Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrochemical Polymerisation of Aniline on Skeleton Nickel Electrodes

N. Plesu [a], A. Kellenberger [b], N. Vaszilcsin [b] & I. Manoviciu [b]

[a] Institute of Chemistry, Timisoara, Romania

[b] University "Politehnica", Timisoara, Romania

Version of record first published: 18 Oct 2010

To cite this article: N. Plesu, A. Kellenberger, N. Vaszilcsin & I. Manoviciu (2004): Electrochemical Polymerisation of Aniline on Skeleton Nickel Electrodes, Molecular Crystals and Liquid Crystals, 416:1, 127-135

To link to this article: http://dx.doi.org/10.1080/15421400490478605

Mol. Cryst. Liq. Cryst., Vol. 416, pp. 127/[383]–135/[391], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490478605

ELECTROCHEMICAL POLYMERISATION OF ANILINE ON SKELETON NICKEL ELECTRODES

N. Plesu
Institute of Chemistry, Romanian Academy, Timisoara, Romania

A. Kellenberger, N. Vaszilcsin, and I. Manoviciu
University "Politehnica" Timisoara, Romania

The polyaniline (PAni) coating was electrochemically deposited on nickel skeleton electrode and nickel foil by potential sweep between −0.2 V and 1.2 V/SCE, with a scan rate of 20 mV s^{-1}; acid aqueous solutions containing 0.027 mol L^{-1} aniline in 1 mol L^{-1} sulphuric acid were used. The PAni film was studied by IR Spectroscopy, UV-VIS Absorption, Scanning Electron Microscopy, X-Ray Diffraction and Cyclic Voltammetry. The X-Ray studies suggest that the PAni films present a good cristalinity, as well as high molecular weight, possible high or intermediate crosslinked.

Keywords: cyclic voltammetry; polyaniline; skeleton electrode

INTRODUCTION

Polyaniline (PAni) can be relatively easy obtained in aqueous acid solutions ($pH = 0 \div 1$) and its conductive form is stable in air or water. The electrical conductivity of polyaniline is due to the dislocation of the π electrons and the possibility of polyaniline to participate in acid-base intern reactions.

In the recent years many studies were dedicated to the deposition of polyaniline on various substrates, generally inert, such as platinum, graphite, glassy carbon or ITO [1–3]. The aim of our paper is to extend the applicability field of this type of conductive polymer, by deposition of polyaniline on original substrates.

Therefore, the formation of polyaniline coatings was studied on un-noble substrate with modified surface and to compare with conventional substrate in the same working conditions.

Address correspondence to N. Plesu, Institute of Chemistry, Romanian Academy, Timisoara, Romania. E-mail: plesu_nicole@yahoo.com

EXPERIMENTAL

PAni film was obtained comparatively by electrochemical polymerisation of aniline in aqueous solutions of sulphuric acid, on both skeleton and bright nickel electrode as substrate. The electrode reaction was studied by cyclic voltammetry, using a Princeton Applied Research Potentiostat Model 273. The potential was swept between -0.200 V and $+1.200$ V versus the saturated calomel electrode (SCE).

The cyclic voltammograms were recorded at a polarisation rate of 20 mV/s, using a 0.027 mol L^{-1} aqueous aniline solution in 1 mol L^{-1} sulphuric acid. In order to compare the properties of the films obtained on the skeleton nickel electrode with those obtained on the smooth nickel electrode, polarisation curves were recorded for both types of electrodes in identical working conditions.

Before being used, the electrodes were treated as follows:

—The smooth nickel electrode, was prepared prior to each experiment through mechanical polishing with Diamond-spray (Struers) with an increased degree of fineness down to 0.25 μm, and washed thoroughly with distilled water.
—The skeleton nickel electrode was obtained by deposition of a nickel-aluminium alloy using the thermal arc spraying technique [4,5]. In order to achieve the skeleton effect, the aluminium was dissolved for 1 h, in 1 mol L^{-1} NaOH, at a temperature of 70°C.

The PAni coatings were characterized by IR Spectroscopy, UV-VIS Absorption, Scanning Electron Microscopy, X-Ray Diffraction and Cyclic Voltammetry.

The morphology of the polyaniline coating deposited on both smooth and skeleton nickel substrate was studied by scanning electron microscopy (Philips XL 30 ESEM) operating at 20 kV.

X-Ray diffraction patterns of the polyaniline coating were registered with a Philips X'pert Diffractometer using the Cu-Kα radiation ($\lambda = 1.54$). The scanning range was $2\theta = 0^\circ - 40^\circ$ and the X-Ray power was 40 kV and 50 mA.

In all experiments, freshly distilled aniline (MERCK), and sulphuric acid (MERCK) were used. The smooth nickel electrode was prepared from Ni folio 0.2 mm (Aldrich).

The working temperature was 25 ± 1°C in all cases.

RESULTS AND DISCUSSION

To study the electrochemical polymerisation of aniline in sulphuric acid, cyclic voltammograms were recorded in the domain were the growth of

the polymer film takes place, on both skeleton and smooth nickel electrode (Fig. 1a, b).

The appearance of peak A on the first cycle in Figure 1a may be attributed to the formation of the passive nickel oxide layer or to the chemisorbed oxygen [6]. The peak appears both on the smooth and on the skeleton nickel electrode. It doesn't appear in the following cycles, due to the passive state, which settles in. On skeleton nickel the appearance of a second peak B was noticed, which may be attributed to the oxidation of the chemisorbed hydrogen, formed at the cathodic limit of the potential domain, were the initial potential was fixed. Peak B appears only on the skeleton nickel because this electrode presents the electrocatalytic effect for the hydrogen evolution, and indicates a large specific surface as compared to the smooth nickel. At the anodic limit of the potential field, the oxygen evolution reaction takes place. It can be seen, that after the first cycle, the rate of the anodic processes, which take place in the potential region were polyaniline grows ($-0.200 \div +0.800$ V/SCE), is negligible, and accordingly, the process of aniline oxidation in sulphuric acid solution can be studied both on the skeleton nickel as well as on the smooth nickel.

Figure 2 presents the voltammograms recorded during the electrooxidation of aniline, on both smooth and skeleton nickel electrode.

In case of smooth electrode, after the appearance of the passive state (cycles 1, 2, 3) starting with cycle 4, an anodic peak appears at $E_p = +0.850$ V/SCE, attributed to the formation of a radical – cation.

In the following cycles (5–11), one notices the appearance of the oxidation peaks C, D, E and F (peak C: $E_p = +0.150$ V; peak D: $E_p = +0.430$ V; peak E: $E_p = +0.510$ V and peak F: $E_p = +0.750$ V). These peaks are shifted towards slightly more positive potentials – the first three peaks – and towards negative potential – the last one of them – with

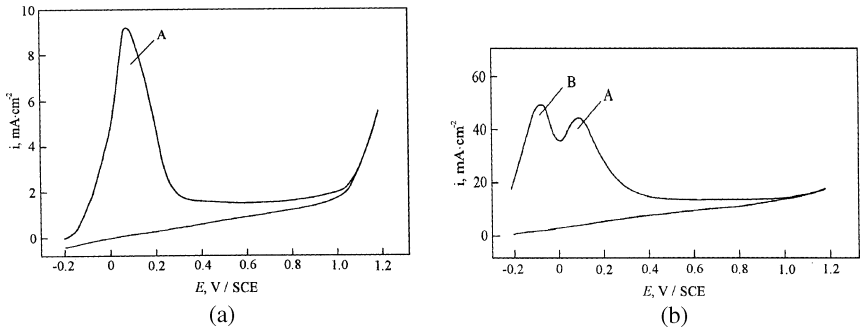

FIGURE 1 Cyclic voltammograms recorded in 1 mol L^{-1} sulphuric acid; Scan rate 20 mV/s. a) Smooth nickel; b) Skeleton nickel.

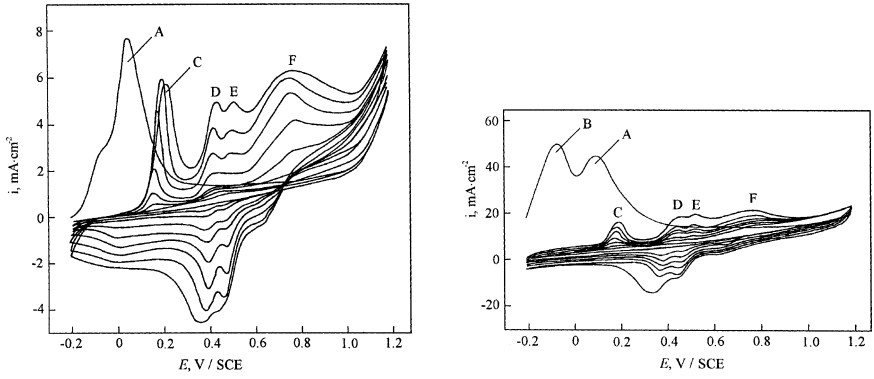

FIGURE 2 Cyclic voltammograms obtained during electrochemical synthesis of PAni films in solutions of 0.027 mol L^{-1} aniline in 1 mol L^{-1} sulphuric acid; Scan rate 20 mV/s; a) smooth nickel electrode; b) skeleton nickel; Number of cycles: 11.

the increase of the number of cycles. Peak C is assigned to the formation of radical – cations in the polymeric chain, and peak F to the oxidation of radical – cations formed in the polymer chain at the corresponding imine, according to [7–10].

Peaks D and E may be assigned either to the oxidation of intermediary compounds or to secondary products of oxidation (benzidine, benzochinone). The intensity of these peaks rises gradually due to the increase of the polymer layer on the surface of the electrode and, consequently, of the intermediate species formed during the reactions on the electrode.

After several cycles in the domain of $-0.200 \div +1.200$ V/SCE, the peak D becomes more pronounced due to the degradation reactions of the polymer layer. The degradation reactions (1, 2) appear because of the overoxidation and of the hydrolytic process of the polymer chains:

$$-N=(C_6H_4)=N-+H_2O \rightarrow -NH_2+O=(C_6H_4)=O \quad (1)$$

$$O=(C_6H_4)=O \underset{-2e^-\,-2H^+}{\overset{+2e^-,\,+2H^+}{\rightleftharpoons}} HO-C_6H_4-OH \quad (2)$$

On the cathodic branch of the cyclovoltammogram two reduction peaks appear at potentials of approximately $+0.460$ V, respectively $+0.390$ V, which are shifted towards slightly more negative values potentials with the increase in the number of cycles and finally overlap. These two peaks probably correspond to the reversible cathodic process associated with the anodic peaks D and E. Also, one may observe a reduction peak at $+0.010$ V,

corresponding to the anodic peak C, shifted to more negative values (−0.05 V) as the number of cycles increases.

The shape of cyclic voltammograms recorded using nickel skeleton in the potential range of −0.200 ÷ +1.200 V/SCE, in 1 mol L^{-1} sulphuric acid solution, with a polarisation rate of 20 mV/s (Fig. 2b), were similar to those recorded on the smooth nickel electrode.

On the skeleton nickel electrode the oxidation process of aniline occurs from the 5th cycle due to the formation of radical – cation. For the following cycles, the appearance of the same anodic peaks at: $E_p = +0.170$ V; $E_p = +0.430$ V; $E_p = +0.530$ V and $E_p = +0.770$ V could be noticed. These peaks are shifted towards slightly more positive potentials – the first three peaks – and towards negative potentials – the last one – with the increased number of cycles.

On the reverse run, the shape of the voltammograms is similarly to that registered on smooth nickel. Two reduction peaks appear, corresponding to the reversible processes associated with peaks D and E.

In both cases during the electrochemical oxidation process the electrode is covered with a polymer layer whose colour changes progressively from yellow – green to dark violet.

By lowering the anodic limit of the working potential range (from 1.200 to 0.700 V/SCE) the shape of the cyclic voltammograms becomes simpler, as shown in Figure 3.

Changing the anodic value of the potential leads to the disappearance of the intermediary peaks of oxidation due to secondary products and to the increase of intensity of the anodic peak C (from approximately 20 mA/cm^{-2} to approximately 40 mA/cm^{-2}).

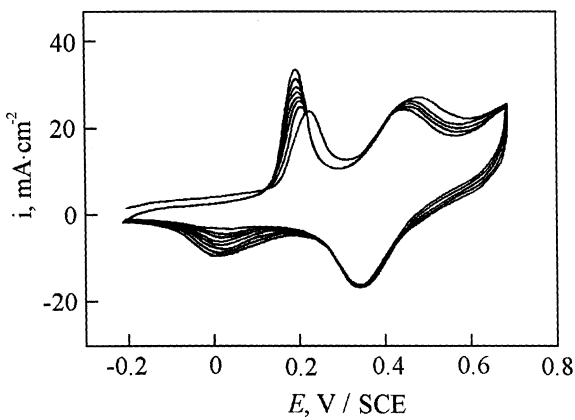

FIGURE 3 Cyclic voltammograms on skeleton nickel in the same solution as Figure 2.; Potential range − 0.200 ÷ 0.700 V/SCE; Scan rate 20 mV/s; number of cycles: 8.

The polyaniline obtained electrochemically was analysed by IR and UV-VIS spectroscopy. The IR spectrum was recorded on KBr pellet, with an Specord IR 75 and the following peaks corresponding to the weave lengths were identified: 659, 830, 1237, 1380, 1480, 1569, 1575, 1600, 2000, 2250, 2700 and 3300 cm^{-1}. The IR spectra of polyaniline were in accordance with the literature data for PAni [8–10].

The UV-VIS spectrum allows the detection of the oxidation state of PAni (salt and base). In solution, according to literature data [10] the UV-VIS spectra of base present two absorption peaks around the value 325 and 625 nm. The salt form presents two absorption peaks, in the same region, as did the base form at approximately 330 and 630 nm, which indicates that a variable amount of PAni base was presented. The protonation of PAni base with acid (sulphuric acid) presents three absorption peaks around 325, 424 and 830 nm.

The SEM micrographs were taken for the surface of the coating, at different magnifications. The specimen revealed a good electrical conductivity therefore gold sputtering was not necessary. The morphology of the PAni coatings deposited on skeleton and smooth nickel substrate is presented in Figure 4.

The PAni films deposited on the nickel electrodes show a porous, granular structure compared to the fibrilar structure of the PAni films obtained on Pt electrodes [11]. We observed that the coating obtained on the smooth nickel electrodes was not continuous.

The elemental composition of the coating was determined by Energy Dispersive X-Ray Analysis. The results of the EDX analysis reveal the presence of C, N, S and O in the samples.

The C/N ratio for the first two samples approximates the theoretical value. When the potential range is extended, a higher value of the C/N ratio indicates the occurrence of overoxidation reactions. The S/N ratio gives information

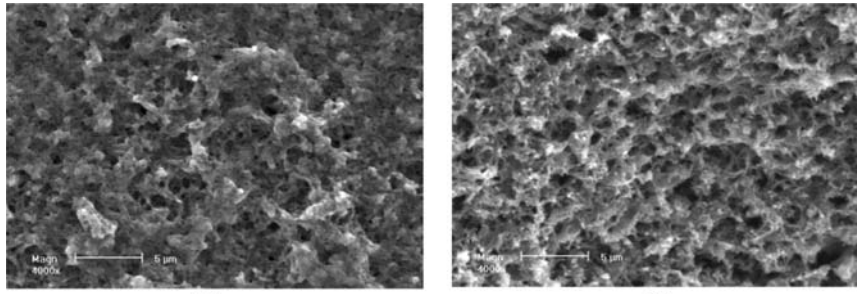

FIGURE 4 Morphology of the PAni coating; magnification 4000×; a) smooth nickel; b) skeleton nickel.

TABLE 1 EDX Results of C/N and S/N Ratios for Different PAni Samples

Sample	C/N	S/N
PAni on smooth nickel (–0.2–0.8 V/SCE)	6.16	0.59
PAni on skeleton nickel (–0.2–0.8 V/SCE)	6.05	0.62
PAni on skeleton nickel (–0.2–1.2 V/SCE)	7.06	0.53

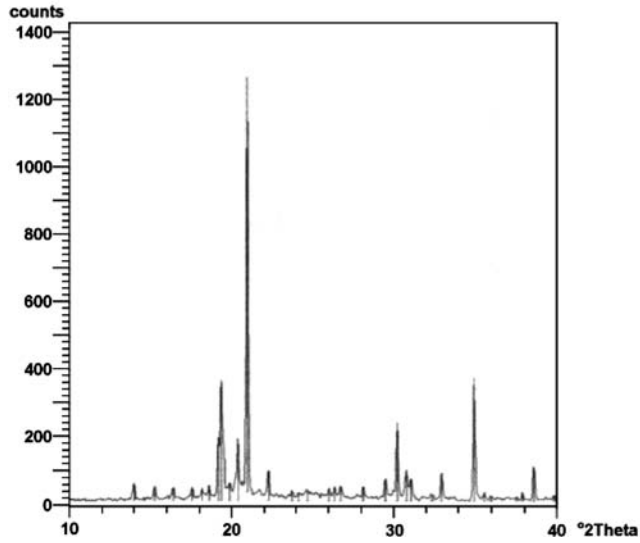

FIGURE 5 X-Ray diffraction pattern for the PAni coating.

about the doping level of polyaniline. The values between 0.53–0.62 demonstrate that polyaniline was obtained in the form of emeraldine salt.

Figure 5 shows the X-Ray diffraction patterns of H_2SO_4 doped PAni obtained at skeleton nickel electrode.

TABLE 2 X-Ray Diffraction Data

d spacing	Relative intensity	2θ
4.63	12.97	19.1
4.59	24.68	19.3
4.36	12.68	20.3
4.24	84.37	20.9
2.96	15.98	30.2
2.57	23.58	34.9

The X-Ray diffraction patterns were similar to those presented by other authors [12,13]. The most important peaks are listed in Table 2.

The presence of sharp peaks reveals the partial crystalline nature of the polymer and indicates the presence of rigid chains and an ordered structure.

CONCLUSIONS

The oxidation of aniline in acid media both on smooth and skeleton nickel electrode allows the obtaining of a polymeric film, of different colour changing from yellow – green to dark violet according to the working conditions.

For both smooth nickel and skeleton nickel, starting the polarization from $-0.200\,\mathrm{V/SCE}$ towards more positive values, the dissolution of nickel takes place until the critical current is reached, when the metal reaches the passive state. After the installation of passive state, the dissolution peaks of nickel are no longer observed. The working domain was anodically limited by the oxygen evolution, starting at the potential of $+1.200\,\mathrm{V/SCE}$.

The oxidation of aniline started at $E = +0.850\,\mathrm{V/SCE}$ on smooth nickel and at $E = +0.750\,\mathrm{V}$ on the modified electrode, after the formation of the passive nickel oxide layer. The initiation process takes place slower on the nickel electrode–as compared to platinum; it requires some time for the generation of the active species–anilinium radical cation–in the initial stage of polymerisation, probably due to the nickel oxide layer formed in the passivation reaction of the electrode in acid media. The shape of the voltammograms is similar to those obtained on platinum and according to literature data.

The SEM micrographs show that the polyaniline film has a granular structure and from the X-Ray data it can be concluded that it presents a good cristalinity.

The skeleton substrate improves the adherence of the polymeric film compared to smooth surfaces and allows preparing in an easy and reproducible manner a modified skeleton nickel–polyaniline electrode.

REFERENCES

[1] Trivedi, D. C. (1997). Polyanilines. In: *Handbook of Conductive Molecules and Polymers*: Vol 2: Conductive Polymers. Synthesis and Electrical Properties. Nalwa H. S. (Eds.), John Wiley & Sons Ltd: London, 503–566.

[2] Huang, W. S., Humpfrey, B. D., & Mac Diarmid, A. G. (1986). Polyaniline, a Novel Conducting Polymer. *J Chem Soc, Faraday Trans I*, *82*, 2385–2400.

[3] Dinh, H. N. & Birss, IV. (1999). Characteristic anodic prepeak. *Electrochim Acta*, *44*, 4763–4771.

[4] Vaszilcsin, N., Brandl, W., Kellenberger, A., & Toma, D. (1998). Characterisation of Skeleton Nickel Cathodes Obtained trough Thermal Arc Spraying Technique. *Chem. Bull "Politehnica" Univ. (Timisoara)*, *43*(57), 330–339.

[5] Fournier, J., Miousse, D., & Legoux, J. G. (1999). Wire-arc sprayed nickel-based coatings for hydrogen evolution reaction in alkaline solution. *Int J Hydrogen Energy*, *24*, 519–528.

[6] Vaszilcsin, N., Nemes, M., Birzescu, M., & Noslopi, L. (1998). Electrochemical behaviour of skeleton electrodes obtained through thermal decomposition of Ni(II)-Al(III)-heteropolynuclear glyoxylates generated in situ. *Glasnik Hem i Teh RS*, *40*, 1–7.

[7] Kitani, A., Kaya, M., Yano, J., Yoshikawa, K., & Sasaki, K. (1987). Polyaniline: Formation reaction and structure. *Synthetic Metals*, *18*, 341–346.

[8] Ohsawaka, T., Kabata, & T., Kimura, O. (1989). Polaronic transition in electrochemical polymerised polyaniline. *Synthetic Metals*, *29*, E203–E210.

[9] Park, S.-M. (1997). Electrochemistry of π-conjugated polymers. In: *Handbook of Conductive Molecules and Polymers*: Vol 3: Conductive Polymers: Spectroscopy and Physical Properties. Nalwa H. S (Eds.), John Wiley & Sons Ltd: London, 429–461.

[10] Zagorska, M., Prori, A., & Lefrant, S. (1997). Spectroelectrochemistry and Spectroscopy of Conducting Polymers. In: *Handbook of Conductive Molecules and Polymers*: Vol 3: Conductive Polymers. Spectroscopy and Physical Properties. Nalwa H. S (Eds.), John Wiley & Sons Ltd: London, 1997:183–215.

[11] Nakajima, T. & Kawagoe, T. (1989). Polyaniline: Structural analysis and application for battery. *Synthetic Metals*, *28*, C629–C638.

[12] Pouget, J. P., Jozefowicz, M. E., Epstein, A. J., Tang, X., & Mac Diarmid, A. G. (1991). X-Ray Structure of Polyaniline. *Macromolecules*, *24*, 779–789.

[13] Luzny, W., Sniechowski, M., & Laska, J. (2002). Structural properties of emeraldine base and the role of water contents: X-Ray diffractions and computer modelling study. *Synthetic Metals*, *126*, 27–35.