

Effect of PANi electrodeposition methods on copper substrate

Efecto del método de electrodeposición de PANi sobre sustrato de cobre

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Abstract

To assess the effect of different electrochemical techniques in the synthesis of polyaniline (PANi) on copper substrates, this paper presents a comparison between cyclic voltammetry and chronoamperometry. For each technique, four synthesis processes were conducted with different potentials using a three-electrode electrochemical set-up with a neutral electrolyte (pH=7). According to the comparison, the oxidation potential sweep associated to cyclic voltammetry results in the synthesis of PANi in three different oxidation states. As synthesis by this technique results in a non-homogeneous layer conformed by different species of PANi, the characteristics of the film are difficult to determine as all three species have different electric, optic and morphologic attributes. On the other hand, selecting an appropriate oxidation potential, chronoamperometry results in the synthesis of a homogeneous layer of PANi. The use of one unique oxidation potential results in a stable process that synthesizes a homogeneous layer of pernigraniline, a stable oxidation state of PANi.

Synthesis; Substrates; Morphologic; Electrolyte; Oxidation; Electrochemical; Comparison

Resumen

Para evaluar el efecto de las diferentes técnicas electroquímicas para la síntesis de polianilina (PANi) sobre sustratos de cobre, en este trabajo se presenta una comparación entre las técnicas de voltamperometría cíclica y cronoamperometría. Para cada técnica, se realizaron cuatro procesos de síntesis con diferentes potenciales utilizando una celda electroquímica de tres electrodos con un electrolito neutro (pH=7). De acuerdo con la comparación, el barrido de potencial de oxidación asociado a la voltamperometría cíclica resulta en la síntesis de PANi en tres estados de oxidación diferentes. Al ser una capa no homogénea conformada por diferentes especies de PANi, las características de la película son difíciles de determinar debido a que las tres especies tienen diferentes atributos eléctricos, ópticos y morfológicos. Por su parte, eligiendo un potencial apropiado, la síntesis por cronoamperometría resulta en una capa homogénea de PANi; un único potencial de oxidación permite un proceso estable que sintetiza una capa homogénea de permigranilina, un estado de oxidación estable de la PANi.

Síntesis; Sustratos; Morfológico; Electrolito; Oxidación; Electroquímica; Comparación

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Introduction

Electrochemical synthesis of polymer films is a reliable alternative to conventional toxic corrosion inhibitors for metallic substrates (Ayalew et al., 2023; Deshpande et al., 2014; Özyilmaz et al., 2005). Coating the susceptible surface with a polymer layer, which is after enriched with chemical corrosion inhibitors, immobilizes the chemical compounds into the polymer layer minimizing their interaction with the environment (Hasanov & Bilgiç, 2009; Shabani-Nooshabadi et al., 2014; Wang et al., 2023). However, the selected process to synthesize the polymer film can tamper the benefits of this technique; it can comprise the use of hard chemicals or thermal treatments, which are harmful to the environment (Bilurbina Alter et al., 2003; Hossain et al., 2023). Synthesizing polymer-based protective layers by electrochemical process results in a sustainable effective approach to protect metals from corrosion (Zhao et al., 2023). Although several electro-chemical deposition methods for polymer coatings on conductive substrates have been reported in the literature (Aljawrneh et al., 2023; Bolaños Ch & Alvarez, 2018; Gutiérrez Pineda et al., 2016; Sebaa et al., 2013; Upreti et al., 2023), a comparison of the most common approaches is conducted in this paper: a comparison between cyclic voltammetry (CVA) and chronoamperometry (CA).

To compare both techniques, polyaniline (PANi) is synthesized on copper using a three-electrode cell with a sodium oxalate solution as electrolyte. The neutral electrolyte eliminates possible interferences due to hydrogen potential, allowing only the performance of the synthesis methods to be compared. The resulting coatings were optically characterized by bare eye inspection as well as under optic microscopy to assess homogeneity. According to the analysis, the best results were achieved under chronoamperometry using a cell potential (pE) above 1100 mV. If pE falls below this value, the aniline cannot oxidize completely in one stable specie, leading to a non-homogeneous coating. As cyclic volt-ammetry requires a repetitive sweep of pE within a selected window, the resulting coating shows different species of PANi even when the potential window was carefully selected according to the Pourbaix (pE/pH) diagrams (González Fernández, 1989; Hernández, 2012; Pedefferri, 2018).

If the oxidation potential is enough, the PANi synthesizes in all three oxidation states possible, leading to the worst results in the comparison.

Experimental details

The substrate for every case in this comparison was a copper plate with a size of 10 x 20 millimeters. To obtain these substrates, a copper sheet was sanded with a 1500 grit sandpaper to eliminate any defects on the surface. Once sanded, the copper sheet was cut into pieces of the desired size and then washed using a deionized water and degreaser mixture in a ratio of 1:1 through an ultrasonic cleaner model 8891 from Cole-Parmer. The sections were after rinsed using deionized water using the same ultrasonic cleaner and then dried by evaporation at room temperature under a bell jar to prevent any further contamination.

The electrolyte for every synthesis was a sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) at a concentration of 0.2 M. The solution was prepared adding 6.7 grams of sodium oxalate with a purity of 99.5% from Fagalab to a volumetric flask, adding deionized water to reach a volume of 250 milliliters. The solution was agitated manually and then mixed using an ultrasonic cleaner to assure a homogeneous result. As monomer, 0.3 milliliters of aniline with a purity of 99% ($\text{C}_6\text{H}_5\text{NH}_2$ A.C.S., Fermont) were added to the cell along with 19.7 milliliters of the sodium oxalate electrolyte for a total of 20 milliliters for each synthesis.

The electrochemical cell for the synthesis processes was a 3-electrode cell. The copper substrate was the working electrode. The reference electrode was an Ag/AgCl electrode model BASMF2056 from Sigma-Aldrich. A piece of stainless steel performed as counterelectrode. The set up used in the synthesis was a potentiostat model 302 from Autolab controlled by computer. All experiments were carried out in an open cell at room temperature and conditions.

Results and Discussions

The comparison between CA and CVA comprises two series of four synthesis. For the case of CVA, the experiments comprise four synthesis processes, each one consisting of 20 redox cycles performed with window potentials of: 300-900 mV, 300-1000 mV, 300-1100 mV and 300-1200 mV respectively against Ag/AgCl. The redox potentials were carefully selected according to the corresponding Pourbaix diagram. The sweep velocity for the potential was 20 mV/s. Table 1 shows the parameters used for the four synthesis using CVA.

Experiment	Reduction Potential vs Ag/AgCl	Oxidation Potential vs Ag/AgCl	Cycles	Voltage Sweep Rate
CVA-A	300 mV	900 mV	20	20 mV/s
CVA-B	300 mV	1000 mV	20	20 mV/s
CVA-C	300 mV	1100 mV	20	20 mV/s
CVA-D	300 mV	1200 mV	20	20 mV/s

Table 1 Parameters for the synthesis of PANi using Cyclic Voltammetry.

Experiment	Fixed Potential vs Ag/AgCl	Time	Sampling interval
CA-A	900 mV	300 s	0.5 s
CA-B	1000 mV	300 s	0.5 s
CA-C	1100 mV	300 s	0.5 s
CA-D	1200 mV	300 s	0.5 s

Table 2 Parameters for the synthesis of PANi using Chronoamperometry.

The experiments to assess CA comprise four synthesis processes at a fixed potential of 900 mV, 1000 mV, 1100 mV and 1200 mV respectively against Ag/AgCl, for a period of time of 300 seconds. Table 2 shows the parameters used for the synthesis using Chronoamperometry.

Synthesis diagrams

The electrodeposition of PANi was first carried out through CVA. Figure 1 shows the voltammogram of the 10th cycle for all the cases. The voltammogram shows in detail the electrochemical response of the system, providing information about the different processes involved in the synthesis.

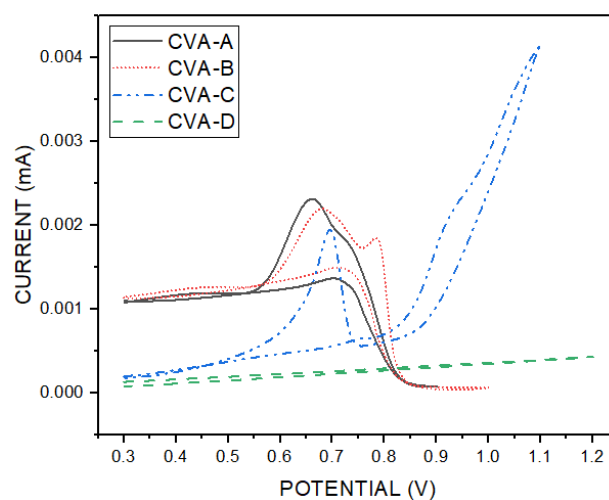


Figure 1 Cyclic voltammogram of the 10th cycle for all four cases

In all cyclic voltammograms, an initial anodic region is observed as the potential increases from 0.3 V. This region is related to the oxidation of aniline and the formation of cationic radicals, which are essential precursors for the polymerization and formation of the PANi film. As the potential increases, the current also increases, indicating a greater number of electroactive species present in the solution. When pE increases to higher regions, a change in the direction of the current occur indicating the beginning of the cathodic region. In this region, the previously generated cationic radicals reduces, building the polymeric structure on the copper substrate.

For CVA-A, current reverses from 650 mV to 900 mV, establishing the cathodic region. Unfortunately, the potential window is too narrow, leading to the redox process to occur prior to the oxidation potential of another PANi species. Because of this, PANi can only synthesize as leucoemeraldine. Same situation occur for the case of CVA-B. The increment in pE only shifts the cathodic region between 675 mV and 1000 mV. This oxidation potential is enough to oxidize pernigraniline, however, the time the cell stays at that specific potential is not enough for pernigraniline to synthesize. As result, pernigraniline started to synthesize, but its growth rate is negligible compared to leucoemeraldine.

For CVA-C, signals shows an initial anodic region related to the oxidation of the monomer. When pE rises above 1000 mV, signal reveals a significant formation of oxidative species of aniline, such as emeraldine and pernigraniline. These cell conditions persists enough time to allow the synthesis of these electroactive species on the substrate.

For CVA-D, it should be noted that there are no characteristic signals for PANi. The cell's performance due to the redox conditions causes aniline to be completely synthesized much before the tenth cycle. To validate this assumption, Figure 2 shows the voltammogram for the whole 20 cycles for CVA-D. The first cycle shows a cathodic peak at about 725 mV, which correspond to the oxidation of aniline. After this peak, a decrement in current indicates a reduction of the radicals previously generated. At 0.8 V, the current increases again until pE reaches 1200 mV, indicating the continuation of oxidative events that results in the formation of electroactive species.

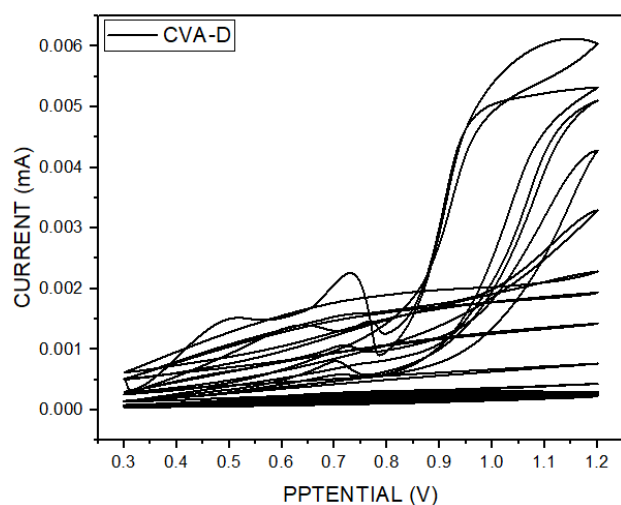


Figure 2 Cyclic voltammogram for CVA-D

For the synthesis of PANi through CA, Figure 3 shows the chronoamperograms for the four cases described in Table 2.

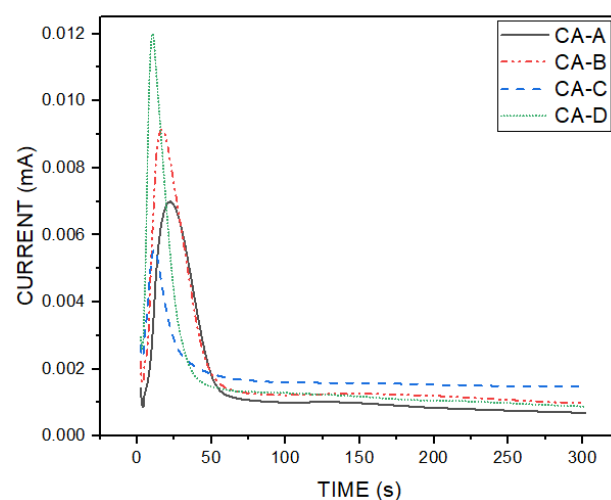


Figure 3 Chronoamperogram from the synthesis of PANi for all cases

Chronoamperograms describes the reaction rate and polymer formation over time at a fixed potential. For all cases, an initial current indicates aniline oxidation and cationic radical formation, which are the essential precursors for the synthesis. As time progresses, this current gradually decreases as the formation of cationic radicals diminishes, indicating the end of the synthesis. Graphs in the comparison shows a higher current for CA-D, suggesting a more efficient and faster generation of cationic radicals. As expected, efficiency and velocity decreases as pE decreases.

Surface Analysis

To compare the results obtained by both techniques, CVA and CA, all the coatings were optically analyzed. Initially, samples were bare eye visually inspected, also, were inspected under an optic microscope at 4X.

Table 3 shows the results for the case of cyclic voltammetry. As shown for CVA-A, the coating have large portions of the substrate uncovered. This lack of coverage is due to the redox potential is not enough to oxidize the monomer into a homogeneous film. When the oxidation potential increases to 1000 mV (CVA-B) coverage improves, but not enough to synthesize a homogeneous film; even when all the substrate is covered, film is thin enough to expose the substrate. According to the microscopy images, CVA-A and CVA-B films synthesizes as leucoemeraldine.

Increasing the oxidation potential to 1100 mV (CVA-C) improve coverage and coating thickness. However, the PANi film synthetizes into different oxidation states. From the corresponding microscopy images, can be identified: white portions corresponding to leucoemeraldine; few green portions corresponding to emeraldine and large blackish areas corresponding to pernigraniline. The non-homogeneity of the film entails penicius consequences. As known, every oxidation state has very different morphological, structural, electric, optic characteristics, therefore, the resulting film will have undetermined characteristics even if it were possible to quantify how much of the film correspond to each oxidation state.






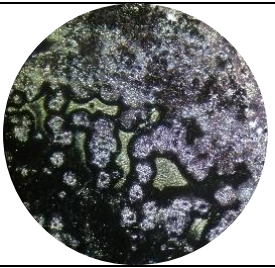

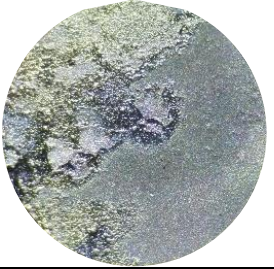
Visual Inspection	Optic Microscopy
CVA-A 	
CVA-B 	
CVA-C 	
CVA-D 	

Table 3 Analysis of the PANi coatings synthetized by cyclic voltammetry.

The homogeneity of the film seems to improve as pE increases to 1200 mV (CVS-D). Through bare eye inspection, the substrate seems fully covered by a blackish film corresponding to pernigraniline. However, by microscopy, all the three oxidation states of PANi were identified.


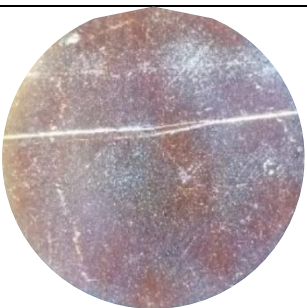

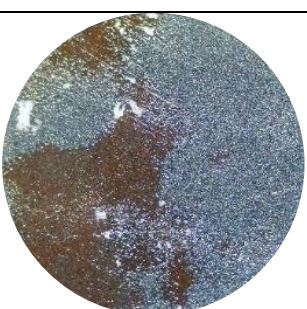
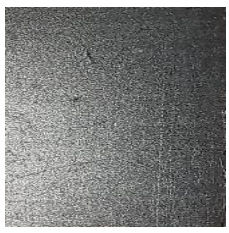
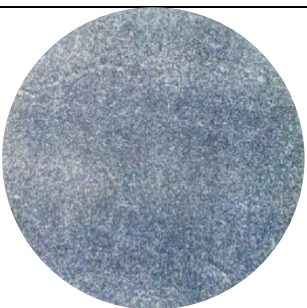


Visual Inspection	Optic Microscopy
CA-A 	
CA-B 	
CA-C 	
CA-D 	

Table 4 Analysis of the PANi coatings synthetized by chronoamperometry

Table 4 shows the results corresponding to CA under the conditions described before. For the case of CA-A the coverage seems enough to cover the whole substrate, but the resulting film is as thin that the substrate remains visible. As in CVA-A, the oxidation potential is not enough to properly oxidize the monomer into a thicker film. As the oxidation potential increases to 1000 mV, the thickness of the film increases. CA-B seems to synthesize a thick homogeneous pernigraniline coating. However, under closer inspection, even when the microscopy images confirm the presence of only pernigraniline, it can be identified sections were permigraniline was synthesized as salt, the protonated form of pernigraniline (Ji et al., 2020), while other sections were synthesized as base, the ladder form of PANi (Macdiarmid et al., 1991). These forms of pernigraniline differ specially in their optic properties, as appreciated in the visual inspection of coating CA-B in Table 4.

The last two cases show a homogeneous coating where the substrate is completely covered with a thick coat of pernigraniline in its base form. Having only one species of PANi assures the film to have known properties useful for the user purposes.

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Conclusions

In this work, PANi was synthesized on a copper substrate using two different electrochemical methods: Cyclic Voltammetry and Chronoamperometry. By setting an appropriate oxidation potential (above 1100 mV), the result is a thick film of PANi that entirely covers the substrate. However, the potential sweep inherent to cyclic voltammetry results in different species to be synthesized in the process. Using one stable sufficient potential (above 1100 mV) as done with chronoamperometry, results in a homogeneous film where only one species of PANi is synthesized.

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