



POLYANILINE NANOFIBER BASED DEVICE ON FLEXIBLE SUBSTRATE

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Received July 27, 2010

The goal of the research is to deposit thin film of nanofiber polyaniline on a flexible substrate in order to develop a new technology for manufacturing miniaturized, rechargeable and flexible batteries based on this polymer. The paper is presenting the synthesis and deposition of polyaniline conductive polymer by electrochemical method on transparent flexible polymeric substrate and the technology for obtaining a half cell battery, using gold electrodes deposited with polyaniline in the form of emeraldine salt. We are using rubylith as polymeric substrate for electrodes patterning, designing a new "mechanical lift-off" process. Rubylith consists of two films sandwiched together. The bottom layer is a clear polyester sheet. The top layer is a translucent, red coloured, self adhesive, emulsion. The red layer is cut and removed leaving open windows for metal deposition (Ti/Au). After metal deposition, the rest of the red layer is removed and the metal is remaining only on the electrodes area. The flexible metal electrode is connected into the three electrodes electrochemical system and the deposition of conductive polyaniline is performed leading to a uniform polyaniline deposited layer, 30 nm thick, on top of gold electrode which is the working electrode of the electrochemical cell.

INTRODUCTION

Conductive polymers are a distinct class within macromolecular compounds characterized by their extraordinary ability to conduct electricity, allowing them to be used as active components in alkaline batteries, biosensors, gas separation membranes, electrochemical capacitor, transistors and conductive textiles. The widespread use conductive polymers is due to reversibility condition doping/undoping that determine the characteristic spectral changes or modifications of optical, chemical properties according to the state of oxidation/reduction. Such a polymer is polyaniline, which can be obtained either through an electrochemical process or by chemical oxidation.¹

The possibility of using it, as material for electrodes of electrochemical batteries was recognized just after 1980, when polyaniline has undergone intensive studies of physical, chemical and electrical characterization.

The interest is motivated by the fact that the monomer is inexpensive and easily accessible and

the polymerization techniques are chemical as well as electrochemical are relatively simple and moreover the polymer is stable under ambient conditions. Unlike other conductive polymers, polyaniline presents another advantage which justifies the interest in the polymer structure: it can be doped to the metallic state using various proton acids, inorganic as well as organic. Scientific and technological interest for polyaniline and its derivatives is due to the variety of physical and chemical properties, such as: electrochemical, magnetic and optical properties changeable by simple synthesis and are leading to a variety of derivatives that are substituted at the nitrogen atom or the phenyl ring.¹

RESULTS

The electrochemical synthesis of polymers is an advantageous method because the obtained polymer is not contaminated with catalysts and can be deposited in a well controlled thickness, directly

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on the electrode. Emeraldine salt was obtained by electrochemical method in order to be directly deposited on gold electrodes.

The polymerization reaction was done in an electrochemical cell using three electrodes into the VoltaLab PGZ 100 system. The three electrodes are: the platinum auxiliary electrode, the reference electrode Ag/AgCl and a working electrode (patterned 200nm thick gold electrode deposited on rutilium substrate). The conductive polyaniline, electrochemically deposited on gold electrode by Cyclic Voltammetry on VoltaLab PGZ 100, has a structure of nanofiber (~ 100nm diameter), as seen in the SEM (Scanning Electron Microscope) picture (Fig. 1). One half cell battery (meaning one

gold electrode deposited with polyaniline) on flexible substrate was produced and it was characterized by the following electrochemical methods: Open Circuit Potential, Potential Cyclic Voltammetry, Chrono Amperometry, Chrono Coulometry and Chrono Potentiometry. Fig. 2 presents the optical photography of electrochemical cell. The cathode of the battery is the gold electrode deposited on rutilium substrate electrochemically deposited with conductive polyaniline and the anode is a thin copper foil (or other more electroactive metal), both immersed in the electrolyte, 0.1 M HClO₄.

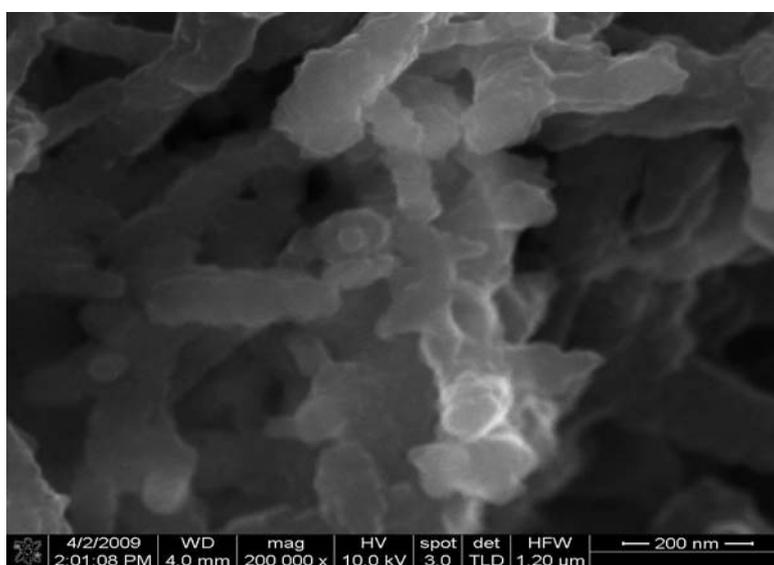


Fig. 1 – SEM picture of polyaniline conductive salt form E deposited as 100nm nanofiber diameter on electrode Ti/Au by Cyclic Voltammetry method.

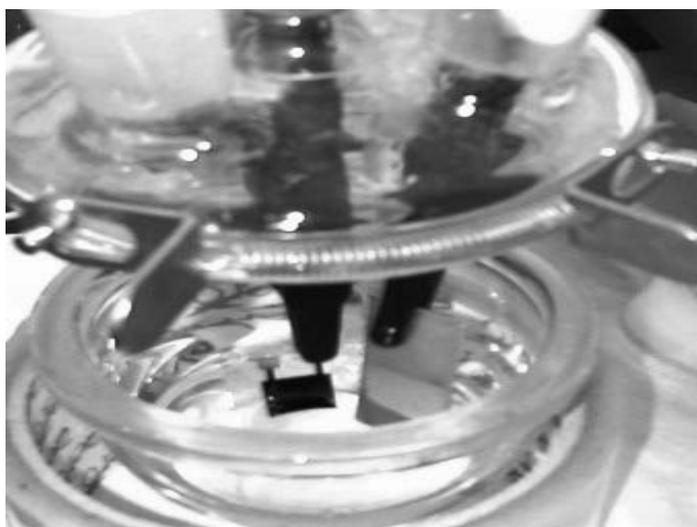


Fig. 2 – Optical photography of experimental cell used to characterize cell battery.

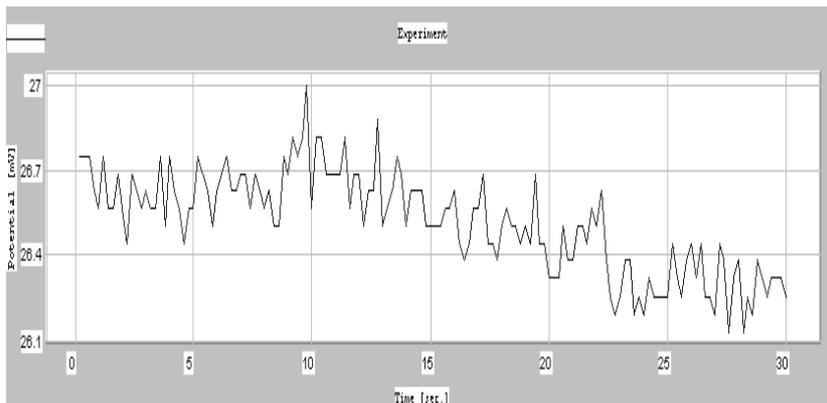


Fig. 3 – The stabilization curve for the WORK potential, using Open Circuit Potential method before deposition polyaniline on working electrode.

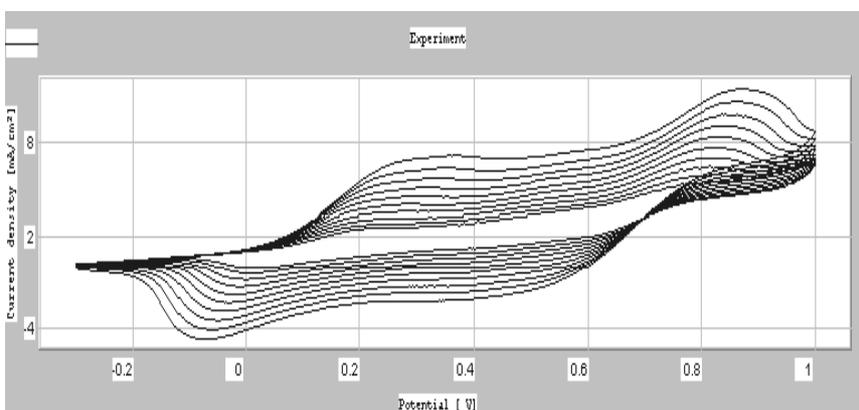


Fig. 4 – The voltammogram of 1M aniline polymerization in 1M perchloric acid by Cyclic Voltammetry method on gold substrate for 10 cycles.

The WORK potential of the half cell battery is measured versus the REF potential before starting the polymerization reaction and the deposition of polyaniline on gold substrate. The curve stabilization at Open Circuit Potential is given in Fig. 3. In Fig. 3, the Work potential measured versus the REF potential before starting the polymerization reaction of aniline and the electrochemical deposition polyaniline on gold electrode is approximately constant at $26\text{mV} \div 27\text{mV}$. After establishing the Work potential at a constant potential versus the REF potential, the Cyclic Voltammetry method is used for aniline polymerization reaction. Aniline polymerization process and the deposition polyaniline by Cyclic Voltammetry method consists of doing the scanning speed potential given the potential between anode and cathode. The experimental curve obtained is known as a polarization curve or “voltammogram” and measures the current (current density). The voltammogram is a series of cyclic polarization curves. Scanning speed is at 100mV/s . In Fig. 4 the voltammogram of

polymerization of aniline on gold electrode during 10 cycles is observed. In Fig. 4, the voltammogram obtained offers information about the evolution process of polymerization of aniline perchlorate solution 1M. As seen in the voltammogram, the oxidation processes take place at the onset of the growth of the potential. As for the reduction processes, they occur once the potential value decrease is lunched. Polymerization of aniline is an oxidative process. The transitions between the three forms of polyaniline (PANI): leucoemeraldine, emeraldine, pernigraniline are marked by two maximums on each route (oxidation, reduction) of the voltammogram.²

The Potential Cyclic Voltammetry method involves a potential given scan rate between anodic and cathodic potential limits and auto ranging for current measurement is available depending on the scan rate. A typical scan rate would be at 100mV/s . The experimental curve obtained is a set of cyclic polarization curves. After polymerization, the electrode potential stabilized at a value of $104\text{mV} \div 105\text{mV}$, Fig. 5.

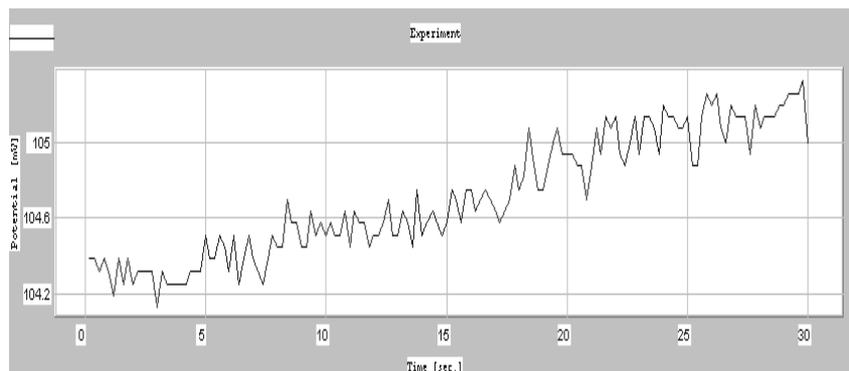


Fig. 5 – The stabilization curve of Open Circuit Potential, after the polymerization and the deposition of polyaniline 1M on the gold substrate.

Electrical properties of polyaniline can be controlled suitably by charge, doping or protonation. Due to its reversible electrochemical response during anodic oxidation and cathodic reduction, it is useful as secondary electrode in rechargeable batteries devices. Our research is focused on polyaniline obtained by electrochemical method and deposited in the form of nanofiber thin layer.³

DISCUSSION

Polyaniline characterization by electrochemical methods is necessary for studying the film conductivity, structure and charge transport at polymer film/electrolyte interface. Deposited nanofiber polyaniline thin layer on gold substrate is considered the cathode of the battery and it was analyzed in the electrolyte, a solution of 1M perchloric acid by Crono Coulometry, Crono Amperometry and Crono Potentiometry methods⁴. In Fig. 6, the data from the cathode reaction with polyaniline in 1M perchloric acid electrolyte using Crono Coulometry method is shown. Crono Coulometry method measures the accumulation of charge (Q) function of time at constant potential. The charge Q [mC/cm^2] is recorded while the WORK potential is maintained at a constant pre-set value versus the REF potential. The charge is the integration of the current versus time. From the curve in Fig. 6 an approximate value for the charge Q by $30\text{mC}/\text{cm}^2$ is observed within the first 10 seconds, as the Work potential electrode is held constant at 600mV. Another method to characterize the cathode based polyaniline in 1M HClO_4 electrolyte medium is Chrono Amperometry method. It consists of recording the current while the WORK potential is maintained at a pre-set

value versus the REF potential. Current measured after stabilization is a measure of current automatic discharge by $0.3\div 0.4\ \mu\text{A}$, as shown in Fig. 7. The last method to characterize the electrode polyaniline is the Crono Potentiometry method which consists of measuring the potential function of time, after imposing a constant current, two successive steps are apparent, representing the charging of two oxidized forms, respectively discharging of two oxidized forms. The charging on the two steps was obtained at +1.2V respectively at +1.8V potentials. The discharging takes place at +0.4V respectively at -0.5V see Fig. 8. The capacity of charging-discharging is maintained by repeating this cycle, as demonstrated by the reversible reactions involved in the process, Fig. 9. To see whether during these cycles of charging-discharging, the polyaniline is affected at the end of the experiments, it has been deemed necessary to characterize it by the Crono Amperometry method to see if it has maintained the same current automatic discharge. As can be seen in the curve in Fig. 10, the current density value was stabilized at $0.3\mu\text{A}/\text{cm}^2$. The cathode polyaniline does not suffer any change during the experiments. Due to the dependence of battery efficiency on the conductivity of the cathode and substrate, these components should be of high conductivity. The conductivity of polyaniline depends on dopant acid (perchloric acid) concentration in the synthesis solution.

Polyaniline structures from reduced state and the oxidized state or intermediate state, in Fig. 11 are shown.⁵ These states depend on the state transition process of polymerization and deposition polyaniline on the gold electrode, in 1M aniline perchlorate solution, $\text{pH}\sim 1$, by Cyclic Voltammetry method, VoltaLab PGZ 100. The anions in medium are incorporated in the matrix

synthesis of PANI as dopant anions. The cathodic reaction involving the oxidation/reduction processes are accompanied by the insertion and elimination of the perchlorate dopant. A constant current mode was chosen for charge-discharge cycling of the battery. When the battery is charged, the voltage increases slowly and the reduced form of polyaniline is changed to its oxidized form. When the cell is discharged, the voltage falls

slowly until polyaniline oxidized form is changed completely to its reduced form. The cell voltage increases rapidly when polyaniline oxidation is completed and polyaniline is degraded to its electrochemical inactive form and similarly when the voltage decreases rapidly leads to irreversible changes in the chemical composition of the polymer.

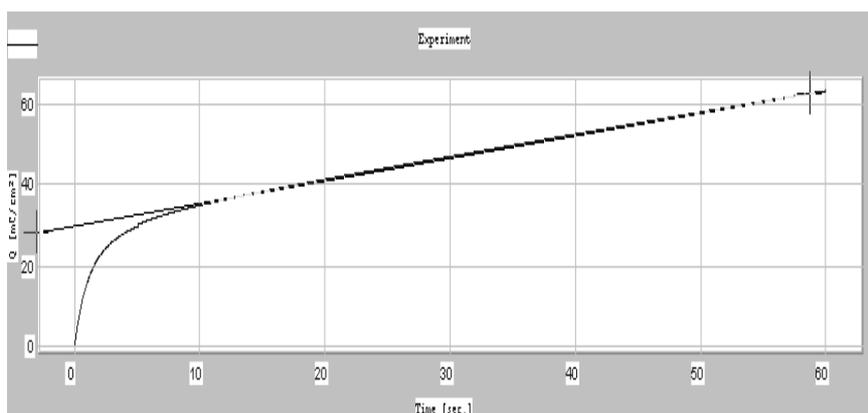


Fig. 6 – Polyaniline cathode in electrolyte medium, perchloric acid 1M, characterized by Crono Coulometry method.

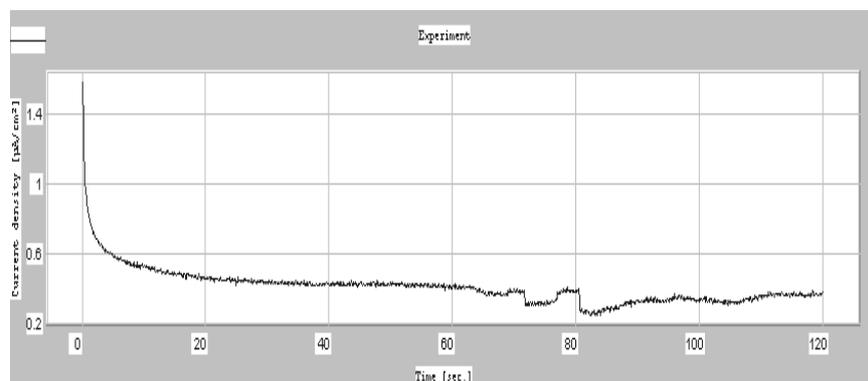


Fig. 7 – Crono Amperometry curve of cathode polyaniline in 1M perchloric acid electrolyte medium.

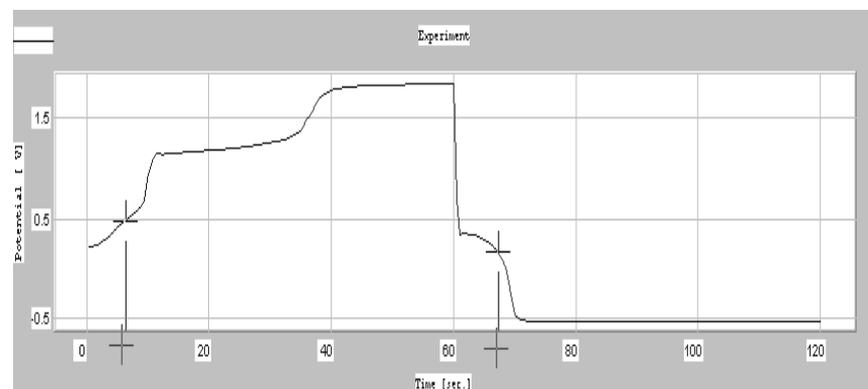


Fig. 8 – Crono Potentiometry curve of cathode polyaniline in 1M perchloric acid electrolyte medium, one cycle.

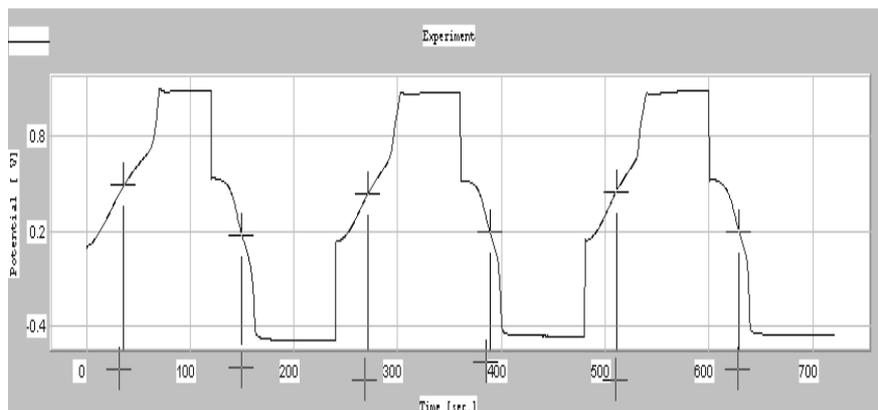


Fig. 9 – The characterization of charging-discharging process for cathode polyaniline made using Crono Potentiometry, 3 cycles.

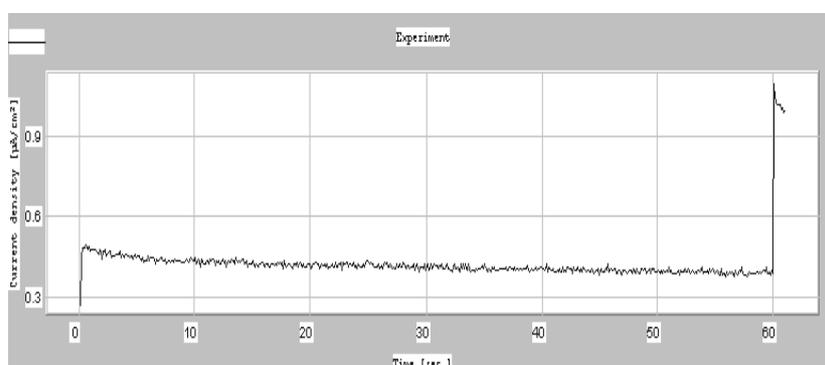


Fig. 10 – The Crono Amperometry curve of cathode polyaniline in 1M perchloric acid electrolyte medium, after a total of 50 charging-discharging cycles.

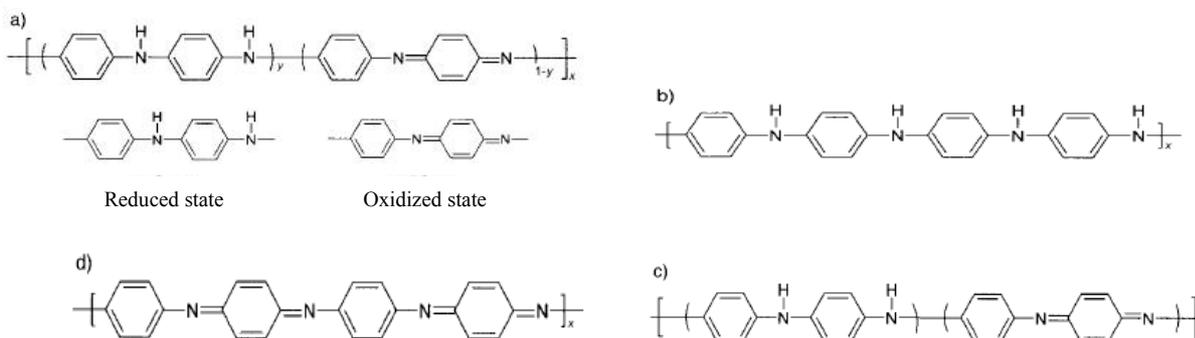


Fig. 11 – The transition states of Polyaniline in the process of polymerization: a) reduced state and oxidized state of polyaniline; b) complete reduced state of polyaniline; c) half-oxidized state of polyaniline; d) complete oxidized state of polyaniline.

EXPERIMENTAL

The technology for obtaining electrochemical devices on flexible substrate includes masking microtechnology and the process of electrode patterning. The design of the electrode is shown in Fig. 12. As shown before, the nanofiber polyaniline film was obtained by electrochemical method and deposited directly on gold surface of the cathode patterned on flexible substrate. Half cell battery on flexible substrate is a cathode made of 0.2 μm gold layer thickness, collector of ion charges, deposited by evaporation method on rubyolith substrate. The

gold electrode was used as a substrate for electrochemical deposition of a thin layer of conductive polyaniline by Cyclic Voltammetry method, 10 cycles. The anode is made of a thin copper foil (or any other more electroactive metal) of 35 μm . The electrolyte used to characterize the cell battery is the perchloric acid 0.1M solution.

Emeraldine salt was deposited in film form using the electrochemical cell VoltaLab-PGZ 100 Radiometer with 3 electrodes: platinum auxiliary electrode; reference electrode Ag/AgCl and working electrode (gold electrode deposited by vacuum evaporation on flexible substrate).

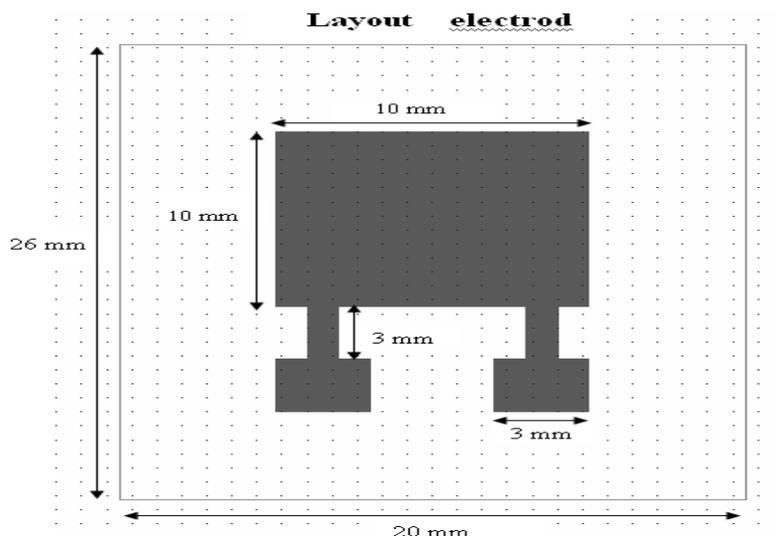


Fig. 12 – Lay-out of the microfabricated battery electrode.

Obtaining and deposition of nanofiber polyaniline film on gold substrate comprise two stages: aniline solution preparation stage and the emeraldine salt deposit on the cathode stage.

The used electrolyte solution contains the following components: aniline, $C_6H_5NH_2$ 1M and perchloric acid, $HClO_4$ 1M which is the dopant.

Aniline solution was prepared according to the following method: in a 50mL volumetric flask 9.2 mL of aniline are introduced and make up to volume with deionized water. Similarly, $HClO_4$ 1M solution was prepared in a 50mL volumetric flask, 10 mL perchloric acid are introduced and make up to volume with deionized water. After the solutions were prepared, the ratio monomer/dopant (aniline/perchloric acid) was 1:1 which are mixed to 100 mL obtaining 1M aniline perchlorate solution, pH~1, and adding a small excess of dopant, perchloric acid ~ 2% to avoid precipitating aniline. Anodic oxidative polymerization of aniline was made at ambient temperature and the electrolyte also had the role of aniline dopant. The emeraldine salt on the substrate of the gold electrode was done with 3 cycles of deposition by Potential Cyclic Voltammetry method with the following program: the scanning speed was at 100mV/sec.; the potential for polymerization of aniline was at 1000mV/sec. and the time of the scanning for one cycle was 62 seconds.

After each cycle, polyaniline was washed with deionized water. In Fig. 13 the aniline polymerization curve and deposition polyaniline on the gold electrode by electrochemical method, Potential Cyclic Voltammetry is shown. In Fig. 13, the curve obtained in the process of polymerization and the deposition of aniline on electrode by the Potential Cyclic Voltammetry method has three peaks. The first peak of the bottom left of the cyclic curve is the process of deposition of polyaniline on the electrode; the second peak in the top right of the cyclic curve, is the process of the polymerization of aniline; and the third peak is a form of transition polyaniline half, 0.5, crossing from left to right side, which shows that only half polyaniline is oxidized (top of curve cycle) or reduced (bottom of the cycle curve). In other words, each cycle is characterized by three polyaniline maximum peaks corresponding to the three forms of polyaniline: reduced form (left), intermediate form (the shift

from left to right) and oxidized form (right). After 3 cycles of polyaniline deposition, a film of polyaniline, emeraldine salt form, on gold electrode was obtained. It is highly conductive, due to the protonated form with perchloric acid present in the reaction environment. The mechanism of the reaction of the aniline polymerization and doping in the experimental conditions, shown above, is given in Fig. 14. Usually, the transfer of electrode structure configurations on a silicon wafers is done by lithographic techniques using a set of masks comprising one mask for each level. Electrode structure configuration was done in one step by removing red rubylith film (20μ), what remains is directly the patterned electrode structure on flexible polymer substrate, transparent rubylith (60μ), like in Fig. 15.⁶ In addition, making an exception processing is therefore to give up at the flux processing as standard integrated circuit processing technology, photolithography technique using positive photoresist absolutely necessary in the process of transferring the device structure on the substrate, when processing problems may occur because of photoresist adhesion at the substrate especially if the humidity of the room or energy to resist exposure were not respected. In this case the entire process of photolithography is re-made, which implies delays and means a longer processing time.

Below, only the most important technological processes of technological steps are described, providing technological solutions for the achievement of feasible electrochemical electrodes using conductive polymers as an active electrode.

The process of chemical cleaning

Before the metal deposition process, the patterned rubylith transparent flexible substrate has to be chemically cleaned in order to remove organic and inorganic contaminants that have reached the surface during the previous process or during handling in order to have a good adhesion of the metal to the flexible polymer surface. If these contaminants are not removed efficiently, they degrade the electrical characteristics of electrode structure. For this stage RIE plasma cleaning was chosen with the following program: P=50W; p=20Pa; O_2 = 99sccm and time=20seconds.

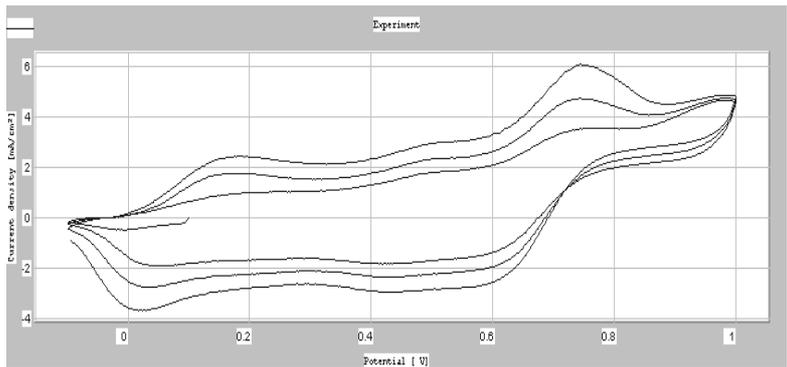


Fig. 13 – Aniline polymerization curve and polyaniline deposition on gold electrode by Potential Cyclic Voltammetry method, 3 cycles.

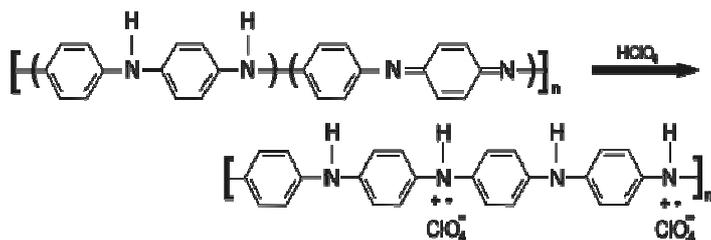


Fig. 14 – Polyaniline polymerization reaction mechanism for obtaining polyaniline emeraldine salt from perchloric acid.

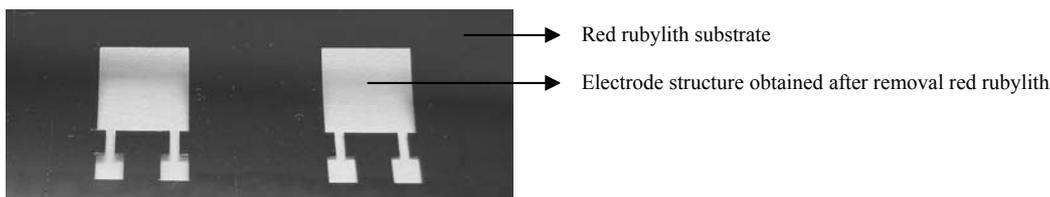


Fig. 15 – Patterned structures on rubylith.

Metal layer deposition

Gold metal, as substrate electrode was chosen since this has a good contact with the film polyaniline conductive thin layer, electrochemically deposited in the form of nanofibre, known as salt emeraldine E.⁷

The deposition of metal layer was done in a vacuum installation (Edwards Auto 500 Vacuum Coating system-BOC Edwards Auto 500), metal layer deposition by vacuum

evaporation. In Fig. 16, the data optical photomicrograph of 0.2µm gold layer thickness deposited on flexible substrate is shown. On the gold electrode substrate a conductive layer polyaniline emeraldine salt form, green, protonated layer due to medium doping with perchloric acid, a 1M aniline perchlorate solution, pH~1 with an excess of 2% HClO₄ was deposited by Cyclic Voltammetry. Optical photomicrograph of polyaniline deposited on gold electrode is given in Fig. 17.

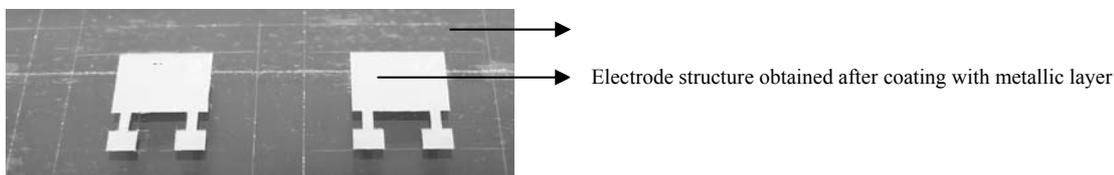


Fig. 16 – Optical photography of the electrode coated with metallic layer Ti/Au on rubylith flexible substrate.

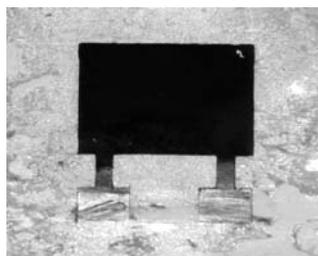


Fig. 17 – Optical photography of gold electrode coated with polyaniline emeraldine salt film, green, high conductive by electrochemical method, Cyclic Voltammetry, on the flexible substrate.

CONCLUSIONS

In conclusion, polyaniline is a conductive polymer that shows great potential for the following reasons: redox reactions consist not only of electron transfer but also of proton transfers; the speed of PANI doping is about two times higher than that of any other conductive polymers; the stability of PANI is probably at its best if the polymer is prepared in appropriate conditions and it may have a low price. During the synthesis of polyaniline, PANI, anions present in the medium are incorporated in the matrix synthesis of PANI as dopant anions. In order to present or analyze the data five available electrochemical characterization methods were used: Open Circuit Potential, Potential Cyclic Voltammetry, Crono Amperometry, Crono Coulometry and Crono Potentiometry to characterize the battery cell function on flexible substrates and confirmed the feasibility and reproducibility of device characteristics on this substrate. The electrochemical methods offer an advantage over the methods involving the chemical oxidation of the monomer in the sense that composite is obtained as coating on a conductive electrode. This is especially important in the applications including batteries and sensors. Active microelectrode is obtained on a substrate of flexible polymer called rubylith, representing an ingenious solution which does not need the entire

manufacturing process of the transfer mask process configuration on a substrate that are commonly used. Thus, microelectrode configuration structure was achieved in one step, directly on red rubylith. By the removing the red rubylith film, the patterned electrode structure on flexible polymer substrate directly remains on the transparent rubylith. By this method aniline can be polymerized and substituted. Polyaniline is known as having the most advantageous combination of stability, conductivity and low costs.

Acknowledgements: The authors acknowledge the POSDRU Project **/89/1.5/S/63 700.*

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