

Effects of The Synthesis Temperature on Electrical Properties of Polyaniline and their Electrochemical Characteristics onto Silver Cavity Microelectrode Ag/C-EM

A. Benabdellah^{1,*}, H. Ilikti¹, H. Belarbi¹, B. Fettouhi², A. Ait Amer², M. Hatti²

¹ Synthesis and Catalysis Laboratory, Ibn Khaldoun University of Tiaret B.P 78, 14000 Algeria.

² Laboratory of the chemistry and electrochemistry of the organometallic complexes. Department of chemistry, Faculty of sciences, University of the Sciences and Technology of Oran (U.S.T.O.MB), BP-1505 Oran El-M'naouer, Algeria.

³ Nuclear Research Center of Birine, B.P 180 Ain Oussera 17200, Djelfa, Algeria.

*E-mail: ben_alk@yahoo.fr

Received: 11 March 2010 / Accepted: 3 May 2011 / Published: 1 June 2011

In this work, the synthesis of a conductive polymer which is polyaniline (PANI) was realized by chemical oxidation of monomer in three different temperatures (5, 30 and 60 °C) to obtain a powder with the best possible electrical conductivity. Electrochemical stability and oxydo-reduction mechanism of the polyaniline synthesized, was studied by cyclic voltammograms with sweeping potential on the polyaniline which presents the best specific conductivity. This study was made by means of a new generation of electrode noted silver cavity microelectrode (Ag/C-EM), developed at the level of electrochemistry catalysis and organic synthesis laboratory (LECSO) of Paris XII university. The using of (Ag/C-EM) was employed to prevent the leaching problems and improve the study of the stability by voltammograms of PANI synthesized by chemical oxidation. The electrical characterization of the three polymers synthesized showed that the best specific conductivity was obtained with the polymer synthesized in the lowest temperature (5 °C). Evolution of intensities, potential of anodic peaks surfaces of the PANI at (Ag/C-EM) with the speeds of sweeping showed that the oxydo-reduction process of PANI is reversible, semi fast, quantitative and stable on all the studied domain of speed. Electrochemical stability of the PANI at (Ag/C-EM) is revealing by the constant shape of voltammograms after 50 cycles of sweeping in acid middle.

Keywords: Polyaniline, silver cavity microelectrode, conductivity, voltammograms of PANI

1. INTRODUCTION

Conductive polymers are new kinds of materials with particular electric-conduction mechanism and electro-chromic. They would be widely applied in the research of chemical modified electrodes, storage batteries, light-emitting diodes, fixation enzymes and so on.

Among a larger number of conductive polymers, polyaniline is one of the most valuable and is attracting much attention because of its low cost, high conductivity, environmental stability, various structures, particular doping/de-doping mechanism and other excellent integrative performance [1-2].

Recently, PANI has been investigated extensively for application in many fields, including the electrode materials of storage batteries, electro-isomerization materials and metal antiseptic materials, etc., where the morphology is believed to play the key role in its applications [3-4].

Up to now, various techniques have been used to synthesize PANI, mostly focusing on mechanical co-blend, solution co-mixing, electrochemical synthesis, chemical synthesis and so on [5-7]. In the chemical synthesis route, a template is often needed to shape PANI into nanostructures.

Microelectrodes offer advantages over conventional larger working electrodes within biosensors since they experience hemispherical solute diffusional profiles, and it is this phenomenon that can impart stir-independence to sensor responses, whilst also offering lowered limits of detection [8-11].

The microelectrode technique has been widely used in electrochemical studies and electroanalytical applications owing to a variety of merits [12-16]. Besides the many advantages of microelectrodes, the powder microelectrode (PME) has a markedly increased real surface area compared with a smooth electrode and therefore, may provide much higher activity for the heterogeneous reactions taking place at the electrode surface.

Cavity microelectrodes C-ME's are greatly attractive because of their low impact on the supported materials (neither special manipulations nor sticking agents are required) and of the offered possibility of quick and reliable renovation of the electrode surface by a rather simple operation of emptying-and reloading with fresh material.

In this paper we report the synthesis of a conductive polymer which is polyaniline (PANI) was realized by chemical oxidation of monomer in three different temperatures (5, 30 and 60 °C) to obtain a powder with the best possible electrical conductivity.

An application of (Ag/C-EM) was employed to prevent the leaching problems and improve the study of the stability by voltammograms of PANI synthesized by chemical oxidation. Microhole electrode, the tip of which is etched with a cavity, is a powerful tool for the investigation of electrochemical processes.

2. EXPERIMENTAL DETAILS

2.1. Reagent and apparatus

Aniline was obtained from Shengyang Federation Reagent Factory. (99%) was distilled under reduced pressure. Ammonium persulfate ($[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, APS) was purchased from Tianjing Bodi Chemical Co. (98%). whereas H_2SO_4 was provided by Harbin Chemical Reagent Co. (99%). All the chemical and reagents were used as received without further purification.

Commercial microcrystalline Ag powder was used (Aldrich, 99.9%, nominal particle mean diameter 2–3.5 μm).

The synthesis of the PANI compound was realized by means of the devices reactionnels following: 1-Balloon, 2- Refrigerating, 3- Light bulb in brome, 4- Heating magnetic agitator, 5- Crystallizer, 6- Boy, 7- Thermometer (as seen Fig.1).

The cyclic voltammograms (CV) measurements of aniline were performed using Volta Lab 40 (Radiometer analytical) potentiostat, driven by Volta Master 4 software; the reactions were performed in single compartment electrochemical glass cell.

The electrochemical cell was assembled with a conventional three-electrode system: an Ag/AgCl/ KCl (3M) reference electrode (Metrohm), platinum (0.072cm^2) as auxiliary electrode and finally a silver cavity micro-electrode ((Ag/C-EM) 10^{-5}cm^3) developed at the level of electrochemistry catalysis and organic synthesis laboratory (LECSO) of Paris XII University as working electrode. Thus, all the potentials reported in this work have been measured versus Ag/AgCl reference electrode.

Electrical conductivity measurements were performed by standard four-probe 4-point method. A Keithley source meter (model 2400) and a Keithley electrometer (model 6514) were used as constant D.C. source and volt meter, respectively. Low temperature conductivity measurements were made using Sumitomo cryogenic (model HC 2), as shown in Fig.2.

The formation of the recess was followed by optical microscope (Olympus BX30) until the desired depth, L (μm), was reached within an uncertainty of $\pm 2\ \mu\text{m}$, corresponding to a division of the micrometric screw.

The deposit homogeneity of micro-sized Ag powder at C-EM was checked using a Wild Photomakroskop M400 optical microscope. Scanning Electron Microscopy (SEM) photographs were acquired with a LEO 1430 and with a Leica Stereoscan 440 (commercial microcrystalline Ag powder).

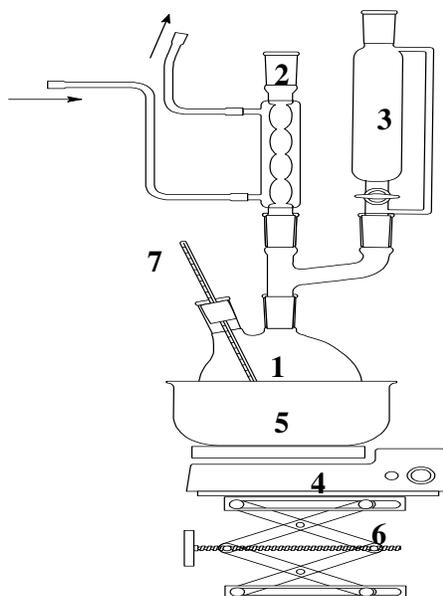


Figure 1. Reactionnel assembly of the synthesis of PANI.

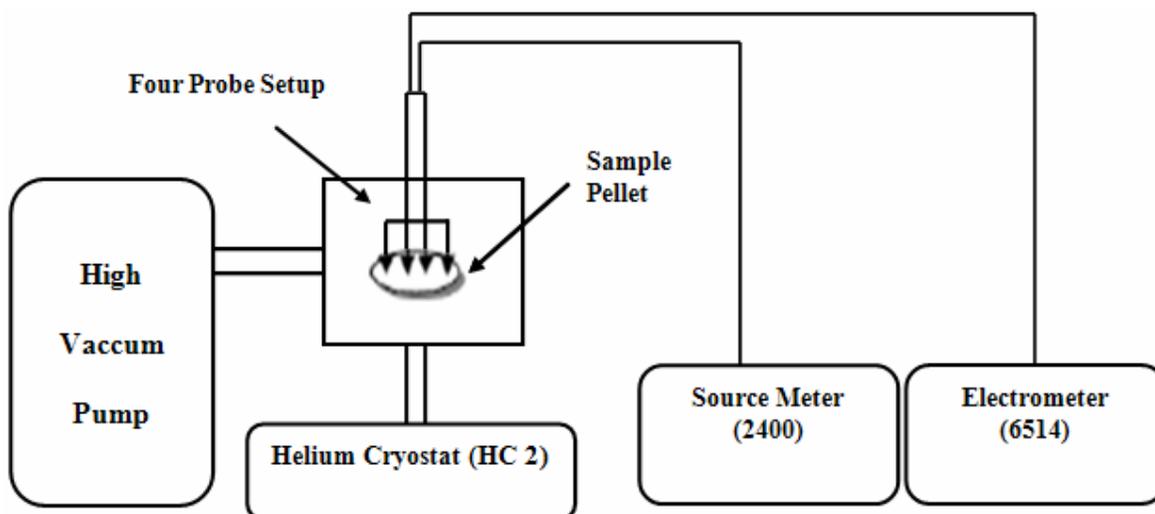


Figure 2. Schematic setup for conductivity measurement.

2.2. Experimental methods

2.2.1. Synthesis of the polyaniline

Polyaniline (PANI) was synthesized with good electrical properties by chemical oxidation of monomer in three different temperatures (5, 30 and 60°C), cooled down to (5°C) by using a bath of glass, and heating for high temperature to obtain a powder with best possible electrical conductivity.

Polyaniline (PANI) was prepared in balloon by oxidative polymerization of aniline in acidic medium by using ammonium peroxydisulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ as an oxidant, all the solutions were prepared in the light bulb in bromine.

In a typical procedure, the monomer aniline (0.005mol) was dissolved in DMF (3ml). If the synthesis temperatures were affected, the polymerization was initiated by the drop wise addition of the oxidant solution containing (0.005mol) of $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, the mixture lead under agitation during 30min. After some minutes this mixtures were transformed in a colloidal solution of dark green colored precipitates of the polymer, were isolated by filtration, washed with de-ionized water and finally dried in an oven for 36hrs. Polyaniline powders obtains were used after in electrical and electrochemical characterization.

2.2.2. Conductivity

Electrical conductivity measurements were performed by standard four-probe technique. Dry powdered samples were made into pellets of ~10mm diameter and ~1mm thickness using a steel die in a hydraulic press under pressure of 300MPa.

A Keithley source meter (model 2400) and a Keithley electrometer (model 6514) were used as constant D.C source and volt meter, respectively. Low temperature conductivity measurements were made using Sumitomo cryogenic (model HC 2). Conductivity measurements were carried out after doping the polymer samples with 0.2M H₂SO₄ solution for 2 h at room temperature after drying at ambient conditions.

The conductivity (σ) was calculated from the relation (1).

$$\sigma = \frac{\ln 2}{\pi d} \left(\frac{I}{V} \right) \quad (1)$$

Where I, V and d are applied current, measured voltage and the thickness of the pellet, respectively.

2.2.3. Preparation of the cavity microelectrodes C-ME

The C-ME were prepared as previously described [17, 18] from a Pt wire of 50 μm diameter, with typical depths of 20–30 μm . The exact value was obtained by measuring the steady state reduction current in Ru (NH₃)₆Cl₃ 1mM solution (using aqueous KCl 0.1M as supporting electrolyte) at 1mV/s and solving for L Eq.2, relevant to planar diffusion in a recess [19]:

$$I_l = \frac{4\pi r F c_b D r^2}{4L + \pi r} \quad (2)$$

where I_l is the steady state current intensity, L and r are cavity depth and nominal radius respectively, c_b and D are the Ru(III) complex concentration and diffusion coefficient, respectively, F the Faraday constant.

The cavity was filled with material particles using the electrode as a pestle. The filling of the cavity was controlled with the microscope, and at the same time, it was verified that no particle remained on the head outside the cavity.

In this work a (C-ME) containing Ag will be denoted Ag powder. At the end of each experiment, the cavity was emptied by sonicating (Ultrasonic Falck UTD18) the electrode dipped in concentrated HNO₃ aqueous solution (10%) and then in acetonitrile (20%). The cavity was then dried at 80°C.

2.2.4. Cyclic voltammogram

For electrochemical study of redox system properties of PANI (powders synthesized in 5°C), an electrochemical cell was set up in a glass container, which had provision to introduce the (Ag/C-EM) working electrode, a Pt coil (0.072 cm²) auxiliary electrode and saturated Ag/AgCl was used as the reference electrode.

An electrolyte solution of 0.5M H₂SO₄ consisting of polyaniline (0.5 M) was taken inside the cell and (Ag/C-EM) electrode was cycled between -0.2 and +0.6 versus Ag/AgCl at a sweep rate of 20mVs.

3. RESULTS AND DISCUSSION

3.1. Electrical measurements

Measurements of the D.C. conductivity of polyaniline have been made in the temperature range (5, 30 and 60°C) table.1.shows the variation in electrical conductivity with temperature. It is observed from the Fig.3 that the conductivity increases with rise in the synthesis temperature, and the best electrical conductivity was obtained in the lowest temperature (5°C).That was explained by in low temperature, chains are better orderly and have a high molecular mass [20].The D.C. conductivity data have been interpreted in light of several results to attribute the most probable mechanism to fit our data.

Table 1. Variation of electrical conductivity with temperature

N°=	Synthesis Temperatures (°C)	conductivity (10 ⁺² S/cm)
1	5	3.34
2	30	2.37
3	60	0.30

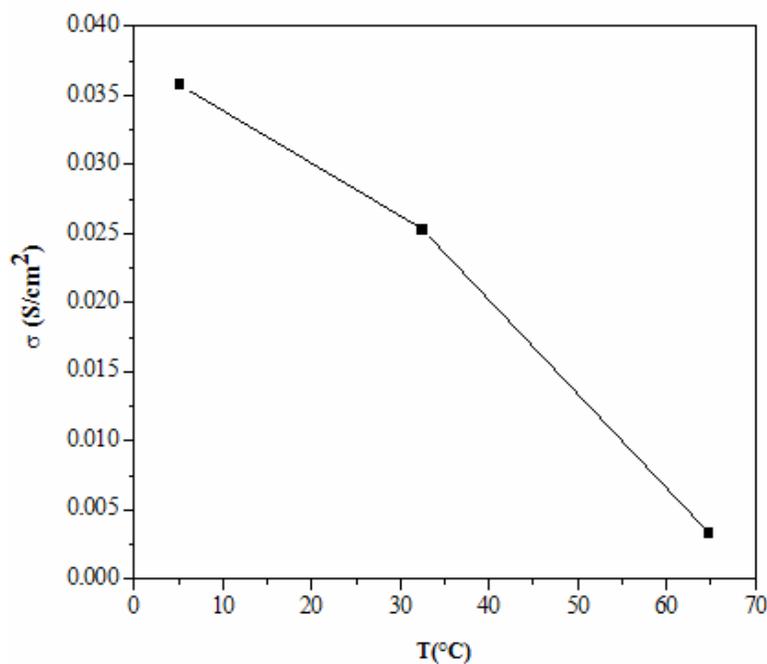


Figure 3. Variation of conductivity of PANI on function to temperature.

3.2. Micro-sized silver (C-ME)

Beside the analytical implications, this represents an indirect proof of the stability of the deposit, which, due to the short deposition time, is far from being dendritic (see Fig4), but rather appears as formed of compact and dispersed grains the sizes of which are between 10 and 30 μm .

The filling of the cavity was highly reproducible; a maximum difference of 9% for repeated electrode filling/emptying procedures.

To this end, the cavity size was tailored to the particle size of the commercial Ag powder (see Fig. 5).

As predicted by the theory, the C-ME behaves as a microelectrode at low scanning rates (almost hemi-spherical diffusion layer) and as a macroelectrode at high scanning rates (planar semi-infinite diffusion layer), in the latter case shows a behaviour similar for electrodeposited Ag layer, although at far higher scan rates V.

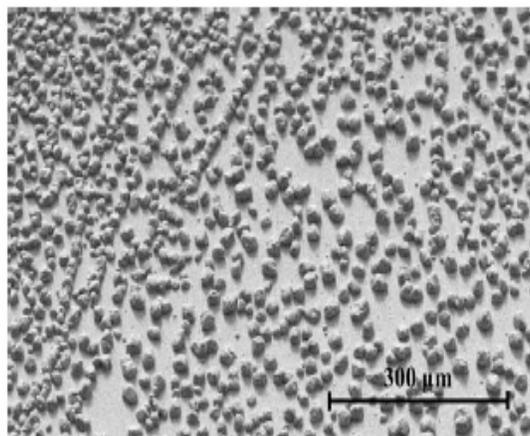


Figure 4. SEM image of the indirect proof of the stability of the deposit Ag.

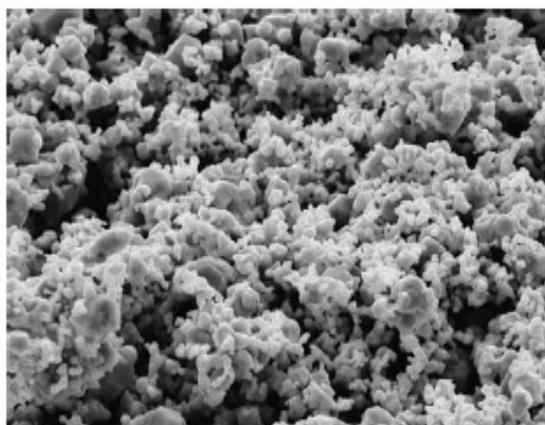


Figure 5. SEM image of the micro-sized Ag cavity onto Pt wire of 50 μm diameter

3.2. Voltammograms studies of PANI on (Ag/C-EM) electrode

Inset in Fig.6. The cyclic voltammograms (CVs) for the pure polyaniline (PANI_{5°C}) recorded at 20mV/s in 0.5M H₂SO₄, in which characterized with two asymmetrical peaks are clearly exhibited. Generally are, anodic oxidation peak (denoted as A), and a reduction cathodic peak (denoted as C). The various characteristics of the anodic peak A are the potential of peak E_A, and the intensity I_A and the area (surface) of the peak Aa corresponding to the load exchanged during the process of oxydo-reduction. The same characteristics can be defined for the cathodic peak C.

The dotted line corresponds to the pure PANI, in which redox peak was observed in the potential range of -0.2 V to +0.6V versus Ag/AgCl.

The voltammograms recorded with the (Ag/C-EM), polymer was kept in its oxidized state (+0.18 V vs.), and show a well-defined cathodic peak at +0.08 V vs. These peaks are identical to those described in the literature and obtained by the other authors for powders and films of polyaniline [21-24].

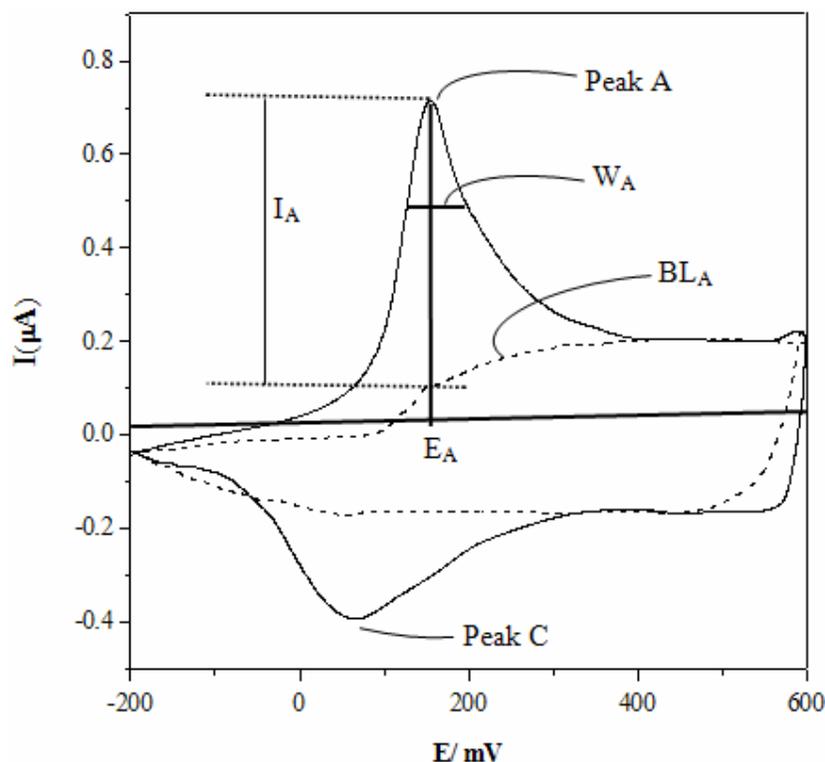


Figure 6. Cyclic voltammograms (CVs) for the pure polyaniline (PANI_{5°C}) at (Ag/C-EM) recorded at 20mV/s.

3.2.1. Voltammograms evolution with speed of sweeping

Redox system of PANI was studied with various speeds of sweepings going of 5 to 1000mV/s, Fig.7 and Fig.8. When speeds of sweeping are increases, the voltammograms was defined are well until 200mV /s, after this speed, the voltammograms speed are deforms gradually. This increase of speeds

of sweeping accompanies with increases in currents intensities [25], by extension of peaks and gap of potential peaks towards positive values for the anodic peaks and negative for the cathodic peaks.

For the biggest values of speed of sweeping, anodic peaks was more marked for which the extension becomes as wide as the cathodic peaks [26, 27]. The voltammograms found at the end of experiment in 50mV/s from at the beginning of experiment Fig.9, what allows verifying that the material did not undergo irreversible modification having been subjected to high speeds of sweeping.

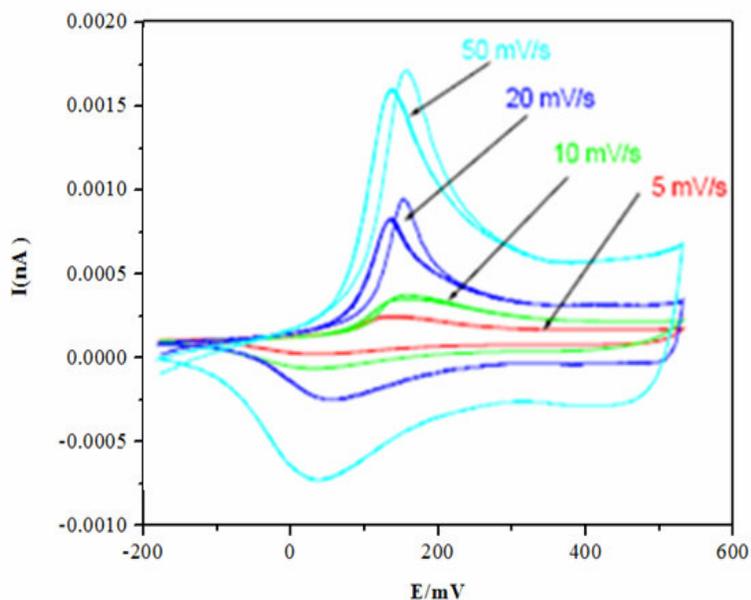


Figure 7. Cyclic voltammograms (CVs) for the pure polyaniline ($\text{PANI}_{5^{\circ}\text{C}}$) at (Ag/C-EM) on different speed of sweeping at 50mV/s.

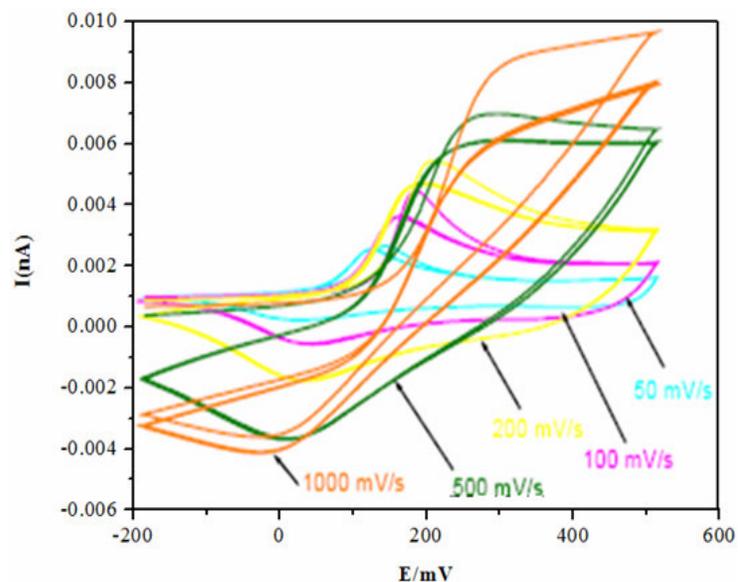


Figure 8. Global cyclic voltammograms (CVs) of pure polyaniline ($\text{PANI}_{5^{\circ}\text{C}}$) at (Ag/C-EM) in the high speeds of sweepings (from 50 to 1000 mV /s).

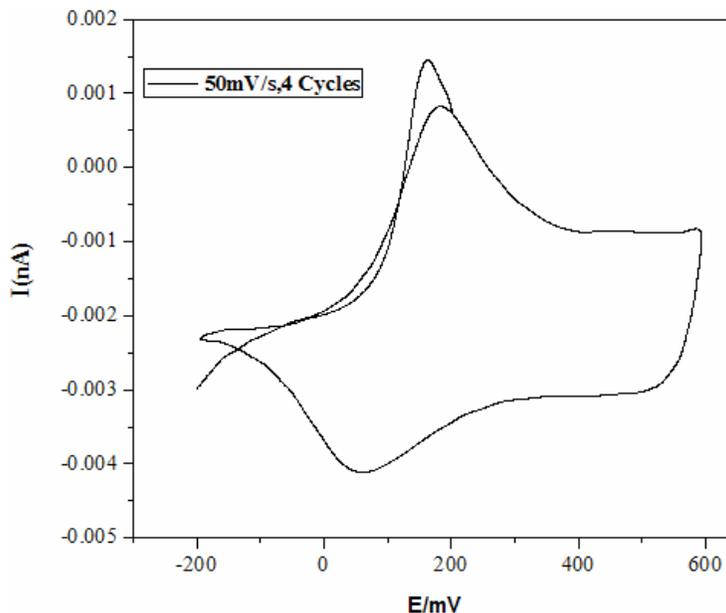


Figure 9. Cyclic voltammograms (CVs) for the pure polyaniline (PANI_{5°C}) at (Ag/C-EM) in the end of experiments in 50 mV /s.

3.3. Exploitation of voltammograms in anodic characterisation of polyaniline onto (Ag/C-EM).

3.3.1. Anodic peaks intensities

The variation of oxidation peaks intensities (I_A) of polyaniline powder a square root in function of speeds of sweeping is straight line, Fig.10, what allows to conclude that the oxydo-reduction kinetics of polyaniline was limited by the broadcasting.

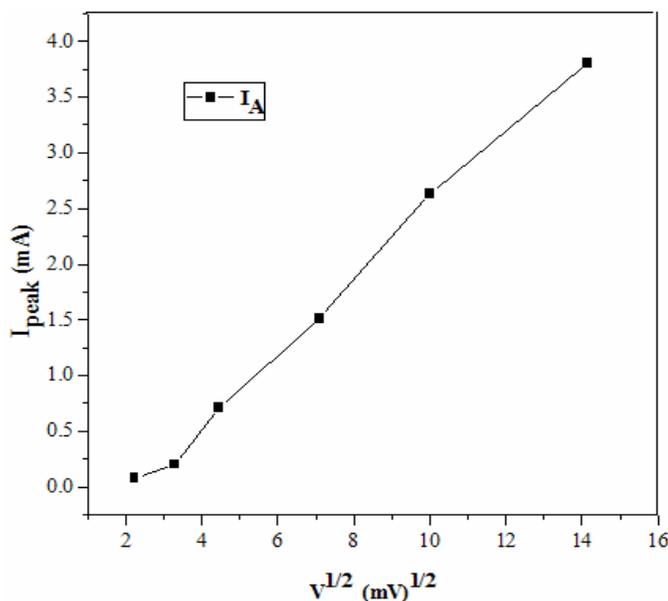


Figure 10. Intensity evolutions of the anodic peak function to the square root of the speed of sweeping.

3.3.2. Anodic peaks potential

For the oxidation peaks potential (E_p) a logarithm in function of speeds of sweeping, which curve varies with an exponential shape, Fig.11, concerning a semi express process of oxydo-reduction [28].

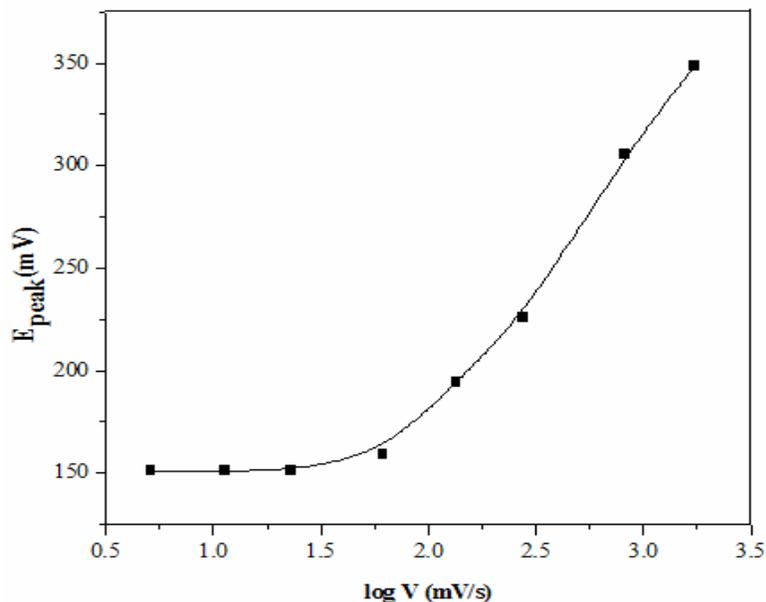


Figure 11. Potential evolutions of the anodic Peak according to logarithm of the speed of sweeping.

3.3.3. Anodic peaks surface

Fig.12, shows the function evolution of the surface to the speed of sweeping. Linear evolution was observed of different slope from zero that was explained an exchanged in oxidation Q_A and all the studied domain of speed are constant.

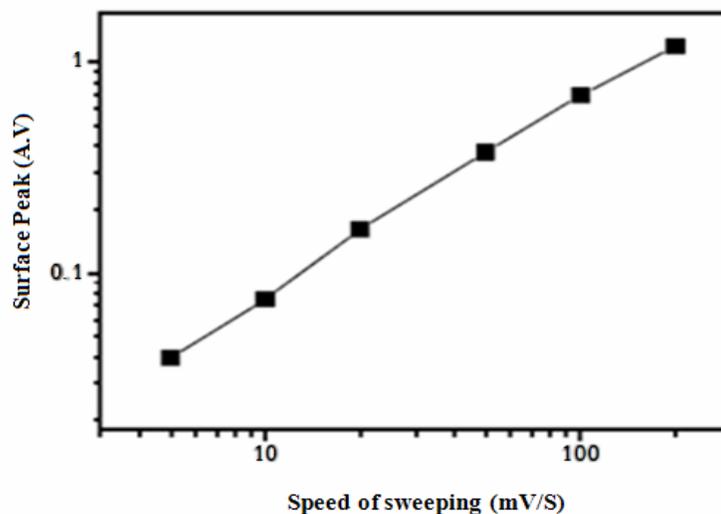


Figure 12. Surfaces Evolutions of the anodic Peak according to the speed of sweeping.

This signifies that all the material participates in the electrochemical reaction (quantitative reaction) [30].

3.4. Evolution of voltammograms with the cycle number

The stability of polyaniline was tested in the length cyclage, Fig.13, shows that the voltammograms speed after 50 cycles are always the same, what means that the oxydo-reduction process of the polyaniline powder is stable in these conditions of employment.

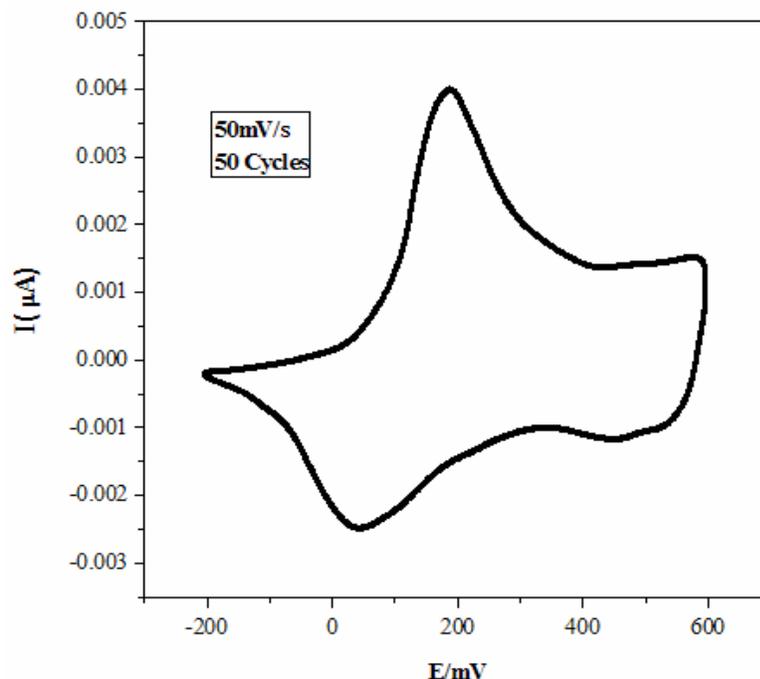


Figure 13. Evolution of Cyclic voltammograms (CVs) for the pure polyaniline (PANI_{5°C}) at (Ag/C-EM) found on the polyaniline during 50 cycles

4. CONCLUSION

The synthesis and protonation doping of the polyaniline was realized by chemical oxidation of aniline in acid middle H₂SO₄. This gave a conductive polymer, the best specific conductivity is observed in the lowest synthesis temperature (5°C).

The use of (Ag/C-EM) would enable substantial saving in both energy and materials.

Evolution of intensities, potential of anodic peaks surfaces of the PANI onto (Ag/C-EM) with the speeds of sweeping showed that the oxydo-reduction process of PANI is reversible, semi fast, quantitative and stable on all the studied domain of speed. Electrochemical stability of the PANI onto

(Ag/C-EM) is revealing by the constant shape of voltammograms after 50 cycles of sweeping in acid middle.

The polyaniline is known to be a reversible and stable system if one limits the cyclage on the first redox step onto (Ag/C-EM).

References

1. J.X. Huang, R.B. Kaner (2004). *J Am Chem Soc* 126 - 851
2. B.K. Yang, K.C. Jae, A.Y. Jeong, W.H. Jin (2002) *Synth Met* 131 - 79
3. D. Marc, D. Jannick, Y.S. Pierre, L. Roger, D.C. Sophie (2000) *Synth Met* 113 - 275
4. J.J. Langer, G. Framski, R. Joachimiak (2001) *Synth Met* 121 - 1281
5. A. H. Elsayed, M. S. Mohy Eldin, A.M.Elsyed, A. H. Abo Elazm, E.M.Younes and H. A. Motaweh. *Int. J. Electrochem. Sci.*, 6 (2011) 206 – 221.
6. N. Kuramoto, A. Tomita (1997) *Polymer* 38 - 3055
7. A.Malinauskas (2004) *J Power Sources* 126 - 214.
8. Abdulilah Dawoud Bani-Yaseen. *Int. J. Electrochem. Sci.* 5 (2010) 1837 – 1846.
9. B. Cassandra Renata. Cordeiro, Aldaléa L. Brandes Marques, Edmar P. Marques, William S.Cardoso, J. Zhang. *Int. J. Electrochem. Sci.*, 1 (2006)343 - 353
10. P. Norouzi, H. Rashedi, T. Mirzaei Garakani, R. Mirshafian and M.R. Ganjali. *Int. J. Electrochem. Sci.*, 5 (2010) 377 – 391.
11. Y. Wang, O. Derek. Northwood. *Int. J. Electrochem. Sci.*, 1(2006) 447 - 455
12. F. Faridbod, M. R. Ganjali, P. Norouzi, *Int. J. Electrochem. Sci.*, 4 (2009) 1679 - 1690
13. U. Chandra, B.E. Kumara Swamy, O. Gilbert, S. S. Shankar, K.R. Mahanthesha, B.S. Sherigara. *Int. J. Electrochem. Sci.*, 5 (2010) 1 - 9
14. S.Reddy1, B.E. Kumara Swamy, U. Chandra1, B.S. Sherigara1, H.Jayadevappa . *Int. J. Electrochem. Sci.*, 5 (2010) 10 - 17
15. M. Saber Tehrani, Mohammad Taghi Vardini, Parviz Abroomand Azar, Syed waqif Husain. *Int. J. Electrochem. Sci.*, 5 (2010) 88 - 104
16. C. S. Cha, C. M. Li, H. X. Yang, P. F. Liu, *J. Electroanal. Chem.*, 1994, 368, 47.
17. V. Vivier, C. Cachet-Vivier, Wu BL, Cha CS, J.Y. Nedelec, L.T. Yu (1999) *Electrochem Solid-State Lett* 2 - 385.
18. C. Cachet-Vivier, V. Vivier, C.S. Cha, J.Y. Nedelec, L.T. Yu (2001) *J Electrochem Soc* 148 - 177.
19. A.M. Bond, D. Luscombe, K. Oldham, C.G. Zoski (1988) *J Electroanal Chem* 249 - 1.
20. J. Stejskal, *Pure App.Chem.*, 74, (2002) 857.
21. W.S. Huang, B.D. Humplhrey, A.G. MacDiarmid, *J. Chem. Soc. Faraday Trans. I*, 82 (1986) 2385.
22. Fallyn W. Campbell and Richard G. Compton, *Int. J. Electrochem. Sci.* 5 (2010) 407 – 413.
23. T. Kobayashi, H. Yoneyama , H. Tamura, *J Electroanal. Chem.*, 177 (1984) 293.
24. A.F.Diaz et J.A. Logan, *J. Electroanal. Chem.*, 111 (1980) 111.
25. A.M. Pharhad Hussain, A. Kumar, *Bull. Mater. Sci.*, 26 (2003) 329.
26. K.G. Conroy, C.B. Breslin, *Electrochim. Acta*, 48 (2003) 721.
27. V. Vivier, *Thèse de doctorat d'état*, Université Paris XII (2000).
28. H. Matsuda , Y. Ayabe, *Z. Electrochem.*, 59 (1955) 494.
29. J. W.YAN, J. Tao LU, P. Fang LIU. *Chinese Chemical Letters* Vol. 10, No. 1, pp. 47 – 50, 1999
30. P. Fang LIU, J. F. HU. *Chinese Chemical Letters* Vol. 13, No. 1, pp 79 – 82, 2002