

Preliminary Studies for Obtaining Polyaniline on Nickel Electrode

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Abstract: In our studies the possibility of obtaining polyaniline films on the nickel electrode through electrodeposition was investigated. The method used was cyclic voltammetry. The working electrode (anode) was glossy nickel. The electrolyte solution was diluted sulfuric acid with or without aniline. The experiments were performed at temperatures ranging from 25 to 45°C and an electrochemical potential interval between $-0.5 \div 1.6$ V. A white green to blue color (depending on the electrochemical potential) polyaniline film was deposited on the nickel electrode. The main reactions that take place on the electrode and the effect of the working conditions on these processes were identified through cyclic voltammetry.

Keywords: polyaniline, nickel electrode, cyclic voltammetry, electrodeposition

1. Introduction

Polyaniline (PANI) is one of the most studied conductive polymers because of its exceptional chemical, electrical and optical properties. It can be obtained through chemical and electrochemical methods.

Through electrochemical synthesis the polymer is obtained directly under the shape of thin films deposited on electrodes (metallic or non-metallic), having an ordered structure, with a high degree of crystallinity. The electrode thus obtained, possibly modified with appropriate structure compounds has many applications. It can be used as a biosensor for biomolecular compounds batching. One such compound is dopamine – a biogenic amine that acts as a neurotransmitter in the brain and is involved in motricity control [1]. A reduction in dopamine concentration leads to muscle stiffening, a decrease in movement speed and trembling while resting, symptoms that indicate a neurodegenerative disease such as Parkinson's disease or schizophrenia.

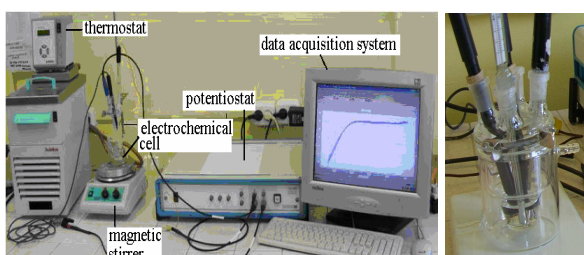


Figure 1. a - Laboratory unit. b - Close-up of the electrochemical cell

The technical literature contains studies performed on the electrochemical polymerization of aniline on platinum electrode [2], skeleton nickel [3], polyaniline film characterization [4], the influence of dopants on the characteristics of obtained films [5], the effect of temperature on the electrochemical synthesis [6] etc.

In our studies the possibility of obtaining polyaniline films on the nickel electrode through electrodeposition was investigated using cyclic voltammetry.

2. Experimental

Aniline electropolymerisation experimental studies in aqueous environment were conducted using a water-jacketed glass electrolysis cell, type BEC/EDI X51V001, equipped with three electrodes: *the working electrode* was a nickel disk electrode with $d = 6.18$ mm, $S = 0.3$ cm²; *the counter electrode* was a platinum wire, $S = 0.25$ cm²; *the reference electrode* was the SCE electrode.

Cyclic voltammetry studies were conducted with a PGZ 301 DynamicEIS Voltammetry potentiostat model equipped with VoltaMaster 4 software and manufactured by Radiometer Copenhagen. The working temperatures (25 and 45°C) inside the cell were ensured with a Julabo F 12 Labortechnik thermostat model. The laboratory unit is shown in figure 1a and a close-up of the electrochemical cell is shown in figure 1b.

Polyaniline film deposition (PANI) on the surface of the nickel electrode was accomplished through aniline electrooxidation in a diluted H₂SO₄ solution. Before conducting the studies, the working electrode was mechanically cleaned using sandpaper with decreasing grit sizes and aluminum polishing cloth, as well as degreased with detergent solution in an ultrasonic bath.

The electrolyte volume used for each determination was 25 ml. Experiments were conducted using 0.1 M and 0.5 M H₂SO₄ solutions, 0.04 M and 0.08 M aniline concentrations and temperatures of 25 and 45°C, respectively. All potentials are referred to the SCE, unless otherwise noted.

The H₂SO₄ and aniline used in the studies were purchased from Merck Company. Aniline was freshly redistilled under vacuum conditions and then stored at a low temperature and in the absence of light. All solutions were prepared using bidistilled water.

Cyclic voltammetry studies were undertaken at a maximum interval potential between $-0.5 \div +1.6$ V. The polarization speed was 0.1 V/s.

3. Results and Discussion

Cyclic voltammograms obtained with the nickel electrode in 0.1 M H_2SO_4 solution are shown in figure 2.

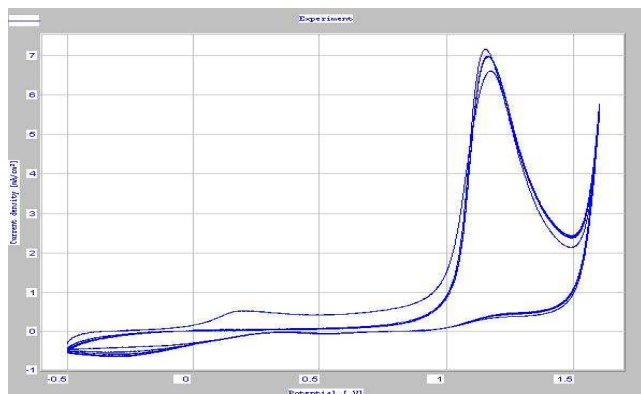


Figure 2. Cyclic voltammograms recorded in 0.1 M H_2SO_4 solution on the Ni electrode, in the absence of aniline; polarization speed: 0.1 V/s; temperature 25°C

At the first polarization cycle, a small intensity peak can be observed at ~ 0.15 V that doesn't appear at the subsequent polarization cycles. Next to it there is a second anodic peak, with higher intensity, at a 1.2 V electrochemical potential. This second peak slowly increases with the number of cycles and then becomes virtually steady. It's possible that this peak is due to the formation of a nickel oxide passivation layer. It would be better if the studied processes were undertaken up to this potential. Under these conditions oxygen release begins at ~ 1.5 V.

Voltammograms obtained on the Ni electrode through electrolyzation of 0.1 M H_2SO_4 solution containing 0.04 M aniline, at the potential interval $-0.5 \div +1.6$ V, are shown in figure 3.

After adding aniline in the electrolyte solution, the presence of three anodic and two cathodic peaks can be observed on the resulting voltammograms (red lines). The first anodic peak appears at a 0.7 V potential, increases with the number of cycles and at the same time moves toward more positive values. This peak corresponds to aniline oxidation (*with anilinium anion formation*) on the initially clean nickel electrode and afterwards on the gradually covered electrode with polyaniline monofilms previously formed on its surface.

The formed anion immediately reacts with another aniline molecule, forms an anilinium anion with a bigger molecular mass and so on. The polymerization reaction keeps propagating. Thus, in the first phase, leucoemeraldine is formed. Under strong oxidizing conditions, the leucoemeraldine film deposited on the anode turns quickly into emeraldine and then into the non-conductive pernigraniline form (highly oxidized state).

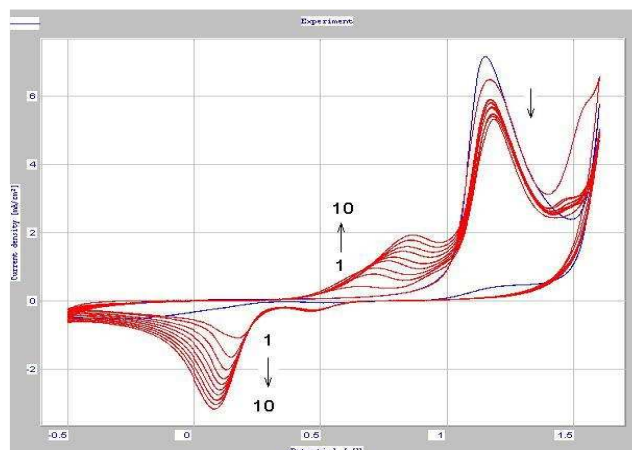


Figure 3. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.1 M H_2SO_4 solution (red) containing 0.04 M aniline; the second cycle of the baseline (blue); polarization speed: 0.1 V/s, polarization interval $-0.5 \div 1.6$ V; temperature 25°C

The oxidation peak corresponding to the 1.2 V potential is also present at the baseline – recorded in the absence of aniline – and thus its presence cannot be attributed to aniline.

At higher potentials – ~ 1.5 V – another anodic process takes place before oxygen release – probably associated with undesired by-product formation due to the advanced degradation of the polyaniline film.

When reversing the potential direction two peaks are observed at potentials of ~ 0.45 V and 0.2 V, respectively.

The first peak, of smaller intensity, is not influenced by the number of cycles. The second peak – first observed at a 0.2 V potential – is of greater interest. It tends towards more negative values and increases in intensity when the number of cycles is increased. This increase is correlated with that of the anodic peak from the 0.7 V potential – these peaks correspond to a reversible process – probably outlining the shift from emeraldine base to emeraldine salt.

After 10 cycles the polarization interval was restricted to $-0.5 \div 0.8$ V and 50 more were recorded, in sets of 10 cycles each, as shown in figures 4 and 5.

The domain was restricted in order to reduce the degradation probability of the polyaniline film formed on the anode, process which takes place at potentials higher than 0.8 V, as established. Thus, the thickness of the polyaniline film was increased only in emeraldine form, with maximum efficiency – without degradation or by-product formation. Even though the first anodic peak is present at a relatively high potential (~ 0.4 V) at which we can consider that pernigraniline is preponderantly formed, the color of the film after 60 cycles, in this restricted interval, is white green – specific to emeraldine.

In the specified range, throughout the whole cyclic polarization process, a continuous increase of the anodic and cathodic currents can be observed.

Peak potentials tend towards more negative values for the anodic peak and towards more positive values for the cathodic one – vice-versa than what was observed after the first 10 cycles. Thus the peak potentials get closer to each other.

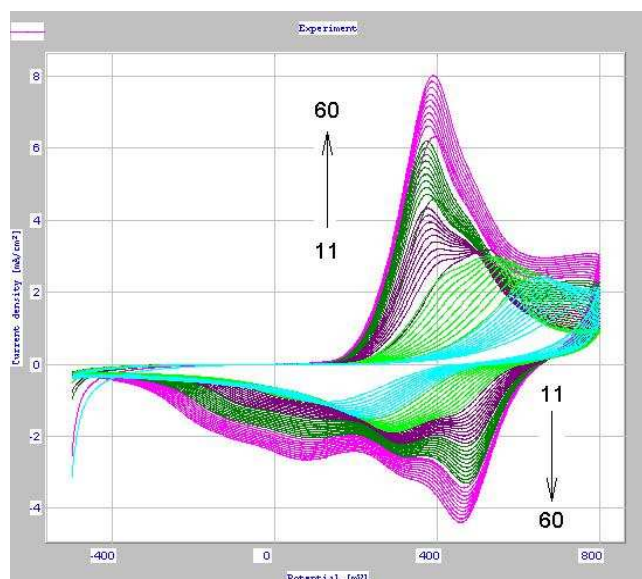


Figure 4. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.04M aniline in 0.1M H₂SO₄ solution, polarization speed: 0.1 V/s; polarization range: $-0.5 \div 0.8$ V; temperature: 25°C

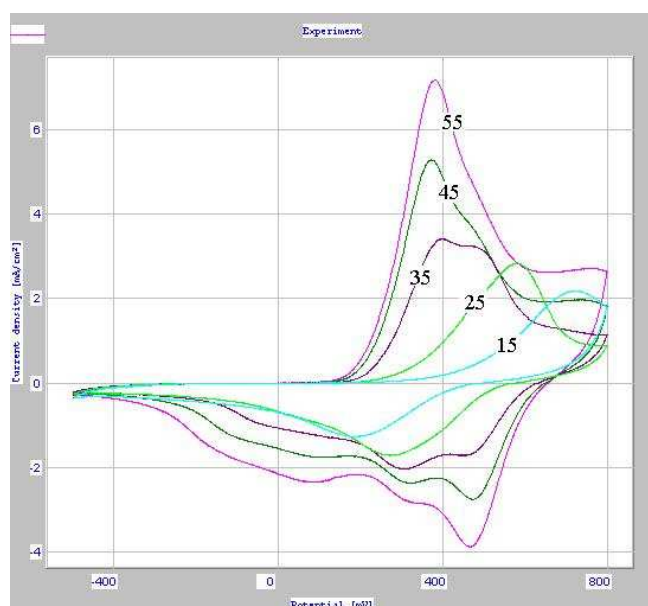


Figure 5. The fifth cycle of every set recorded on the Ni electrode during PANI deposition from the 0.04M aniline in 0.1M H₂SO₄ solution; polarization speed: 0.1 V/s; polarization range: $-0.5 \div 0.8$ V; temperature: 25°C

At cycles 29 and 30 the initiation of a division of both the anodic as well as the cathodic peak is observed. Judging by the shape of the newly formed peaks it can be considered that these are also due to a reversible process which takes place next to the already attributed one.

A continuous increase in the number of cycles – from 30 to 40 and then to 50 – shows a faster increase of the newly formed anodic peak at an approximately 350 mV potential in comparison to the old one, at approximately 500 mV. The shape of these peaks continuously shows the involvement of reversible processes.

There are two more new peaks on the cathodic branch – at potentials of ~ 100 mV and ~ -150 mV, respectively – that have no correspondent on the anodic branch and were attributed to irreversible reduction processes, probably due to the formation of some degradation by-products on the electrode.

In order to better point out the peak current increase, figure 4 was simplified by representing the 5th cycle from every set of 10 cycles each, thus obtaining figure 5. This way it's easier to observe the initial peaks, their evolution, the appearance of new peaks, their evolution etc.

In these preliminary studies the processes taking place on the electrode were also present after an increase in aniline concentration. The voltammograms shown in figure 6 were obtained using the Ni electrode, an electrolyte solution with 0.08M aniline in 0.1M H₂SO₄, a polarization speed of 0.1V/s and the extended polarization interval.

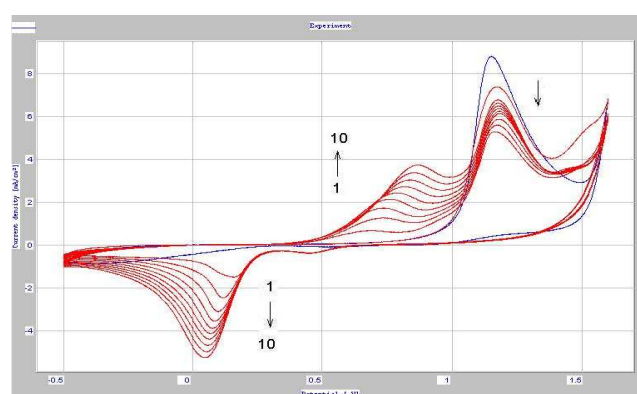


Figure 6. Cyclic voltammograms obtained on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution (red); the second cycle of the baseline (blue); polarization speed: 0.1V/s; polarization interval: $-0.5 \div 1.6$ V; temperature: 25°C

By taking into account the first 10 cycles recorded under these new conditions, it can be observed that the shape of the voltammograms is the same as the one from figure 3.

The peaks appear at the same potentials, their evolution is the same and the peak intensity is higher – 3.9 mA/cm² as compared to 2 mA/cm² at 0.04M aniline concentration, at the anodic peak present at a 0.7 mV potential, cycle 10.

The cyclic voltammograms shown in figures 7 and 8 were obtained, after the first 10 cycles, by restricting the polarization interval.

Increasing the number of cycles – between 10 and 20 – peak potential evolution changes again, the same way it did at a 0.04M aniline concentration in the electrolyte solution. Unlike the peaks observed in figure 4, peak division starts from the 16th cycle and thus, a new anodic peak appears at a 430 mV potential next to the 550 mV one. The similar division of the associated cathodic peak leads to the conclusion that the ionic species involved are the components of a reversible process.

The increase of the newly formed anodic peak starting from the 430 mV potential is more emphatic than that of the previous anodic peak. It's tendency towards more positive values is also more emphatic and it even covers the

initial anodic peak (basically the old peak can no longer be seen on the last voltammograms – starting with the 40th cycle).

After 60 cycles the peak potential for this process reaches 550 mV and the peak current 18 mA/cm².

The associated cathodic peak shows a similar evolution – it divides at the same time as the anodic one. The intensity of the newly formed peak increases but not as much as that of the anodic peak (previously mentioned). The association between the two new peaks – anodic and cathodic – constitutes strong evidence for a new reversible process present in the polyaniline film.

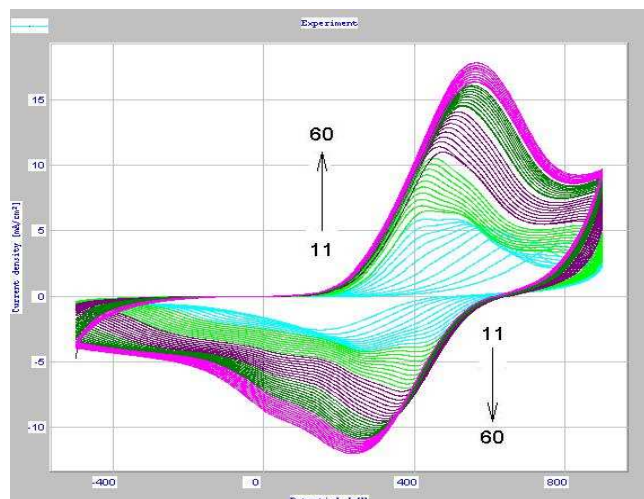


Figure 7. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution; polarization speed: 0.1 V/s; polarization range: -0.5 ÷ 0.9V; temperature: 25°C

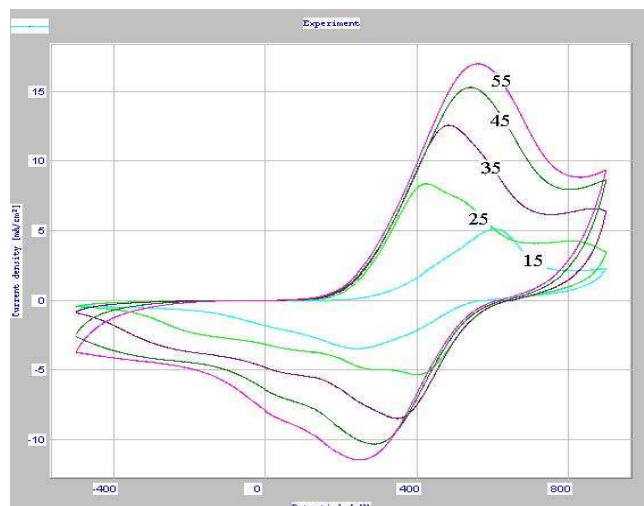


Figure 8. The fifth cycle of every set recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution; polarization speed: 0.1V/s; polarization range:- 0.5 ÷ 0.9V; temperature:25°C

Figure 8 was obtained by removing all voltammograms from figure 7 except the 5th cycle from each set of 10 cycles and it better points out the evolution process previously discussed. These voltammograms show that apart from the peaks previously analyzed there are two

new cathodic peaks, rather poorly defined in the potential range 400 ÷ -100 mV. These peaks have no correspondent on the anodic branch.

A comparison between the recorded voltammograms (cycles 14 from figures 4 and 7) during polyaniline film deposition from two solutions – a 0.04M aniline in 0.1M H₂SO₄ solution (curve 1) and a 0.08M aniline in 0.1M H₂SO₄ solution (curve 2) – is shown in figure 9.

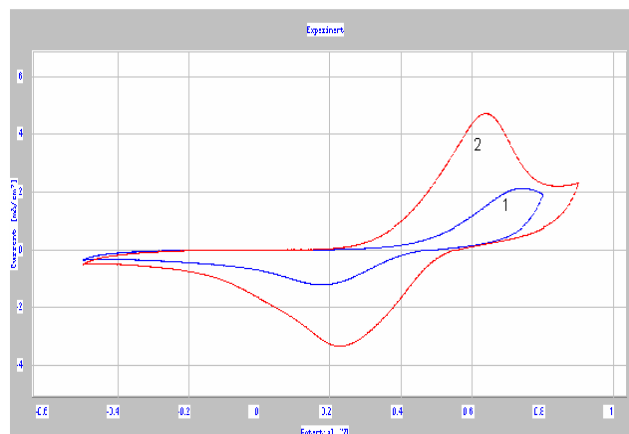


Figure 9. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from two solutions: 1) 0.04M aniline in 0.1M H₂SO₄ solution; 2) 0.08 M aniline in 0.1M H₂SO₄ solution; cycles 14; polarization speed: 0.1 V/s; temperature: 25°C

The observed peak intensities (anodic and cathodic) are significantly higher when the aniline concentration is also higher. The observed processes are reversible.

The voltammograms shown in figures 10 – 13 were recorded after increasing the concentration of the electrolyte support – from 0.1 to 0.5M H₂SO₄.

Figure 10 shows voltammograms recorded on the Ni electrode, over an extended potential range. The baseline (blue) shows just one oxidation process starting before oxygen release, at the ~ 1.1 V potential. In the presence of aniline, two anodic peaks can be observed – one just after the 0.2 V potential and the other approximately at the 0.5 V potential – as well as a cathodic one around 0.35 V. The intense anodic peak present from 1.1 V also appears in the absence of aniline.

Figure 11 shows the voltammograms recorded during PANI deposition from the 0.04M aniline in 0.5M H₂SO₄ solution, over a restricted potential range.

By restricting the maximum potential to 1 V the peaks become more visible. Thus, 3 peaks on the anodic branch become better defined by increasing the number of cycles. The peak observed at the 0.35 V potential has a high intensity, strongly emphasized due to an increase in the number of cycles. The other two anodic peaks remain rather small and can be seen at a 0.5 V potential and a 0.85 V potential, respectively. It's probable that the first anodic peak is associated with aniline film formation, most likely in emeraldine salt form (current – conducting form).

There are also 3 peaks on the cathodic branch – at potentials of 0.11, 0.4 and 0.55 V.

It's probable that the corresponding processes of these peak pairs are reversible, especially the last two.

Concerning the first peak pair, there is a visible disproportion between anodic and cathodic peak intensities (anodic peak intensity is very high). The associated process has a small degree of reversibility. The possibility of a strong adsorption at the 0.35 V potential cannot be excluded.

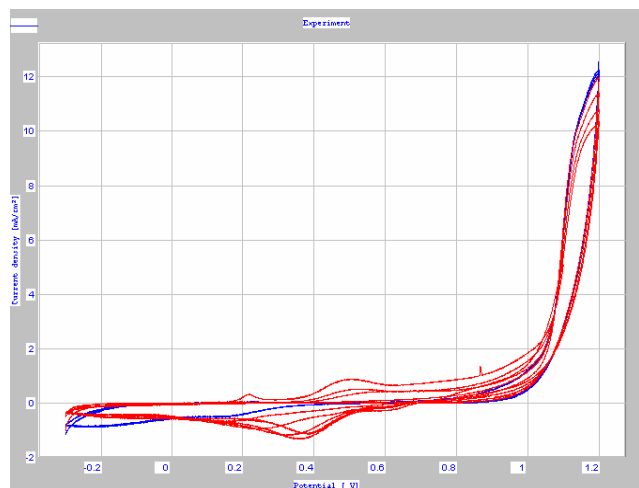


Figure 10. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.04M aniline in 0.5M H₂SO₄ solution; polarization speed: 0.1 V/s; extended potential range: $-0.3 \div 1.3$ V; temperature: 25°C

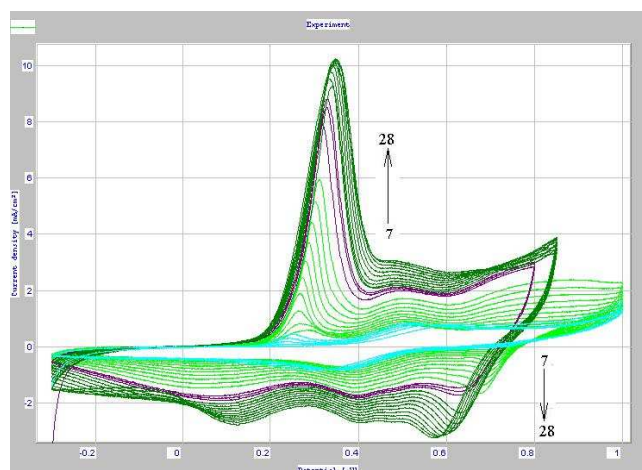


Figure 11. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.04M aniline in 0.5M H₂SO₄ solution; polarization speed: 0.1 V/s; restricted potential range: $-0.3 \div 1.0$ V; temperature: 25°C

The next figures show cyclic voltammograms recorded during PANI film deposition from 0.08M aniline in 0.5M H₂SO₄ solution. Initially a large polarization range was used. This way the polymerization reaction on the surface of the anode was initiated (figure 12). This process was followed by film generation on a restricted polarization range (figure 13).

It can be observed that starting from the 5th cycle there are 3 well defined anodic peaks as well as 3 cathodic ones. These peaks increase with the number of cycles.

Reducing the limit of the anodic potential to 0.8 V emphasizes the relevant peaks and protects the polyaniline film from possible degradation at high potentials.

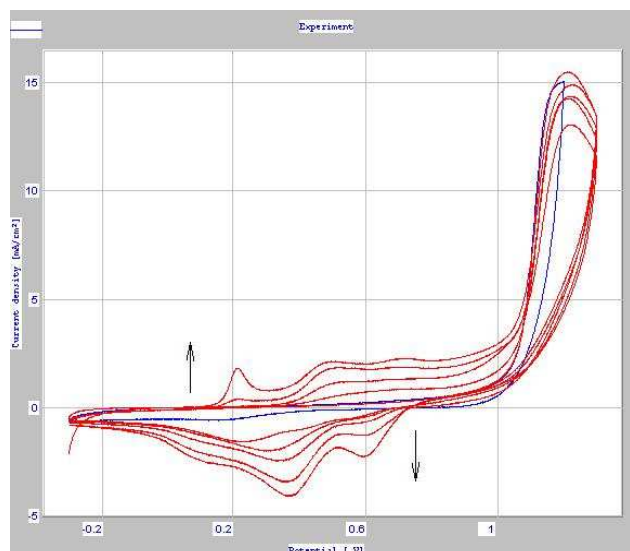


Figure 12. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.5M H₂SO₄ solution (red); the second cycle of the baseline (blue); polarization speed: 0.1 V/s; extended potential range: $-0.3 \div 1.3$ V; temperature: 25°C

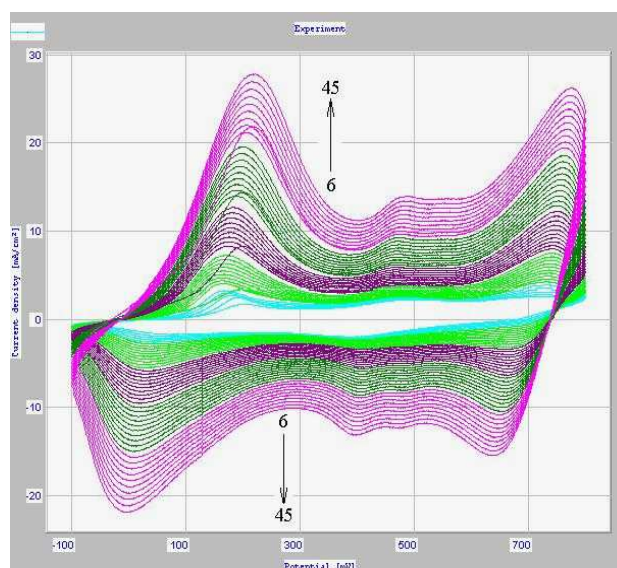


Figure 13. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.5M H₂SO₄ solution; polarization speed: 0.1 V/s; restricted potential range: $-0.3 \div 0.8$ V; temperature: 25°C

On the restricted interval 4 anodic peaks can be observed – at 0.21V, at 0.47V, at 0.55V (poorly defined but still present) and at 0.8 V – as well as 4 cathodic ones – at 0V, at 0.40 V, at 0.45 V and at 0.65V. The four peak pairs – that keep getting better defined as more cycles are added – are associated with reversible processes.

Compared with the peaks in figure 11, these ones have a higher intensity and are much better defined. The associated processes are almost entirely reversible. It is clear that the processes appear and develop as the number of cycles increases by becoming better defined and more intense.

Figure 14 shows the 40th cycle from the voltammograms recorded during polyaniline film deposition from two electrolyte solutions – a 0.04M aniline in 0.5M H₂SO₄ solution (curve 1) and a 0.08M aniline in 0.5M H₂SO₄ solution (curve 2). Even though the shape of the voltammograms is basically the same – the same anodic and cathodic peaks can be observed – the intensity of the peaks is considerably higher when the aniline concentration is also higher.

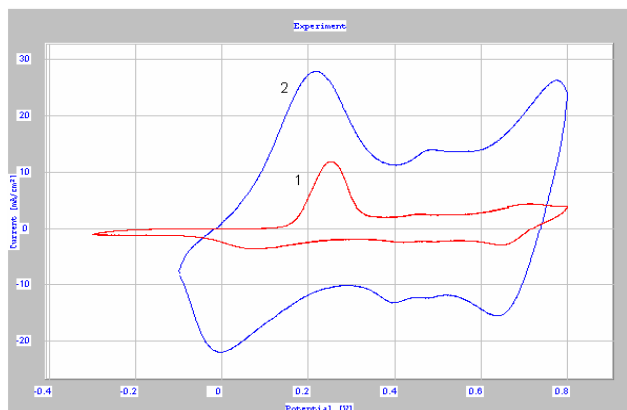


Figure 14. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from two solutions: 1) 0.04M aniline in 0.5M H₂SO₄ solution; 2) 0.08M aniline in 0.5M H₂SO₄ solution; cycles 40; polarization speed: 0.1 V/s; temperature: 25°C.

The electrode processes don't change, but are clearly favored by a higher aniline concentration in the electrolyte.

A comparison between the 20th cycle of the voltammograms recorded during polyaniline film deposition from two solutions with the same aniline concentration but with different H₂SO₄ concentrations – 0.1M (curve 1) and 0.5M (curve 2), respectively – is shown in figure 15.

There are significant differences between the recorded voltammograms. If the first cycle shows one peak pair – one anodic peak at 0.7 V and one cathodic peak at 0.25 V – associated with a reversible process, the second cycle shows three pairs – three anodic peaks and three cathodic peaks at different potentials from those present on the first cycle.

The peak aspect is also different – the first peak, from approximately the 0.3 V potential is very sharp and has an intensity of about four times higher than the other two. The corresponding cathodic peak is very small which means the associated process is basically irreversible. For anodic polarization the interference of an adsorption process is not excluded. The other two peak pairs – from the more positive potentials – correspond to processes much closer to full reversibility.

It seems that by increasing the H₂SO₄ concentration in the electrolyte solution, the polyaniline film formation mechanism changes significantly. This change might be due to a higher degree of proton involvement.

Also, at an aniline concentration of 0.08M (cycle 40) the aspect of the voltammograms is completely different (figure 16). At a 0.1M H₂SO₄ concentration there is still a single observable peak pair, specific to a reversible process.

At potentials lower than 0.1 V two small waves can be observed that don't have any correspondent on the anodic branch – they are probably irreversible reductions.

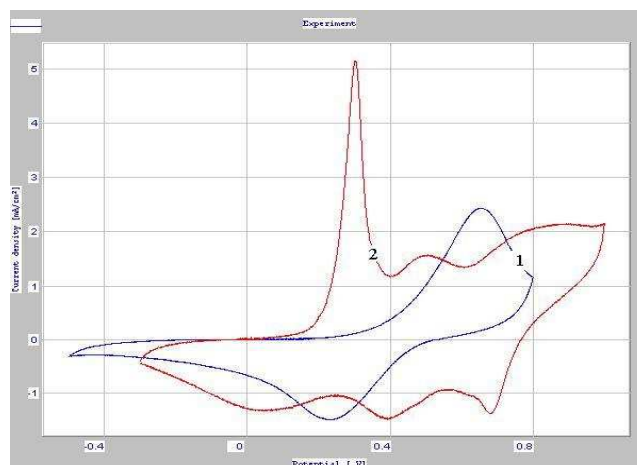


Figure 15. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from two solutions: 1) 0.04M aniline in 0.1M H₂SO₄ solution; 2) 0.04M aniline in 0.5M H₂SO₄ solution; cycles 20; polarization speed: 0.1 V/s; temperature: 25°C.

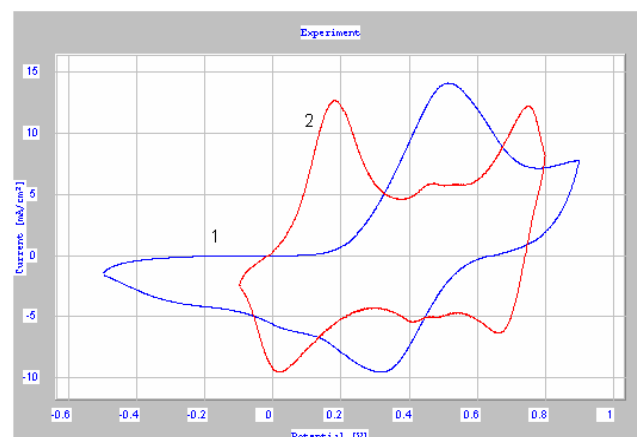


Figure 16. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from two solutions: 1) 0.08M aniline in 0.1M H₂SO₄ solution; 2) 0.08M aniline in 0.5M H₂SO₄ solution; cycles 40; polarization speed: 0.1 V/s; temperature: 25°C.

Increasing the H₂SO₄ concentration to 0.5M, leads again to the formation of four peak pairs associated with reversible processes. The intensity differences seen in figure 15 are no longer present.

It is clear that by increasing H₂SO₄ concentration, aniline oxidation – the first anodic peak – takes place at more negative potentials thus favoring emeraldine formation. Despite all of this, the color of the film formed on the anode is white green, specific to emeraldine.

It's probable that at higher aniline concentrations in the electrolyte solution the effect given by an increase in H₂SO₄ concentration is no longer as strong as before and aniline protonation is quicker.

Figures 17 and 18 show the temperature effect on the recorded voltammograms.

The blue voltammogram from figure 17 was recorded on the Ni electrode at a temperature of 45°C in the absence

of aniline. In the presence of aniline, by increasing the number of cycles, several anodic and cathodic peaks appear and grow at potentials lower than 1V. Three anodic peaks – at potentials of 0.3V, 0.45V and 0.85V – and two cathodic ones – at 0.37V and 0.15V – can be observed. All these peaks increase with the number of cycles.

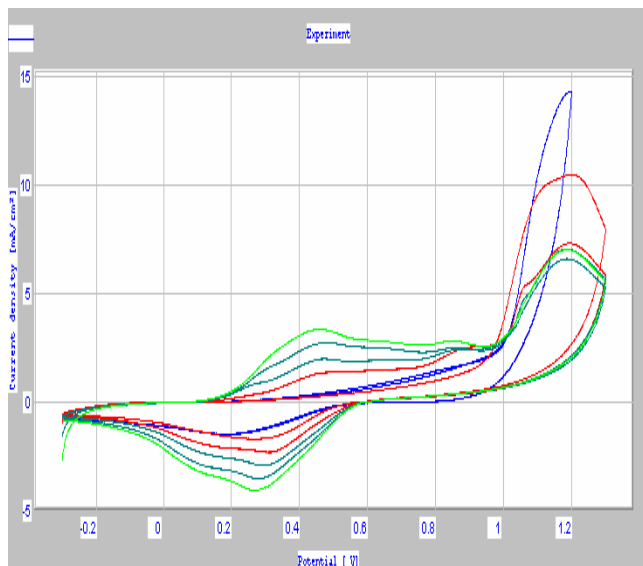


Figure 17. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution; first 5 cycles; the second cycle of the baseline (blue); polarization speed: 0.1 V/s; polarization range: $-0.3 \div 1.3$ V; temperature: 45°C

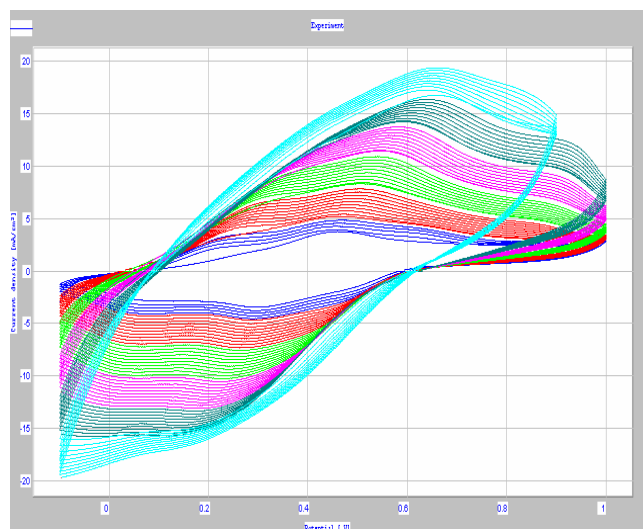


Figure 18. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution; cycles 5 - 60; polarization speed: 0.1 V/s; polarization range: $-0.3 \div 1$ V; temperature: 45°C.

By increasing the number of cycles all anodic peaks tend toward more positive potentials while cathodic ones tend toward more negative ones.

Figure 19 shows the 44th cycle from the voltammograms recorded during polyaniline film deposition at temperatures of 25 and 45°C, respectively. At 25°C, just one anodic peak and three cathodic ones – associated with one reversible process and two irreversible

cathodic ones – can be observed. At 45°C, three anodic peaks – one at a potential similar to that of the peak obtained at 25°C – and two cathodic peaks can be observed.

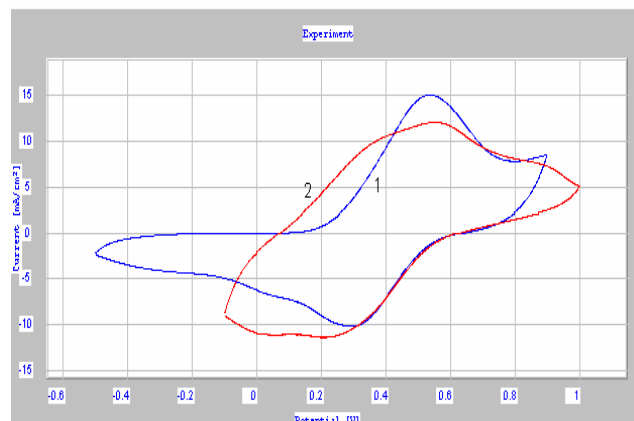


Figure 19. Cyclic voltammograms recorded on the Ni electrode during PANI deposition from the 0.08M aniline in 0.1M H₂SO₄ solution; cycles 44; polarization speed: 0.1 V/s; temperatures: 1) 25°C; 2) 45°C.

The deposition on the Ni electrode of a polymer layer was observed during electrochemical oxidation. The color of this layer alternatively changes from white green to blue depending on the value of the electrochemical potential (figure 20). The first deposited layers (after the first cycles) are white green. As the number of cycles increases (and implicitly that of the formed polyaniline layers) the color switches to dark green and at a high potential value it becomes blue. During cathodic polarization, down to the 0V potential and even to -400 mV, the film color turns back to green.



Figure 20. PANI films deposited on the Ni electrode

4. Conclusion

The behavior of the Ni electrode in H₂SO₄ solutions with aniline content was investigated through cyclic voltammetry.

The first cycles were recorded on a large potential range ($-0.5 \div +1.6$ V).

When using the 0.04M aniline in 0.1M H₂SO₄ solution, at a temperature of 25°C, polyaniline formation takes place at the 0.7V potential. The recorded peak corresponds to aniline oxidation (anilinium anion formation).

By restricting the polarization interval to $-0.5 \div 0.8$ V and adding 50 more cycles the degradation probability of the polyaniline film formed on the anode was reduced.

This way the thickness of the polyaniline film was increased with maximum efficiency only in emeraldine form – without degradation by-products. The color of the

film is white green, same as the one obtained in 0.5M H₂SO₄. It seems that at the cycles 29 – 30 a division of both the anodic and cathodic peaks is initiated.

Increasing the aniline concentration in the electrolyte solution leads to a significant increase in peak intensity for both anodic and cathodic ones.

The effect of the electrolyte support was also analyzed by increasing H₂SO₄ concentration from 0.1 to 0.5M. It seems that by increasing H₂SO₄ concentration in the electrolyte the polyaniline film formation mechanism changes significantly. This change might be due to proton concentration.

Temperature increase from 25 to 45°C also had an important effect on the recorded voltammograms. At 45°C there are two more anodic processes that probably involve intermediaries in the aniline polymerization process.

The adherent polyaniline film formed on the Ni electrode alternatively changes from white green to blue depending on the value of the electrochemical potential.

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