Electrochemical behaviour of conducting polymers obtained into clay-catalyst layers. An in situ Raman spectroscopy study

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Received 28 August 2005; accepted 17 October 2005

Abstract

In this paper we present the study of the electrochemical properties of the following conducting polymers: poly(*o*-anisidine), polyaniline and copolymers of aniline and *o*-anisidine obtained by a new synthetic method. The polymers are synthesized in free-of-acid conditions, using an activated montmorillonitic clay catalyst, known as Maghnite-H⁺ (Mag-H) as proton source. The electrochemical behaviour of poly(*o*-anisidine) created using Mag-H (PoANI-MagH) and their copolymers with aniline is quite different of those polymers created in HCl solution. In situ Raman data suggest that the structure of PoANI-MagH is a mixture of conducting (polyaniline-type) and redox (phenoxazine or phenazine-type) segments.

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Keywords: Conducting polymers; Montmorillonite clay; Nanocomposites; In situ Raman spectroscopy

1. Introduction

Due to its remarkable thermal and environmental stability, polyaniline (PANI) presents great interest for both real and potential technological applications such as electrocatalysis, microelectronics, electrochromic displays, sensors, etc. It is known that high molecular PANI can be produced mainly by electrochemical and chemical oxidation of aniline in strong acidic solutions [1]. In the last years, PANI nanoparticles [2,3] and nanofibers [4,5] have been

produced by polymerisation in emulsion and interfacial polymerisation, respectively. In all cases the synthesis is carried out in strong acidic conditions using mainly sulphuric and hydrochloric acids. However, it is known that the rate of polymerisation (mainly) and the structure of the polymers depend on the anion of the acid used in the synthesis [6–9]. Recently, the synthesis of PANI-clay nanocomposites has been explored because the clay minerals have large surface and ionic-exchange properties [10–12]. Firstly, the oxidative synthesis has been performed in aqueous medium adding the oxidant (ammonium peroxodisulphate) to a mixture of sodium-montmorillonite clay (Mag-Na), aniline and hydrochloric acid (proton sources) [12]. Also,

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Yoshimoto et al. reported the mechanochemical synthesis of the same nanocomposites [11,12]. In this method the oxidation was carried out in solid state grinding aniline salts (sulphate and fluoride), the Mag-Na clay and ammonium peroxodisulphate (free of solvents). However, in the two methods described, the materials have been characterized by X-ray diffraction and some spectroscopic techniques but the final structure and the electrochemical properties have not been studied.

Here, we reported a preliminary spectroelectrochemical study of conducting polymers created using non-toxic cationic catalyst, known as Maghite- H^+ (Mag-H) [13]. The properties of polyaniline, poly(*o*-anisidine) and copolymers of aniline and *o*-anisidine have been compared with those synthesized by bulk polymerisation.

2. Experimental

Aniline (from Aldrich) was distilled under vacuum prior to use and *o*-anisidine (from Aldrich) was used as received. Perchloric acid (from Merck) used in all experiment was suprapur quality. In a typical experiment Mag-H catalyst was obtained by pre-treating sodium montmorillonite—a naturally occurring clay—with strong acids (the catalyst composition in wt.% after the treatment with H_2SO_4 0.25 M is SiO_2 71.70, Al_2O_3 14.03, Fe_2O_3 0.71, CaO 0.28, MgO 0.80, Na_2O 0.21, K_2O 0.77, TiO_2 0.15, SO_3 0.34). After that, 1 g of Mag-H was dried at 105 °C over night. After cooling to room temperature, 0.022 mol of monomers (aniline or *o*-anisidine) was added to the mineral and the mixture kept under magnetic stirrer at room temperature for 30 min. The chemical synthesis starts when 100 ml of 0.1 M potassium peroxodisulphate solution was slowly added to the mixture (thus, the final concentration of aniline and *o*-anisidine is 0.22 M). The reaction was carried out under magnetic stirring for 1 h and then the solid product was filtered under vacuum and washed with hydrochloric acid and distilled water to remove all traces of oxidant and oligomers. All the materials were dried at 60 °C. The polymer remain into the catalyst layers forming a nanocomposite at the last of the synthesis. However, the Mag-H is easy to separate by filtration because it is insoluble in the solvents in which the polymers are soluble.

The same procedure was used for the copolymer synthesis, keeping always the concentration of the aniline units equal to 0.22 M (aniline units come from aniline and *o*-anisidine).

The XPS spectra were measured with a VG-Microtech Multilab electron spectrometer using non-monochromatized Mg $K\alpha$ (1253.6 eV) from a twin anode source operated at 300 W (20 mA, 15 kV). Photoelectrons were collected into a hemispherical analyser working in the constant energy mode at a pass energy of 50 eV. The binding energy (BE) of the Cls peak at 286.4 eV was taken as standard internal. Peak synthesis was done with missed Gaussian/Lorentzian function lineshape by using the Peak-fit program implemented in the control software of the spectrometer. The pressure in the analysis chamber was always lower than 2×10^{-9} Torr. Thermal degradation of the samples not occurs because the time required to collect the XPS spectra is low.

In the XPS measurements have been performed in the Mag-H-polymer samples. That is, the polymer has not been separated from the catalyst.

The cyclic voltammogram were obtained at a constant sweep of 50 mV s⁻¹ using 1 M $HClO_4$ solution. In all cases, the solutions were prepared from Merck suprapur and ultrapure water (Purelab Ultra from Elga-Vivendi, 18.2 M Ω cm). Potentials in this work are referred to a reversible hydrogen electrode (RHE) immersed in the same solution. For all the electrochemical and spectroelectrochemical experiments the polymers were separated from the catalyst by dissolving the mixture in NMP and filtrating. Then polymer films were obtained by casting a drop of these solutions over the working platinum disk electrode and heating with an infrared lamp to remove the solvent.

Raman spectra were obtained with a LabRam spectrometer (from Jobin-Ivon Horiba). The system has an extremely high detecting sensibility and it uses a single spectrograph equipped with a notch filter in order to filter the Rayleigh scattering and holographic gratings (1800 and 600 grooves mm⁻¹). The slit and pinhole employed were 200 and 700 μ m, respectively. The excitation line was provided by a 17 mW He-Ne laser at 632.8 nm, and the laser power delivered at the sample was held at 4 mW. The laser beam was focused through a 50 $\times$ long-working objective (0.5 NA). The diameter of the laser beam spot on the sample surface was 2 μ m. The sample viewing system consisted of a colour television camera attached to the microscope. The spectrometer resolution was better than 3 cm⁻¹ and the detector was a Peltier cooled charge-coupled device (CCD) (1064 $\times$ 256 pixels). The time needed for the analysis (averaging included) was 27 s. The spectroelectrochemical cell used for the acquisition of Raman

spectra was made in Teflon[®] with the working electrode facing up as the LabRam spectrometer utilized a backscattering configuration to collect the Raman scattering through a confocal microscope vertically. The cell was designed with a silica window to form a closed system in order to prevent the etching of the lens and to eliminate any possible pollution of solution from the air. For in situ Raman spectroscopy measurements a Au working electrode imbedded in a Teflon[®] rod was used.

3. Results and discussion

Poly(*o*-anisidine), polyaniline and copolymer of them at different feed ratio (20/80, 50/50 and 80/20 aniline/*o*-anisidine ratio) were obtained using the procedure described in the experimental section and characterized by X-ray photoelectronic spectroscopy (XPS) and Raman spectroscopy.

Fig. 1 shows the XPS spectra for poly(*o*-anisidine) synthesized using both the conventional and our method. The C1s signal for poly(*o*-anisidine)

prepared using Mag-H (PoANI-MagH) (Fig. 1a) is similar to those obtained in hydrochloric acid (PoANI-HCl) (Fig. 1b). The C1s of poly(*o*-anisidine) can be deconvoluted into three peaks, the first one at 284.6 eV is assigned to aromatic carbons. The peak at 286.1 eV could be attributed to carbon atoms in quinonimine units or carbons on the ether group. And the peak at 287.1 eV has been attributed in polyaniline and derivatives at charged species [14,15] such as $-C-N^+$ and $-C=N^+$. However, this peak could correspond also to carbon atoms on the ether group.

Table 1 shows the relative areas of the C1s peak for PoANI and copolymers of aniline and *o*-anisidine at different feed ratio. Here, it can be noted that while the area of the peak at 286.1 eV does not change significantly with the feed composition (C_2/C in Table 1, where C refers to total carbons area), the area of the peak at 287.1 eV (C_3/C in Table 1) increases when the amount of *o*-anisidine in the feed increase. Therefore, this signal at 287.1 eV has contribution of the carbon linked to the oxygen atom in

Fig. 1. XPS of poly(*o*-anisidine) for both C1s of PoANI-MagH (a) and PoANI-HCl (b) and for N1s signal of PoANI-MagH (c) and PoANI-HCl (d).

Table 1

Relative areas variation of the XPS signal of C1s and N1s for homopolymers of *o*-anisidine and copolymer of them

Polymers	C1s signal areas			N1s signal areas	
	C_1/C	C_2/C	C_3/C	N^+/N	
PoANI-MagH	0.438	0.359	0.203	0.296	
Copolymer ^a 20/80 ^b	0.416	0.395	0.189	0.908	
Copolymer ^a 50/50 ^b	0.545	0.384	0.070	1.372	
Copolymer ^a 80/20 ^b	0.518	0.434	0.048	0.907	
PoANI-HCl	0.459	0.423	0.118	0.397	

C refers to total carbons area, C_1 refers to BE 284.1 eV, C_2 correspond to 286.1 eV and C_3 to 287.1 eV.

^a Synthesized using Mag-H.

^b Feed composition corresponding to aniline/*o*-anisidine ratio in the reactor.

Fig. 2. Cyclic voltammograms for a Pt electrodes covered by PoANI-MagH (solid line) and PoANI-HCl (dashed line) in 1 M HClO_4 solution. $v = 50 \text{ mV s}^{-1}$.

the ether group and the peak at 286.1 eV only corresponds to carbon atoms in quinoneimine units.

The N1s signal for both PoANI-MagH (Fig. 1c) and PoANI-HCl (Fig. 1d) can be deconvoluted into two principal peaks attributed at both neutral amino or imine groups (399.5 eV) or positively charged nitrogen atoms (401 eV) [15]. In Table 1, the ratio between charged and neutral nitrogen atoms (N^+/N) increases remarkably when a small quantity of aniline is added to the feed. In polyaniline substituted with anionic groups, the N^+/N ratio is related to either the doping level or the charge localization [15,16]. However, the increase of N^+/N in this case is only related to the increase in the doping level because the substituting group ($-\text{OCH}_3$) is not an ionic species and therefore it is unable to fix charge.

To study the electrochemical response of PoANI, a conventional cell of three electrode was used. To separate the polymers from the catalysts, they were dissolved in *N*-methyl-2-pyrrolidone (NMP). Films of the polymers were made by casting a drop of a solution of them in NMP over the working platinum disk electrode and heating with an infrared lamp to remove the solvent. Fig. 2 shows the voltammograms obtained with the two electroactive PoANI films in 1 M HClO_4 solution. The current densities have been normalized in order to clearly compare between the two polymers, due to the thickness of the films could vary from different samples. The electrochemical behaviour of the PoANI-MagH exhibits a broad anodic peak around 0.62 V however, on the reverse scan two reduction peaks around 0.54 V and 0.3 V are observed. This behaviour differs from those obtained when the polymer is created in acidic conditions (PoANI-HCl, Fig. 2, dotted line). The polymer created in HCl shows the

similar electrochemical response reported by Motheo et al. [17], that is three redox peak at 0.46 V, 0.6 V and 0.8 V, although the last redox pair is not clearly observed. The existence of three redox processes in PoANI (one additional peak compared with PANI) could be explained by the presence of oligomers occluded in the polymeric films [17]. However, the middle peak could be also related with a degradation product (quinone/hydroquinone redox couple), as it is observed in the case of polyaniline in aqueous acidic medium. To try to clarify this aspect, we have synthesised PANI and copolymer of aniline and *o*-anisidine with Mag-H as proton source. The cyclic voltammogram of polyaniline synthesized with Mag-H (PANI-MagH) shows an intense redox peak at 0.46 V and a shoulder around 0.62 V (figure not shown). In addition, all the copolymers shows the same behaviour (one clear redox process). Therefore, besides that the properties of this kind of conducting polymers does not depend on the type of anion used in the synthesis [16], the electrochemical properties depend strongly on the proton source (inorganic acids or Mag-H catalyst).

The electrochemical behaviour is being studied more in detail using in situ spectroscopic (FTIR) and optical techniques and the results will be reported elsewhere. Nevertheless, we presented here some preliminary results. Fig. 3 shows the surface Raman spectra of PoANI-MagH collected at different electrode potentials. In Table 2 are detailed the Raman bands of PoANI-MagH film over an Au working electrode at reduction potential 0.05 V. The new materials present the most of the bands

Fig. 3. Surface Raman spectra of a PoANI-MagH-modified Au electrode in 1 M HClO₄ solution at different electrode potentials.

Table 2

Vibration modes on Raman spectroscopy in Au electrodes modified with PoANI-MagH at 0.05 V_{RHE} in 1 M HClO₄ solution

Wavenumber (cm ⁻¹)	Vibration modes
1632	–C–N–C in heterocyclic six-membered rings
1602	>C–C< stretching in benzenoid units
1570	>C=C< stretching of quinoid units or N–H ⁺ deformation of secondary amines
1446	>C=N– stretching of emeraldine-type units
1346	>C–N ⁺ – stretching
1231	>C–N– in benzenoid units
925	Perchlorate vibration band
830	Amine deformation
776	Imine deformation
615	Ring deformation
574	Benzenoid ring deformation or stretching of tertiary nitrogen in cyclized structures

bands at 1317 and 1338 cm⁻¹ when camphorsulfonic acid-doped PANI was irradiated with a He–Ne laser ($\lambda_{\text{exc}} = 632 \text{ nm}$ [21]. These bands coalesce at 1336 cm⁻¹ in secondarily doped PANI (with *m*-cresol) and the authors attributed this broad band at extended polarons [21]. In addition, Cochet et al. noticed the same behavior for emeraldine salt excited with red laser at $\lambda_{\text{exc}} = 676.4 \text{ nm}$ [22]. The authors reported two bands at 1320 and 1337 cm⁻¹ which overlap in a broad band at 1332 cm⁻¹ when the polymer is treated with HCl vapors, confirming the existence of a bipolaronic structure [22]. Therefore, in our case it can be suggested that PoANI-MagH has only one polaronic species either isolated or extended polarons.

However, two additional bands at 1632 and 574 cm⁻¹ are observed in Fig. 3. These bands appear in polymers with cyclized phenazine-type structures [19,21] and the same bands have been observed in ladder polymer such as poly(*o*-aminophenol) [23], which presents a like-phenoxazine structure. In addition, it have been recently reported that copolymers of aniline and aminonaphthalene-disulfonic acid which have heterocyclic structure (like phenazine) show a Raman band at 1630 cm⁻¹ [24]. Therefore it is possible that the structure of PoANI-MagH is formed by both open (like-polyaniline) and cyclical (like-poly(*o*-aminophenol)) units. This fact will be discussed later.

The areas of the Raman bands strongly depend on the applied potential (Fig. 3). The fitting of the bands by Lorentz curves (using the Origin 6.0 software) allows to quantify the evolution with the potential of the species related to these bands. Due to this, the evolution of the integrated Raman intensities have been obtained referring the areas of the bands to the area of that corresponding to the symmetrical stretching of the perchlorate anion, at 925 cm⁻¹, which does not change significantly with the potential (internal standard). Despite the fact that the perchlorate anions can enter or leave the polymer film during the redox processes, the variation of the Raman band at 925 cm⁻¹ is negligible considering the concentration of these anions in the solution. Fig. 4 shows the evolution with the applied potential of the integrated Raman intensities for PoANI-Mag-H (the right y-axis correspond to the intensities of 574 and 1632 cm⁻¹ bands and the left y-axis to the 1346 cm⁻¹ one). The band at 1346 cm⁻¹ assigned to the polarons, displays a typical behaviour of intermediate species, it increases to reach a maximum at 0.45 V and later decreases as the poten-

obtained in similar conducting polymers obtained by chemical or electrochemical oxidation [18]. It is interesting to note that already at low potential (0.05 V), the absorbance of the Raman band attributed to the >C–N⁺– stretching of semiquinoid species (1346 cm⁻¹) is appreciable. In polyaniline, this band shifts from 1340 to 1310 cm⁻¹ as the potential is increased [19]. The first band at 1340 cm⁻¹ is attributed to isolated polarons and the last one at 1310 cm⁻¹ to polaron lattice formed by organization of two isolated polarons [19]. It has been also reported that the band at 1310 cm⁻¹ is never obtained in substituted polyanilines [19]. But, the wavelength used in Ref. [19] is 514.5 nm (in this work $\lambda_{\text{exc}} = 632.8 \text{ nm}$) and it is known that Raman spectra depend on the laser excitation wavelength [20]. However, Pereira da Silva et al. observed two

Fig. 4. Dependence of the integrated Raman intensities relative to 925 cm^{-1} of 1346 (triangle) (see intensities in left y-axis), 1632 (square) and 574 (circle) cm^{-1} (see intensities in right y-axis) Raman band on the electrode potential for a PoANI-modified Au electrode in 1 M HClO_4 solution.

tial is increased. This behaviour supports the hypothesis that the broad oxidation peak observed by cyclic voltammetry can be the overlapping of two peaks (Fig. 2) in which the intermediate species (semiquinone) is formed in the first process and consumed in the second one to give iminic or quinoid species.

Identical behaviour with maximum at 0.45 V is observed analyzing the Raman band at 1632 cm^{-1} (see intensity in right y-axis). This behaviour has been also observed in poly(*o*-aminophenols) and attributed to charged quinoniminic intermediates [23]. In ladder polymer, such as poly(*o*-aminophenol), the broad oxidation peak corresponds to two peaks that can be separated changing the protons concentration in the electrolyte because one process is dependent on the pH of the medium [23]. Also, in the copolymer of aniline and aminonaphthalenedisulfonic acid, the Raman band at 1630 cm^{-1} (collected at $\lambda_{\text{exc}} = 632.8\text{ nm}$) grows during the oxidation reaching a maximum and after that decreases [24]. Therefore, the dependence of the band at 1632 cm^{-1} on the applied potential supports the presence of phenoxazine or phenazine-type segments in PoANI created into a layered catalyst clay.

Fig. 4 also shows the variation of the Raman band at 574 cm^{-1} (see intensity in right y-axis). This band has been usually assigned to the ring deformation in benzenoid units [18,23]. In polyaniline-type materials the intensity of the band attributed to benzenoid units decreases as the potential increases

because this species are being consumed. However, the area of this band increases significantly as the potential increases until reach a maximum at 0.45 V and at higher values the intensity becomes independent on the applied potential. Pereira da Silva et al. proposed for polyaniline, doped with camphorsulfonic acid, that several bands at 574 , 1381 and 1643 cm^{-1} appeared as the polymer was heated. The authors proposed that the band at 574 cm^{-1} could be related to the vibrational modes of cyclic structures containing tertiary nitrogen formed by cross-linking [21]. Therefore, PoANI-MagH could be formed by both electroactive polymer segments and redox segments. However, it is also possible that the polymer is heated during the Raman experiment due to the high power density in the irradiated region. Thus, the intensity of the band at 574 cm^{-1} would not depend on the applied potential but on the time of the experiment. Nevertheless, as is shown in Fig. 4 the area reaches a maximum suggesting that the structural change is produced by the applied potential. More detailed in situ studies are being carried out using Fourier transformed infrared spectroscopy to clarify these features.

4. Conclusions

We have developed a new synthetic method to produce conducting polymers, which does not use inorganic acid but a non-toxic clay catalyst as proton source. Preliminary results about the spectroelectrochemical properties have been shown. However, we can conclude that the electrochemical behaviour of PoANI-MagH is quite different from those observed for PoANI-HCl given broad peaks in the voltammogram that can be produced by the overlapping of two different processes. The polymers synthesized using Mag-H could show a structure that is a mixture of conducting (polyaniline-type) and redox (phenazine-type) units.

Acknowledgment

The authors thank the financial support from the Ministerio de Educación y Ciencia (MAT2004-01479 project) and Generalitat Valenciana (GRU-POS04/75).

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