18], but unlike literature procedure, we used as precursor material the Emeraldine Salt (ES) instead of Emeraldine Base (EB). The designed transition of electron conducting PANI (ES) to proton conducting SPANI is given in Fig. 2.

By supplementary doping of polyaniline in sulfuric acid media, actually we introduced multiple charge carriers which determine an improvement of the electrical conduction along the polymer chain. Moreover, we assume that the total conduction in SPANI is given by summing the electrical conduction and ionic conduction that occurs by sulfonic groups on the aromatic rings. This aspect will be supplementary studied in further works.
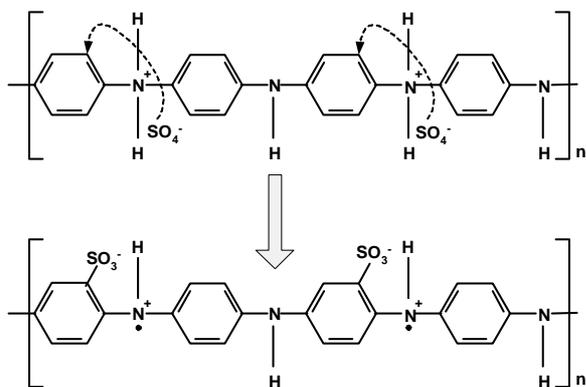
Fig. 2. The designed transition of electron conducting PANI (ES) to -SO_3 doped polyaniline (SPANI).

The FTIR spectra of a PANI and SPANI samples show similar characteristics with literature reports [19,20], with characteristics bands of a doped polyaniline structure at 1610, 1570, 1480, 1300, 1240, 1139, 1050, 870 and 820 cm^{-1}, Fig. 3. The characteristic peaks of sulfonated aromatic rings appear clear in SPANI spectra at 620, 700 and 1100 cm^{-1}, Fig. 4.

Changing different parameters in aniline's polymerization, we have changed the morphology of polyaniline, passing from spherical particles of about 0.5 μm to nanotubes / nanofibers with a diameter of about 80 nm and a length of about 300 nm. These changes in PANI morphology are represented by SEM diagrams, Fig. 5-8.

Electrical conductivity of PANI vs. Ketjen Black EC 300 J was measured in a special designed two-points probe equipment, Fig. 9, in a range of temperatures between 25 °C and 120 °C. In this measurement we have been using a cylinder mold, designed by two SS electrodes and a teflon tube having the inner diameter of 1 cm^2. Applying DC current in a range between 20 mA and 1 A, we measured the voltage as response of the passing current through the particulate conductive / resistive sample.

The obtained electrical conductivity of PANI is about 3 S/cm, Fig. 10, corresponding with literature reported data regarding the conductivity of Emeraldine Salt doped with sulfuric acid [15]. The conductivity of polyaniline, in dry state, is in the same range with the Ketjen Black sample conductivity.
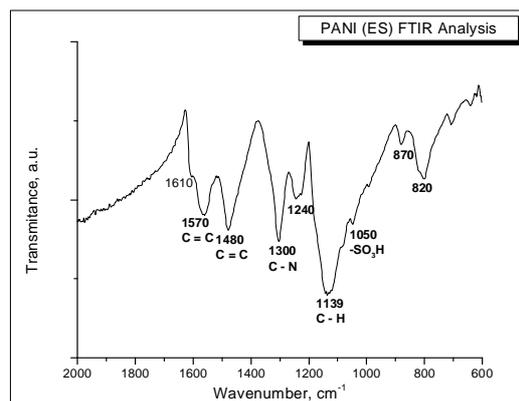
Fig. 3. FTIR spectra of a PANI obtained by Self Assembly Polymerization.
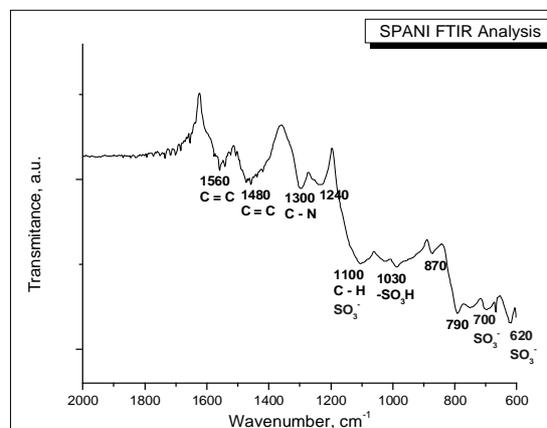
Fig. 4. FTIR spectra of -SO_3 doped polyaniline (SPANI).
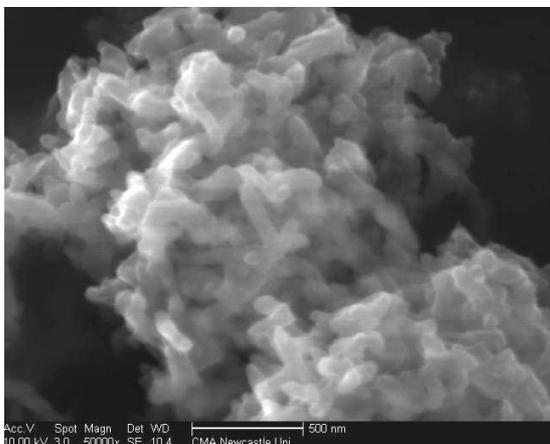
Fig. 5. SEM on a PANI sample obtained by Self Assembly Polymerization Method x 50000.
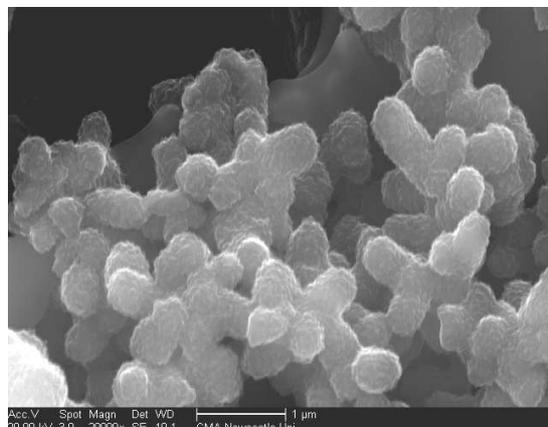
Fig. 8. SEM on a electrodeposited PANI sample by Pulse Galvanostatic Method x 20000.
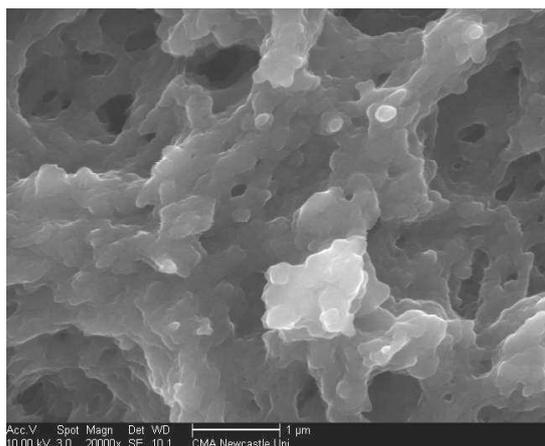
Fig. 6. SEM on a electrodeposited PANI sample by Cyclic Voltammetry Method x 20000.

R1 - Measured resistance
R2 - Variable Resistance

Fig. 9. Designed two-points probe equipment for electrical conductivity measurement.

Fig. 7. SEM on a electrodeposited PANI sample by Galvanostatic Method x 20000.
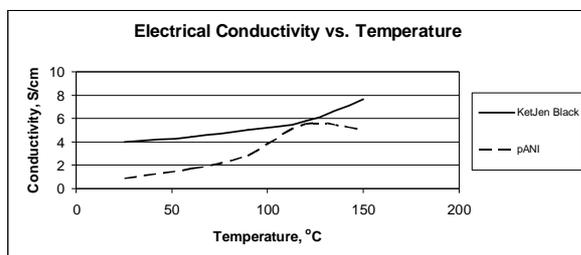
Fig. 10. Dry state electrical conductivity comparison: PANI vs. Ketjen Black (two points probe measurement).

4. Conclusions

While the carbon is quiet limited regarding the conductivity and chemistry aspects, due to easier manipulation of PANI's conduction properties, particle size, surface area and polymer morphology, by controlling its chemistry and polymerization process parameters, PANI offers a large set of desirable properties with high potential for successful utilization in fuel cell technology.

A better understanding of PANI conduction mechanisms and the investigation of PANI as a proton conducting polymer could bring new opportunities for the realization of a new proton conducting membrane for fuel cell technology.

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