

Morphological and electrochemical characterisation of graphite electrodes coated with SPANI and Ni-cyclam

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Abstract The preparation of the composite graphite–sulphonated polyaniline (SPANI)–Ni-cyclam was investigated with the purpose of dispersing a catalyst in a conducting matrix that allows a better electronic transfer from the surface of the electrode towards the reaction site. The graphite is a material with a high porosity, big area and cheaper than other materials. The electrochemical and morphological characterisations show that the best conditions for obtaining SPANI over graphite were reached with an anodic limit of 1,000 mV in H₂SO₄. The deposit of the Ni-cyclam over graphite–SPANI in basic medium allows the formation of a spongy and open material, which permits better accessibility to the catalytic sites, showing good catalytic properties. These results illustrate that the importance relays on the morphology and dispersion of the catalyst and not on the amount of catalytic material present in the composite. The electrocatalytical properties Ni-cyclam over graphite–SPANI was studied for the methanol oxidation in basic medium.

Keywords Graphite · Orthanilic acid · Ni-cyclam · Methanol · Copolymer · Electrocatalysis

Introduction

Research on new electrode materials is currently an area of great impact due to the multiple applications of electrodes in different fields, such as the catalysis of electroorganic reactions [1], studies of interfacial electron transfer [2] and the design of electrochemical sensors [3]. Many research groups are dedicated to obtain electrodes with specific features, such as optical, catalytic or enantiomeric properties, etc. [4]. The final objective is to overcome the problems presented by conventional electrode materials, such as slow electron transfer rates, passivation phenomena and the generation of undesirable products, among others.

For most electrode materials, the electrochemical reaction is limited to the catalytic surface. One way of obtaining a better response is to disperse the catalytic species in a matrix that allows efficient charge transfer from the surface of the electrode to the site of the reaction [5].

Conducting polymers may act as such matrix to support catalysts, since they adhere strongly to the electrode surface and possess high conductivity and good durability. Polyaniline (PANI) is characterised by its conductivity at low pH [6], which is achieved by means of oxidative doping in acidic media. The choice of doping agent is very important since it modifies the material's properties. For instance, electrodes modified with PANI films doped with camphor-sulphonic acid have extended their electroactivity in neutral and alkaline media [7]. On the other hand, in order to maintain the system's conductivity at neutral and alkaline pH, the formation of PANI has been proposed with aniline monomers replaced with (–SO₃H) groups to act as a source of

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protons, thus, assuring that the polymer's conductivity does not depend on the pH of the medium [8]. Another example is that of the synthesis of self-doped PANI films from a mixture of 3-amino-benzyl-sulfonic acid or metanilic acid with aniline [9–11], which gives rise to sulphonated PANI (SPANI). Although SPANI's conductivity is lower than the one of PANI, the electroactivity of SPANI extends to neutral and alkaline media with increased stability and degradation resistance compared to the film synthesised with other dopant (doping species).

Alternatively, many species have been used as co-catalysts with Pt for methanol oxidation, such as phthalocyanines of Co, Fe, Ni, Ru and Sn [12], and other Ni complexes such as Ni(II) 1,4,8,11-tetraazacyclotetradecane (Ni-cyclam) have been reported to be able to form conducting polymeric films on the electrode surface in an alkaline medium, reacting in a similar way to nickel hydroxide electrodes [13]. For instance, several nickel catalysts have been immobilised on polymeric bases. Godínez et al. [14] immobilised Ni-cyclam on a non-conductive matrix of a polyamidoamine dendrimer for the oxidation of methanol at high pH. In our group, it was reported [15] the deposition of this composite on glassy carbon (GC). The result showed good catalytic properties. However, the application in fuel cell is more convenient to find a material like graphite which has a higher porosity, bigger area and is cheaper than GC. Hence, it is interesting to prepare composites based on a copolymer (SPANI) upon which Ni-cyclam may be deposited on graphite for its possible application in the oxidation of methanol in alkaline medium.

The present work studies the morphological, electrochemical and structural characteristics of sulphonated polyaniline deposits on graphite prepared in different conditions (orphanilic acid/aniline ratios, anodic potentials) in order to find the optimum composite preparation requirements and know the feasibility of graphite as a substrate for this catalytic material. Once these conditions had been defined, the deposition of Ni-cyclam on this matrix was assessed in order for its study in the electrocatalysis of methanol in an alkaline medium.

Experimental

Materials and equipment

All reagents were analytical grade and were used without further purification, except for aniline which was distilled and kept refrigerated. These reagents were 2-amino-benzyl-sulphonic acid, also known as orphanilic acid (Aldrich);

sulphuric acid (Baker 97.2%); the macrocycle 1,4,8,11-tetraazacyclotetradecane (Aldrich); NiCl₂ (Baker, dehydrated); NaOH (Baker); and CH₃OH (TQ). All the solutions were prepared with 18 MΩ deionised water (Millipore–MilliQ system). The Ni-cyclam complex was prepared by mixing the 1,4,8,11-tetraazacyclotetradecane macrocycle with nickel chloride in anhydrous ethanol. The mixture was refluxed for 4 h and slowly cooled up to –4 °C. The precipitate was filtered to dryness, previously washing it with anhydrous ethanol and then with diethyl ether.

All electrochemical experiments were performed in a conventional three-electrode electrolytic cell: using as the working electrode, a graphite bar of 6 mm diameter, in which walls were insulated with Teflon[®] tape to allow only the circular base to come into contact with the solution, along with a platinum wire as counter electrode and a Ag/AgCl/KCl_{sat} as reference electrode, all the electrode potential values are given to this electrode. The working electrode was cut after use in order to renew the surface, polishing it first with abrasive paper and then with soft paper. All the studies were carried out at room temperature, maintaining a nitrogen atmosphere in the solution.

Electrochemical experiments were carried out using a PAR potentiostat, model VerSastat. The polymeric growth was performed by cyclic voltammetry in 0.1 M H₂SO₄ at a potential sweep between –0.2 and 1.3 or 1.0 V and a scanning rate of 50 mV/s for 30 cycles. The considered orphanilic acid/aniline (OA/ANI) ratios were 10:1 (0.1/0.01 M), 20:1(0.2/0.01 M) and 30:1 (0.15/0.005 M). The deposition of Ni-cyclam was performed on the copolymer coating by cyclic voltammetry applying ten potential cycles between 0 and 900 mV at 100 mV/s, using 5 mM solution of Ni-cyclam in 0.1 M NaOH.

Characterisation of the deposits

Micrographs were performed using a Philips XL30 scanning electron microscope coupled to an EDAX DX4i analyser.

Results and discussion

Graphite presents a much greater porosity than GC and other metals like platinum or gold. This represents an advantage over other electrodes, since the material is deposited on a larger active area. So, the electrodeposited materials on this surface will lead to a larger amount of useable active material, e.g. in this case for the catalysis of methanol.

When OA and similar compounds are electrooxidised over graphite, no polymerisation occurs over the surface of

the substrate [15, 16]. The electropolymerisation process is inhibited by the nature of the structure of these compounds, where the sulphonic groups decrease the nucleophilic character and increase steric impediment hindering the formation of long chains. During the polymerisation process, the oxidation rate was slow, and only a small amount of soluble oligomer was formed. These oligomers, once formed, diffuse toward the solution matrix.

The electrodeposition of ANI with different ratios of OA was performed on graphite electrodes in a potential range of -200 to $1,300$ mV/Ag/AgCl. Figure 1 shows the cyclic voltammograms for the obtention of SPANI at OA (0.1 M)/ANI (0.01 M) concentration ratio of 10:1 in 0.1 M H_2SO_4 . Curve (a) corresponds to the first scan potential cycle and curve (b) to scan 30 cycles. In the first scan, it is seen that copolymerisation starts at approximately 780 mV and that the current increases above this potential, while in the return scan, a current loop is observed which indicates a nucleation and growth process characteristic of polymer formation on the electrode. During the return scan, a reduction peak is noted around 400 mV as a consequence of partial reduction of the polymer formed during the oxidation process. After 30 cycles (curve b), two oxidation peaks are seen at potentials of 300 mV (P1) and 700 mV (P2). In the return scan, only one reduction peak is observed at 0 mV (P3). This great shift indicates that the polymer oxidation and reduction process is becoming increasingly irreversible. These processes may be attributed to the well-known leucoemeraldine–emeraldine and emeraldine–

pernigraniline redox processes of the PANI film. Comparing the potential values with those appearing in similar processes on a platinum electrode [17], it can be seen that in the present case, these are of the order of 100 and 300 mV more positive. This behaviour is attributed to the lower conductivity of the graphite used for electrodeposition, which requires higher potentials for these redox processes to take place, as it is also due to the formation of a deposit less conductive than polyaniline [10]. For the GC case [15] the potentials of both processes observed appears at the same potential as in graphite, although in a less apparent fashion. However, peak P2 is in a higher proportion than process represented by P1, which indicates that the polymerisation reaction occurred in a different way. This behaviour may produce a polymeric film with different properties.

After 30 polymerisation cycles the graphite surface is coated with a copolymer layer (anodic limit of 1,300 mV). The morphology of this layer is shown in Fig. 2. Two well-differentiated zones can be seen. The first zone (a) corresponds to a porous and open structure which may be suitable for electrodepositing the Ni-cyclam polymer. The appearance of the second zone (b), associated to a more compact and darker rounded zone, leads us to think that some degradation of the polymer takes place ($E=1,300$ mV) at these points, due mainly to the process of oxygen evolution which over-oxidises the film at certain points. It is worth to mention that this degradation does not occur in the case of GC, which confirms that a different electrochemical behaviour and different properties are obtained for the generated material. For this reason, the anodic limit of polymerisation for graphite was changed to 1,000 mV.

Figure 3 shows the cyclic voltammogram obtained after 30 cycles of potential scanning of the 10:1 (OA/ANI) copolymer at 1,000 mV in 0.1 M H_2SO_4 . Peaks P1 and P2 correspond to the characteristic redox potentials of the two polyaniline oxidation processes mentioned before. Comparing the results obtained for this potential limit with voltammogram of Fig. 1, it can be seen that the peaks are better defined, appearing both reversible systems, which were mentioned previously (differing to what occurs when the anodic limit is increased to values of 1,300 mV), with a uniform current increase and a shift towards more negative values for system P2. This proves that when electrodeposition of the copolymer is performed at anodic potential limit of 1,300 mV, there is a decrease in the redox activity due to a degradation process.

The morphology of the deposit obtained at an anodic limit of 1,000 mV, and can be seen in Fig. 4a (5 μm), shows that the desired spongy porous structure was achieved. Compared with the compact globular structure of polyani-

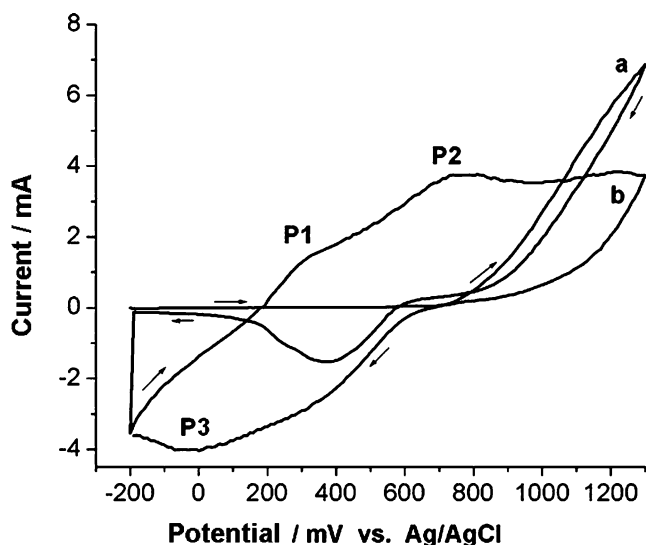


Fig. 1 Cyclic voltammograms on graphite electrode in a solution containing AO/ANI 10:1 mixture solution, scan rate 50 mV/s. **a** First scan and **b** 30th scan

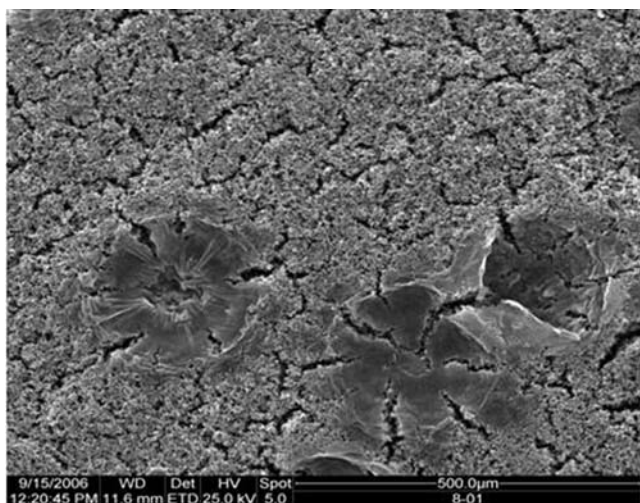


Fig. 2 Scanning electron micrograph of the film electrodeposited from AO/ANI 10:1 in 0.1 M H₂SO₄, anodic limit 1,300 mV at scan rate 50 mV/s

line [18], this porous morphology is due to the sulphonate groups on the orthonilic acid. The presence of these sulphonate groups in the polymeric structure destabilises the polaronic form of PANI, generating repulsive interactions within the structure and causing it to open. In order to observe the surface, the sample was measured at a lower magnification (500 μm ; Fig. 4b). The surface does not present degraded areas as in the case of Fig. 2, being highly homogeneous and coating perfectly the graphite electrode.

On the other hand, the morphology of these copolymers depends greatly on the orthonilic acid/aniline ratio. An increase in the amount of orthonilic acid from 20:1 to 30:1 does not alter the shape of the voltammograms (data not

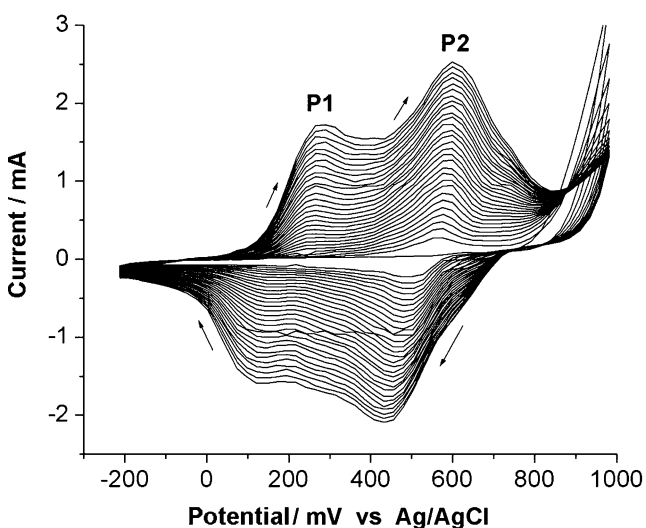


Fig. 3 Cyclic voltammograms of the electrodeposition of SPANI from a AO/ANI 10:1 mixture solution, anodic limit of 1,000 mV at scan rate 50 mV/s

presented) compared to those shown in Fig. 3 (OA/ANI ratio 10:1), since they continue to present the two redox processes mentioned before, although the current intensity is somewhat lower and the definition of the redox processes is poorer. The morphology of these copolymers with high orthonilic acid concentrations is depicted in Fig. 5a (20:1) and b (30:1). As it can be seen in the micrographs, a porous structure does not appear; instead, there is a compact granular morphology which is similar to the morphology of polyaniline. The reason is that at high OA concentrations, the growth is inhibited by the steric impediment of the sulphonic groups mentioned before. Hence, the 10:1 ratio and anodic limit 1,000 mV is the optimum for the porosity, conductivity and morphology of the deposit to be suitable for subsequent use as an insertion matrix.

This 10:1 OA/PANI base composite was used to perform depositions by cyclic voltammetry (10 cycles) of the Ni-cyclam polymer in NaOH 0.1 M. Figure 6 shows the voltammograms obtained after ten potential scanning cycles of the Ni-cyclam deposit on SPANI (Fig. 6a) and on unmodified graphite (Fig. 6b). Two processes appear for

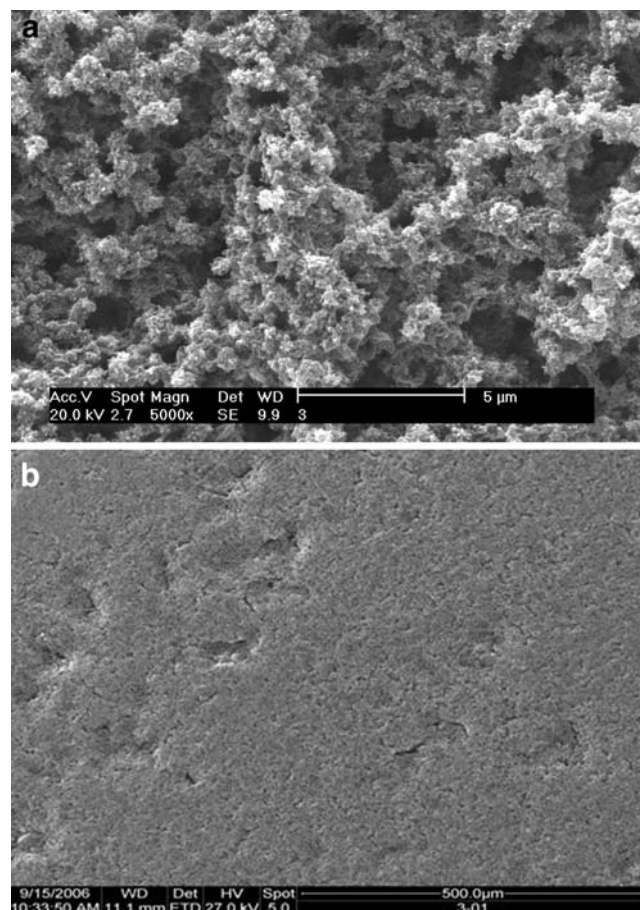


Fig. 4 Scanning electron micrographs show two different magnifications of SPANI's film deposited from AO/ANI 10:1 mixture solution, anodic limit 1,000 mV, **a** 5 μm and **b** 500 μm

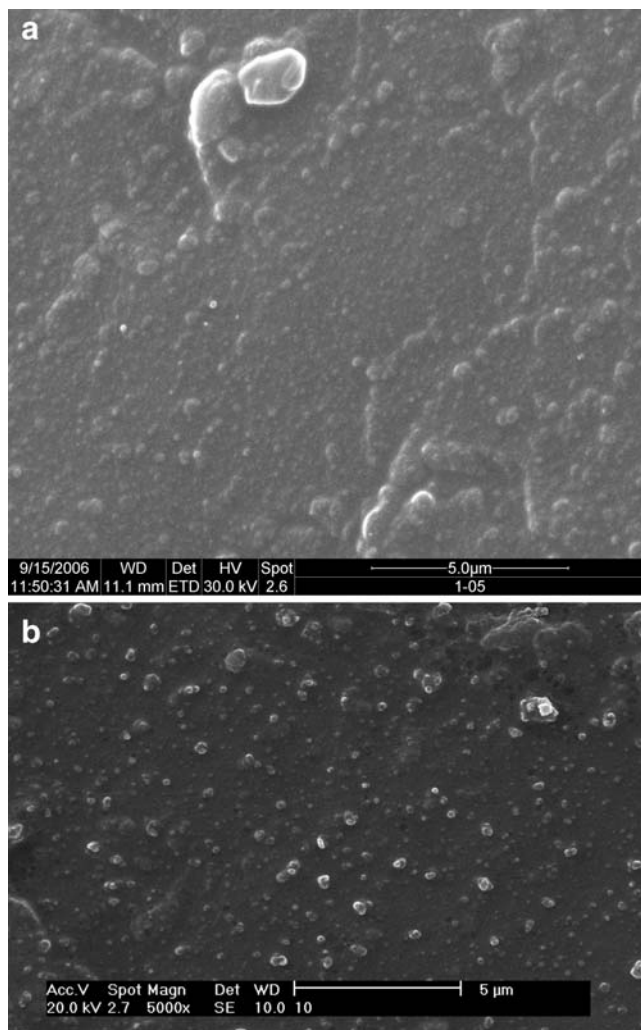


Fig. 5 Scanning electron micrographs of SPANI's films deposited from different concentration ratio **a** AO/ANI 20:1 and **b** AO/ANI 30:1

both electrodes. The first is an irreversible anodic (peak P1) at a potential of about 350 mV attributed to the known adsorption of the complex to the electrode surface. A similar peak has been observed the Ni-cyclam curves at Au electrode during the modification of the electrode surface in strongly alkaline solutions [18]. The second process is observed at potentials of 675 mV for SPANI (peak P2 Fig. 6a) and at 525 mV for graphite (peak P2 Fig. 6b), along with the corresponding redox reduction signal at 350 and 300 mV, respectively, corresponding to the Ni(II)/Ni(III) system [19]. This second process is more irreversible over the SPANI electrode due to its lower conductivity towards the bare graphite electrode. For thicker coatings, the potential of the Ni(II)/Ni(III) system moved towards more positive values, and the peak separation increased with increasing film thickness. It is important to state that these processes are more reversible over other electrodes [15]. This suggests that the rate of

charge transfer is limited by the film thickness and the nature of the substrate.

The amounts of Ni-cyclam over both electrodes were calculated in an approximated way by measuring the area below the voltammetric curve. The amounts obtained were very similar for the two electrodes (graphite and SPANI), where the limit was under 6×10^{-8} mol/cm². In this case, if the mass of Ni-cyclam is practically the same for both electrodes, the catalytic effect towards the oxidation of methanol would have to be analogous as well. In order to verify this, cyclic voltammetry was performed with these electrodes in methanol basic medium solution. The results are shown in Fig. 7. Curve (a) depicts alkaline methanol oxidation on the 10:1 copolymer electrode with Ni-cyclam, showing that oxida-

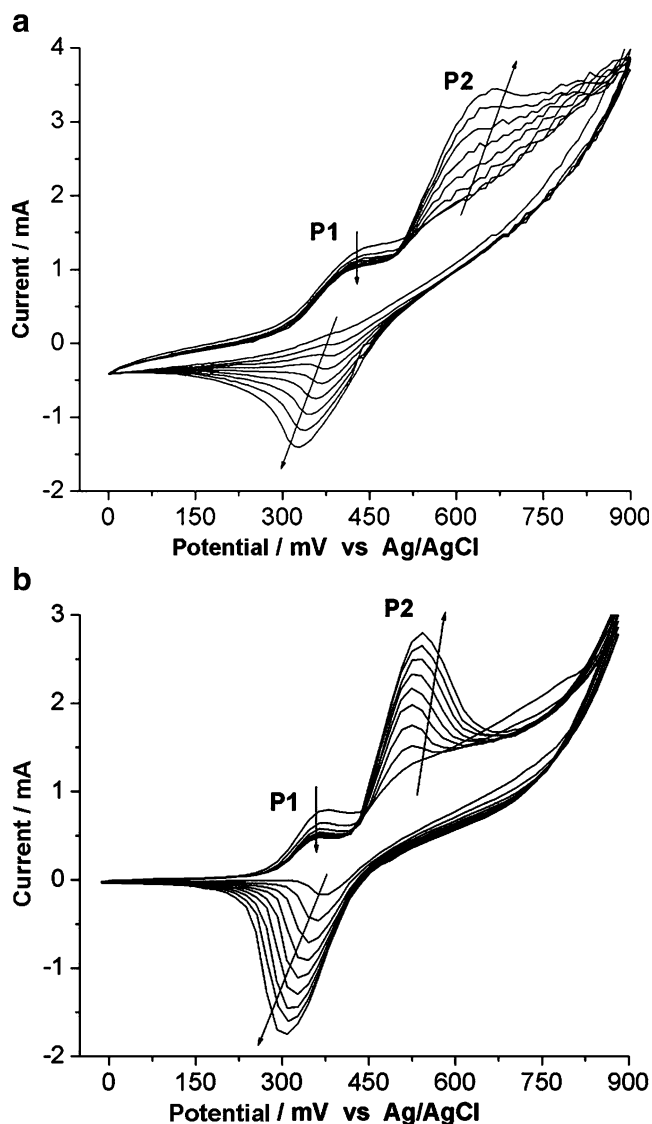


Fig. 6 Cyclic voltammograms for the deposition of Ni-cyclam on: **a** SPANI and **b** graphite

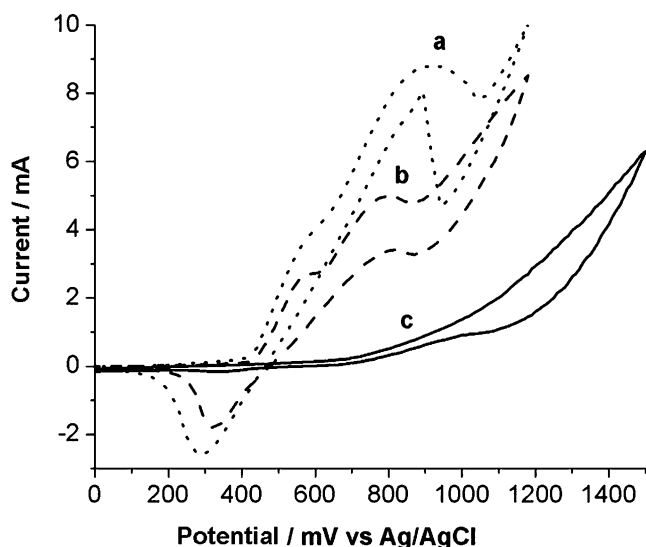


Fig. 7 Cyclic voltammograms of 0.1 M methanol oxidation in 0.1 M NaOH on: **a** graphite-SPANI-Ni-Cyclam and **b** graphite-Ni-cyclam and **c** graphite

tion starts at 640 mV, with the oxidation peak appearing at approximately 900 mV and in the return scan presenting the characteristic peak of these processes (anodic current). In the case of graphite/Ni-cyclam (curve b), there is a small peak around 789 mV, and it is seen that the current of this process is lower than that developed on the composite. Curve (c) is the case for the graphite electrodes, where no oxidation peak is observed due to oxidation of methanol. The adsorption of the complex is still detected ($E=550$ mV), but it does not interfere in the catalysis.

It is noted that the latter voltammetric curve does not show the characteristics of methanol oxidation process, which means that there is no oxidation of the adsorbed species. It is observed that the catalytic effect differs, being higher for the SPANI-Ni-cyclam electrode, which is closely associated with Ni-cyclam's morphology over these substrates and not due to the amount of Ni-cyclam present (6×10^{-8} mol/cm²).

To confirm, the above morphologic studies were performed on Ni-cyclam over SPANI (Fig. 8a) and over graphite (Fig. 8b). The difference in morphology adopted by Ni-cyclam can be detected for both substrates. When it is deposited on graphite, the structure is of the granular kind, dispersed along the electrode. On the other hand, when it is deposited over SPANI, it presents a spongy morphology, with a higher contact area where a close adherence exists between catalyst and substrate. This morphology produces a more open structure, where methanol can have a better access to the catalytic sites of the material. More detailed studies about the oxidation

mechanism of methanol on these electrodes are being performed at this moment.

Conclusions

SPANI with a porous open structure has been electro-deposited by copolymerisation of aniline and orthonilic acid on graphite electrode in ratio 10:1 (orthonilic acid/aniline) in H₂SO₄. The potential limit for oxidation cannot be higher than 1.0 V, since the polymer degrades at higher potentials, giving a very different electrochemical behaviour than over GC. The composite graphite-SPANI-Ni-cyclam in an alkaline medium has a spongy morphology and shows electrocatalytic activity towards methanol oxidation; better than that presented by Ni-cyclam on graphite. For these reasons, graphite could be thought as a substrate for the application of this composite in fuel cells.

From the results obtained, it can be deduced that the catalytic properties of the composite depend to a great extent on the substrate's morphology and on the catalyst distribution in the composite, allowing better the methanol access towards the active catalytic sites.

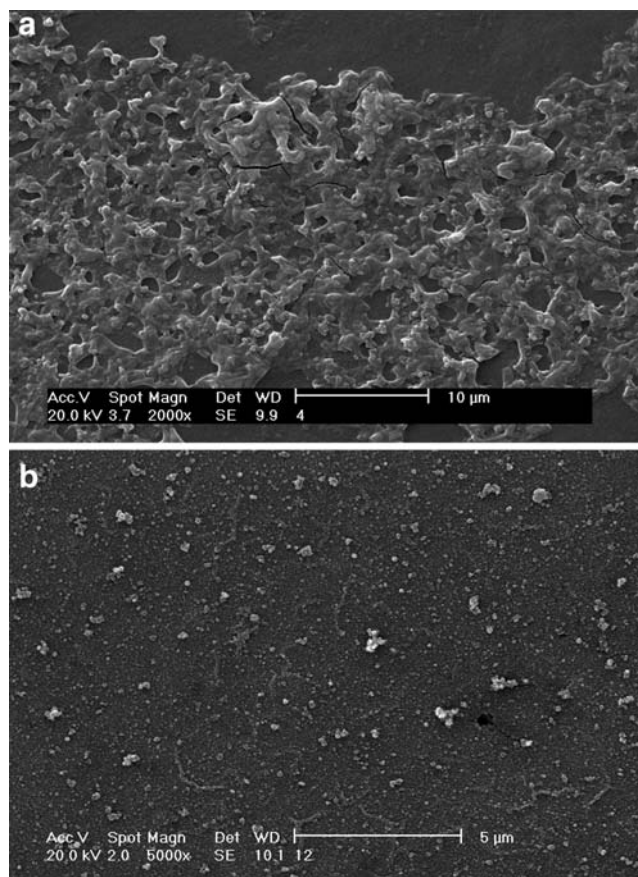


Fig. 8 Scanning electron micrographs of Ni-cyclam on **a** SPANI and **b** graphite

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References

1. Malinauskas A (1999) *Synth Met* 107:75 doi:[10.1016/S0379-6779\(99\)00170-8](https://doi.org/10.1016/S0379-6779(99)00170-8)
2. Pandey RK, Suresh KA, Lakshminarayanan B (2007) *J Colloid Interface Sci* 315:528 doi:[10.1016/j.jcis.2007.07.044](https://doi.org/10.1016/j.jcis.2007.07.044)
3. Tang LH, Zhu YH, Xu LH, Yang XL, Li CZ (2007) *Talanta* 73:438 doi:[10.1016/j.talanta.2007.04.008](https://doi.org/10.1016/j.talanta.2007.04.008)
4. Lipkowski J, Ross PN (1994) *Electrochemistry of novel materials. Frontiers of Electrochemistry*. Wiley, Hoboken
5. Laborde H, Lèger JM, Lamy C (1994) *J Appl Electrochem* 24:1019
6. Focke WW, Wnek GE, Wei Y (1987) *J Phys Chem* 91:5813 doi:[10.1021/j100306a059](https://doi.org/10.1021/j100306a059)
7. Karyakin AA, Vuki M, Lukachov LV, Karyakin EE, Orlov AV, Karpacheva GP et al (1999) *Anal Chem* 71:2534 doi:[10.1021/ac981337a](https://doi.org/10.1021/ac981337a)
8. Mažeikienė R, Niaura M (2003) *Synth Met* 139:89 doi:[10.1016/S0379-6779\(03\)00037-7](https://doi.org/10.1016/S0379-6779(03)00037-7)
9. Lee JY, Cui CQ (1996) *J Electroanal Chem Interfacial Electrochem* 403:109
10. Mu S (2004) *Synth Met* 143:259 doi:[10.1016/j.synthmet.2003.12.008](https://doi.org/10.1016/j.synthmet.2003.12.008)
11. Zhang J, Shan D, Mu S (2006) *Electrochim Acta* 51:4262 doi:[10.1016/j.electacta.2005.12.005](https://doi.org/10.1016/j.electacta.2005.12.005)
12. Bett JS, Kunz HR, Aldykiewicz AJ Jr, Fenton JM, Bailey WF, McGrath DV (1998) *Electrochim Acta* 43:3645 doi:[10.1016/S0013-4686\(98\)00122-4](https://doi.org/10.1016/S0013-4686(98)00122-4)
13. Manríquez J, Gutiérrez-Granados S, Alatorre-Ordaz A, Bedioni F (1999) *Anal Chim Acta* 378:161 doi:[10.1016/S0003-2670\(98\)00564-9](https://doi.org/10.1016/S0003-2670(98)00564-9)
14. González-Fuentes MA, Manríquez J, Gutiérrez-Granados S, Alatorre-Ordaz A, Godínez LA (2005) *Chem Commun (Camb)* 31:898 doi:[10.1039/b412442a](https://doi.org/10.1039/b412442a)
15. Vilchez F, Gutiérrez Granados S, Alatorre Ordaz A, Galicia L, Herrasti P (2008) *J Electroanal Chem Interfacial Electrochem* 614:8
16. Lee JY, Cui CQ, Su XH (1993) *J Electroanal Chem Interfacial Electrochem* 360:177
17. Motheo AJ, Santos JR, Venancio EC, Mattoso LHC (1998) *Polymer (Guildf)* 39:6977 doi:[10.1016/S0032-3861\(98\)00086-X](https://doi.org/10.1016/S0032-3861(98)00086-X)
18. Barbero C, Miras MC, Schnyder B, Haas O, Kotz R (1994) *J Mater Chem* 4:1775 doi:[10.1039/jm9940401775](https://doi.org/10.1039/jm9940401775)
19. Roslonek G, Taraszewska J (1992) *J Electroanal Chem Interfacial Electrochem* 325:285