

Characterization of copper manganite oxide-polypyrrole composite electrodes cathodically polarized in acidic medium

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Abstract

We have studied the electrochemical behaviour induced by polarization in sandwich-type composite electrodes with the structure GC/PPy/PPy(Ox)/PPy where GC stands for glassy carbon, PPy for polypyrrole and Ox for $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ nanoparticles. The electrodes were polarized at -0.45 V/SCE in 0.15 M KCl aqueous solution at pH 2.2 either saturated in Ar or O_2 at 25 °C. The changes occurring on these electrodes were studied using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (EXAFS and XANES) techniques. In previous work we have shown that when the oxide particles are incorporated into the PPy matrix the Cu^+ present in the initial oxide suffers dismutation to give Cu^{2+} and metallic Cu. In this work we show that the polarized electrodes also reveal the presence of metallic Cu and Cu^{2+} . The data also show that the oxide particles embedded in the polarized electrodes contain Mn^{3+} and Mn^{4+} , although the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio is different from that found in the fresh electrodes. The Cl 2p XPS data show that in the electrode polarized in O_2 there is an enhancement of the Cl covalent contribution that appears at 200.8 eV (which is already present in the fresh electrode although with a very small intensity). This result suggests that the oxygen reduction reaction leads to an increase of the OH^- concentration inside the composite electrode that explains the charge transport in PPy at negative potentials.

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1. Introduction

Nanoparticle transition metal oxide electrodes are important materials due to their low cost, high-surface area, potential electrocatalytic activity for the oxygen reduction reaction (orr) and for being suitable materials to be used in fuel cell vehicles and light batteries. The use of conducting layers of polypyrrole PPy prevents the dissolution of metal oxide-based electrocatalysts, as we have reported recently in the case of copper manganite oxide [1]. In previous work we have confirmed the electrocatalytic activity for the orr of multilayer composite electrodes GC/PPy/PPy(Ox)/PPy, Ox being a copper- and manganese-containing spinel oxide with composition $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ [2,3] or a nickel- and

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cobalt-containing spinel oxide with composition $\text{Ni}_{0.3}\text{Mn}_{2.7}\text{O}_4$ [4,5]. During the orr on the Cu–Mn oxide covered by a PPy film taking place at negative potentials, two important features were observed: (i) the conservation of the electrical conductivity of the composite film in conditions at which generally the polymer PPy is insulator and (ii) the occurrence of a remarkable electrochemical stability of the electrocatalyst at acidic pHs, a situation where the oxide is normally destroyed by electroreduction. This experimental behaviour can be explained by the local formation, by the orr, of OH^- ions in the $\text{PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)$ inner layer, which arises from the consumption of the H^+ ions. Their presence plays a determining role for the anion exchange process between OH_{ads}^- on PPy and Cl^- in electrolytic solution, allowing for the preservation of good electrical conductivity of PPy [6]. In addition to that, the milder local activity medium improves the oxide stability.

In recent work [7] we have reported on the surface and structural characterization of $\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$ composite electrodes. The XPS data indicate that the $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ oxide contains Cu^+ , Cu^{2+} , Mn^{3+} and Mn^{4+} . On the other hand, XPS, XANES and EXAFS results indicate that when the oxide is incorporated into the PPy matrix, all the Cu^+ present in the original oxide suffers dismutation to give Cu^{2+} and metallic Cu^0 giving place to the formation of a large number of vacancies (\square) and to the approximate cation distribution: $\text{Cu}_{1.17}^{2+}\square_{0.23}\text{Mn}_{1.20}^{3+}\text{Mn}_{0.40}^{4+}\text{O}_4$. The Mn K-edge XANES and EXAFS data reveal that, in this spinel-related oxide, Mn is present as Mn^{3+} and Mn^{4+} and that these cations occupy octahedral sites in the structure. The Cu K-edge EXAFS data indicate that copper exists in two oxidation states: Cu^{2+} , which predominantly occupies tetrahedral sites in that structure but having a large degree of disorder in the second and higher coordination shells, and Cu^0 , which is in good agreement with the XPS data [7].

We report here on the use of X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (EXAFS and XANES) to determine the influence of the polarization conditions in oxygenated and non-oxygenated KCl aqueous solutions (pH 2.2) on the bulk and surface structure of $\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$ composite electrodes.

2. Experimental

The oxide synthesis and the preparation of the electrode with the composite structure $\text{GC/PPy/PPy}(\text{Ox})/\text{PPy}$ have been already described elsewhere [3,7]. The description of samples is given in Table 1. The amount of copper manganite incorporated in the electrode composite was 0.3 mg cm^{-2} [1,2].

The electrochemical behaviour of $\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$ composite electrodes was studied between -0.8 and 0.8 V/SCE using cyclic voltammetry in 0.15 M KCl aqueous solution, at room temperature and pH 2.2 in Ar atmosphere. The pH of this solution was obtained using the adequate amount of 1 M HCl . Three electrodes were analyzed: (i) a freshly prepared one denoted by E, (ii) a cathodically polarized electrode at -0.45 V/SCE during 4 h in a solution saturated by Ar (P_1) and (iii) an electrode polarized as electrode (ii) but in an oxygenated solution (P_2) (see Table 1). An electrode polarized as P_1 was treated by immersion in a 1 M NaOH solution.

The electrochemical equipment used was a three-electrode cell comprising the composite electrode, a Pt auxiliary electrode and SCE as the reference electrode. An Autolab PGSTAT 20 potentiostat equipped with a data acquisition system completed the electrochemical system.

The XPS data were recorded using a CLAM2 analyzer with three channeltrons under a vacuum better than $1 \times 10^{-8} \text{ Torr}$, using Al $\text{K}\alpha$ radiation and a constant analyzer transmission energy of 100 eV for the wide scan spectra, and 20 eV for the narrow scan spectra. All the spectra were recorded at a take-off angle of 90° . The binding energy (BE) values were referenced to the main C 1s peak of the PPy ring (284.5 eV). The BE values are accurate to $\pm 0.2 \text{ eV}$. The relative atomic concentrations were calculated using tabulated atomic sensitivity factors [8].

The XANES and EXAFS measurements were performed at the Synchrotron Radiation Source at Daresbury Laboratory operating at 2.0 GeV and an average current of 200 mA . The data were collected at 298 K using a Si(1 1 1) double crystal order sorting monochromator in fluorescence mode using 50% harmonic rejection. The energy scale

Table 1
Description of samples

Designation of sample	Composition
E	$\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$
P_1	$\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$ polarized at -0.45 V/ECS in a 0.15 M KCl solution at pH 2.2 saturated in Ar
P_2	$\text{GC/PPy/PPy}(\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4)/\text{PPy}$ polarized at -0.45 V/ECS in a 0.15 M KCl solution at pH 2.2 saturated in O_2

was calibrated using a 6 μm Mn foil in the case of the manganese K-edge and a 6 μm Cu foil for the copper K-edge. The position of the Mn foil edge was taken at 6538 eV and that of the Cu foil edge at 8982 eV. All the manganese and copper XANES data were referred to these two values. All the edges were recorded at least twice and at different times separated by several hours but within the lifetime of the beam. The reproducibility in the determination of the edge positions was found to be better than 0.2 eV. The edge profiles were separated from the EXAFS data and, after subtraction of the linear pre-edge background, normalized to the edge step. The EXAFS oscillations were isolated after background subtraction of the raw data using the Daresbury program EXBACK and converted into k space. The data were weighted by k^3 , where k is the photoelectron wavevector, to compensate for the diminishing amplitude of the EXAFS at high k . The data were fitted using the non-linear squares minimisation program EXCURV90 [9] which calculate the theoretical function using the fast curved wave theory [10].

3. Results and discussion

3.1. Electrochemical behaviour

Fig. 1 (curve 1) shows the cyclic voltammogram of the freshly prepared electrode in 0.15 M KCl aqueous solution, at room temperature and pH 2.2, in Ar atmosphere. It displays the classic electrochemical behaviour of composite electrodes characterized by insertion/expulsion processes of Cl^- doping anions into/from polymer PPy matrix. The positions and heights of the peaks varied with the scan rate but they remained unchanged with the number of cycles. The shape and characteristics of voltammograms obtained on this electrode at the 100th scan were practically identical to those recorded at the first scan. The voltammograms recorded on composite electrodes previously polarized at -0.45 V/SCE prior to the cyclic voltammetry experiment (Fig. 1, curve 2), in the same conditions of the fresh one, showed that after a prolonged polarization at negative potentials almost all Cl^- anions are expelled from the PPy matrix leading to an important loss of conductivity. Consequently, its electrochemical properties are quasi null. The expulsion of the chloride anions from the PPy matrix at negative potentials such as -0.45 V/SCE would lead to a reduction of the conjugated chain and consequently to a loss in conductivity. However, regarding the results obtained by Van Dyke in the case of acetonitrile [6], it is possible to extend the conductive state of PPy films to very high-negative potential such as -1.1 V/SCE using a simple chemical treatment consisting of immersion of the electrode in NaOH aqueous solution. It has been suggested that such treatment [6], gives rise to an exchange reaction between the OH^- and Cl^- ions placed inside the polypyrrole matrix. Therefore it is possible to accept that at negative potentials the PPy conductivity is assured by the OH^- anions. In fact, when the blocked electrodes were treated via immersion into 1 M NaOH solution, their electrochemical properties were virtually the same than those exhibited by the fresh electrode (Fig. 1, curve 3). On the other hand, when the composite electrode is polarized at the same potential (-0.45 V/SCE) in the solution but now saturated with O_2 , the voltammogram is similar to that obtained after NaOH

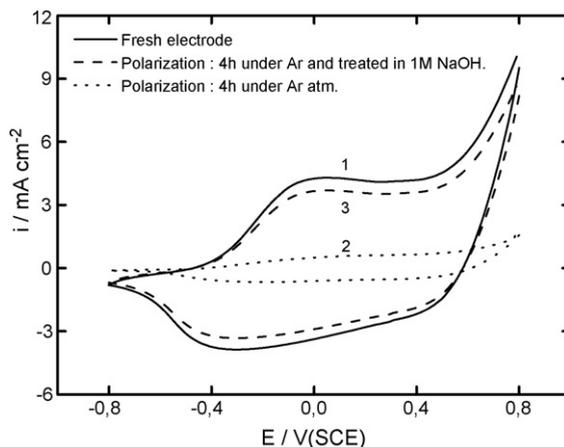


Fig. 1. Cyclic voltammograms recorded from the fresh electrode and from the electrodes polarized for 4 h at -0.45 V/SCE under an inert atmosphere in the presence and in the absence of treatment in 1 M NaOH solution during 2 h. Electrolyte: 0.15 M KCl solution, pH 2.2, room temperature, scan rate $\nu = 10$ mV s^{-1} .

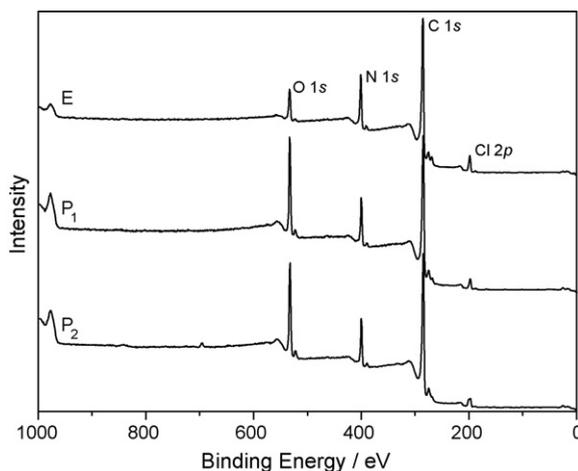


Fig. 2. Wide scan XPS spectra recorded from samples E, P₁ and P₂.

treatment (Fig. 1, curve 3) confirming the OH⁻ formation during the electrocatalytic orr $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ on Cu_{1.4}Mn_{1.6}O₄ particles incorporated to PPy. The composite electrode is particularly stable in acidic solution (pH 2.2) because the H⁺ ions are consumed by the orr favouring the increase of local pH and stabilizing the oxide. The OH⁻ ions existing in the pores of PPy may play a role similar to that played by those involved in the chemical treatment in NaOH solution cited before.

3.2. Spectroscopic characterization

Fig. 2 shows the wide scan XP spectra recorded from the polarized electrodes P₁ and P₂ as well as from the freshly prepared, non-polarized PPy/PPy(Cu_{1.4}Mn_{1.6}O₄)/PPy electrode (E). The spectra recorded from samples E, P₁ and P₂ show the signals for C 1s, N 1s and Cl 2p, as expected. All the spectra show an extra oxygen contribution that is more intense on the polarized electrodes, which we attribute to adsorbed oxygen at the surface of the electrodes. Since the oxide loading of the electrodes is small and the oxide particles are covered by a protective PPy overlayer (which must attenuate most of the photoelectron flux coming from the oxide particles) it is difficult to observe in these general spectra any significant signal in the Cu 2p and Mn 2p spectral regions above the spectral background. The N 1s spectra recorded from samples E, P₁ and P₂ were all similar amongst themselves and also similar to those reported previously for the system Ni–Co–O/PPy [11] which is not shown here. Several contributions were observed which correspond to pyrrolium nitrogen atoms (–NH–; BE = 399.7 eV), charged nitrogen atoms (–N⁺N–) belonging to the pyrrole structure (characterized by BE's of 401.2 and 402.8 eV) [11] and =N– structures (BE = 397.8 eV) [12]. The Cl 2p spectra recorded from samples E and P₁ were very similar to those reported previously [11] (Fig. 3). Three spin–orbit doublets characterized by a BE of the Cl 2p_{3/2} level of 197.2, 198.9 and 200.8 eV were observed. The lowest and the highest BE components correspond to ionic and covalent chlorine species (Cl⁻ and –Cl), respectively [12], while the contribution appearing at 198.9 eV could be associated to an intermediate situation between that of an ionic Cl⁻ species and the covalent –Cl species, arising from an increase in the number of positively charged nitrogen atoms in the polymer chain. The spectrum recorded from sample P₂ is very different and shows a considerable enhancement of the intensity of the contribution corresponding to the covalent –Cl species (Fig. 3) which in this sample accounts for ca. 56% of the spectral area. The relative contribution of the ionic Cl⁻ species to the total Cl 2p signal has decreased in this sample with respect to the contribution observed in the fresh electrode (sample E). This result illustrates the determining role of the O₂ presence on the increase of the covalent –Cl species strongly linked to the PPy chain in the composite electrodes. The chloride anions favour the electrical conductivity of PPy so contributing to the electrocatalytic behaviour of composite electrodes at negative potentials as previously reported [3]. The relative atomic concentrations derived from the spectra are shown in Table 2. The experimental N/C ratio, which is very similar for all samples (0.16–0.17), is lower than that calculated for a pyrrole unit in PPy (N/C = 0.25). The difference can be attributed to the presence of an adventitious hydrocarbon layer on the surface of the electrode. Using the N/C ratios, the C_{ppy} corresponds to 66% of the total carbon C ($C = C_{\text{ppy}} + C_{\text{other}}$). On the other

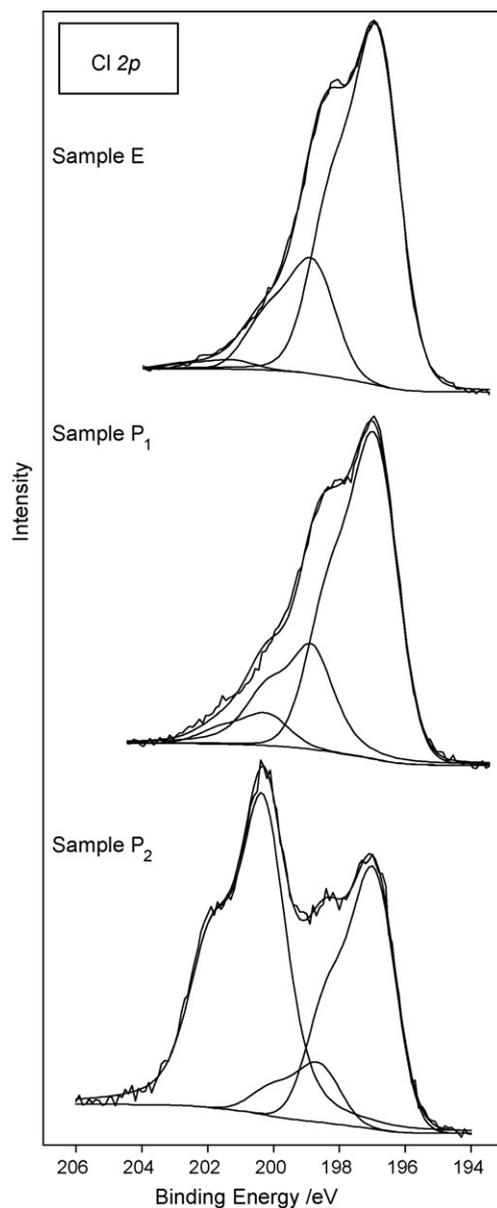


Fig. 3. Cl 2p spectrum recorded from samples E, P₁ and P₂.

hand, the calculated N/Cl ratios vary between 0.13 and 0.24, values that are similar to those of the non-polarized electrodes [7]. It can be also observed that the surface of the electrodes P₁ and P₂ contains much more oxygen than the fresh electrode (E). This oxygen contribution disappears very rapidly after the effect of Ar⁺ sputtering. Actually its intensity is reduced to a tenth of its initial intensity just after removing the outermost 2 nm from the surface by Ar⁺

Table 2
Relative atomic concentrations obtained from the XPS data

Sample	N/C	Cl/C	O/C	N/Cl
E	0.17	0.04	0.08	0.24
P ₁	0.16	0.02	0.21	0.13
P ₂	0.16	0.03	0.23	0.19

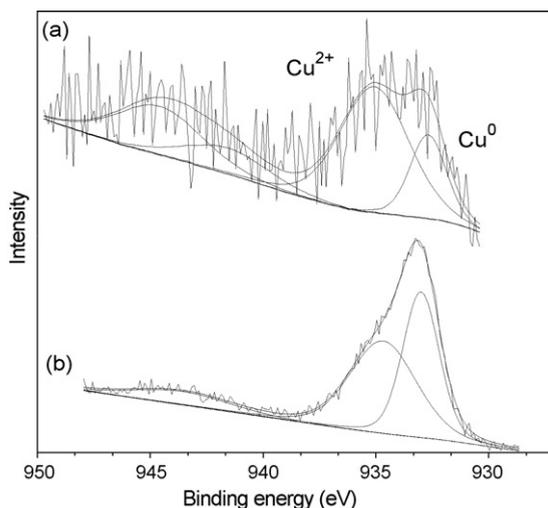


Fig. 4. Cu $2p_{3/2}$ spectra recorded from (a) sample E and (b) sample P₁.

bombardment. The main component in the O 1s spectra recorded from these samples appears at 533.2 eV, with a smaller component at 531.2 eV. These binding energies are characteristic of adsorbed water and hydroxyl groups, respectively, and can come from the electrolyte in which these two samples have been treated electrochemically. In the case of the sample P₂ another source of water can come from the oxygen reduction reaction mentioned before.

As mentioned in Section 1, previously reported results [7] have indicated that the powdered oxide $\text{Cu}_{1.4}\text{Mn}_{1.6}\text{O}_4$ contains Mn^{3+} , Mn^{4+} , Cu^+ and Cu^{2+} . The XPS Cu $2p_{3/2}$ spectra recorded from the polarized electrodes also show the presence of metallic Cu and Cu^{2+} as the fresh electrode [7]. Regarding the XPS Cu $2p_{3/2}$ spectrum recorded from the polarized electrode P₁ (Fig. 4) it is possible to observe that the metallic copper signal has increased significantly respect to that observed in the spectrum of the freshly prepared composite electrode E. This indicates that a fraction of the Cu^{2+} initially present in the composite electrode has suffered reduction to metallic Cu as a consequence of the electrode being cathodically polarized.

Fig. 5 shows the Mn K-edge XANES recorded from samples E, P₁ and P₂ together with those of the reference compounds MnO, Mn_2O_3 and MnO_2 . As already reported, the shape of the edge spectral features recorded from the electrodes are all characteristic of an octahedral spinel cation [14]. The position of the Mn K-edge of all the composite electrodes is situated between that of Mn_2O_3 and MnO_2 indicating that the composite electrode contains both Mn^{3+} and Mn^{4+} placed only in B sites of the spinel structure. It is also evident that the absorption edge corresponding to the

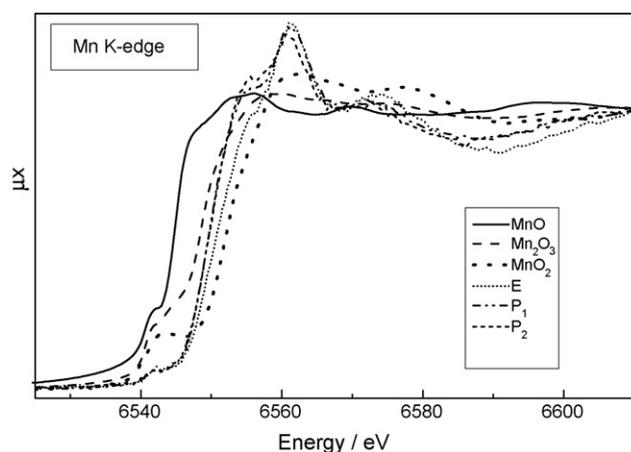


Fig. 5. Mn K-edge XANES recorded from samples E, P₁ and P₂ and the reference compounds MnO, Mn_2O_3 and MnO_2 .

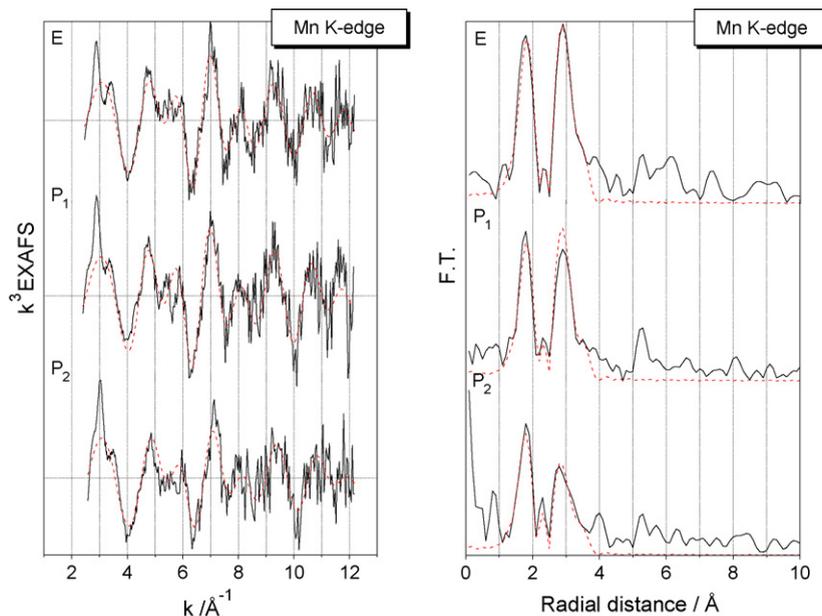


Fig. 6. Left: Mn K-edge EXAFS recorded from samples E, P₁ and P₂. Right: the corresponding Fourier transforms of the spectra are shown on the left. The solid line depicts the experimental data, while the dashed lines represents the fitted curve.

polarized electrodes (P₁ and P₂) is shifted to lower energies than that of the non-polarized electrodes (sample E) showing that the samples P₁ and P₂ contain more Mn³⁺ than the fresh electrode E. This indicates that the Mn⁴⁺ ions are reduced to Mn³⁺ ions as a consequence of the electrodes being cathodically polarized.

The Mn K-edge EXAFS recorded from samples E, P₁ and P₂ together with their corresponding Fourier transforms are shown in Fig. 6. These Fourier transforms are characterized by a first shell situated at ca. 2 Å and a second shell situated at ca. 2.9 Å, which is consistent with what was observed for transition metal cations occupying the octahedral sites of a spinel-related structure [13–17]. Considering that the XANES results suggested the existence of both Mn³⁺ and Mn⁴⁺ the EXAFS was fitted to a model which considered the presence of these two oxidation states of Mn. The results obtained from the fit using a procedure already described [15] are shown in Table 3. The shortest Mn–O distance at ca. 1.90 Å is characteristic of Mn⁴⁺ [18]. Since Mn³⁺ is a JT-cation, a distorted octahedral geometry results which are characterized by four short Mn–O distances of about 1.90 Å and two longer distances of about 2.2–2.3 Å [18]. Therefore, the distance at ca. 1.90 Å also stands for the shorter Mn³⁺–O distance while the distance at 2.18–2.21 Å corresponds to the longer Mn³⁺–O distance [19]. Since the ratio of the corresponding coordination numbers for each distance is representative of the Mn³⁺/Mn⁴⁺ ratio, the results presented in Table 3 indicate that the percentage of Mn³⁺ increases in the order E < P₁ < P₂. This is in good agreement with what was suggested by the XANES data. It is also observed that the intensity of the second shell diminishes in amplitude in the order E < P₁ < P₂ suggesting the existence of disorder in the second shell. In fact the FT corresponding to the electrode P₂ resembles more that characteristic of the Cu–Mn amorphous oxides with proto-spinel structures [17].

Table 3
Results regarding fitting the Mn-K edge EXAFS data

Sample	Atom type	Coordination number	R (Å)	2σ ² (Å ²)
E	O	6	1.92	0.023
	O	2	2.21	0.011
P ₁	O	5.5	1.90	0.024
	O	2	2.20	0.012
P ₂	O	5.5	1.90	0.026
	O	2.5	2.18	0.013

The Cu K-edge XANES and EXAFS data obtained from sample E (not shown) were compatible with the presence of Cu⁰ and of Cu²⁺, the latter occupying tetrahedral sites in the spinel-related structure, a situation that was described and reported elsewhere [7]. The data recorded from the polarized electrodes P₁ and P₂ were qualitatively similar to those recorded from sample E. In the case of sample P₂ the data showed a remarkable increase of the Cu⁰/Cu²⁺ ratio with respect to the E sample (0.36 and 0.28, respectively). As opposed to what was observed by XPS, in the case of sample P₁ no increase of the Cu⁰/Cu²⁺ was observed. This discrepancy can be explained in terms of the surface sensitivity of the XPS technique versus the bulk character of the XAS technique.

4. Conclusions

Two important conclusions can be pointed out:

- (i) When the composite electrodes are polarized at -0.45 V/ECS in 0.15 M KCl solution (pH 2.2) under O₂ or Ar atmosphere, the Mn³⁺/Mn⁴⁺ ratio increases, which suggests that some of the Mn⁴⁺ has been reduced to Mn³⁺ during the process of cathodic polarization. A similar effect has been pointed out for copper since a fraction of the Cu²⁺ present in the freshly prepared composite electrode appears to be reduced to Cu⁰ in the polarized electrodes.
- (ii) The XPS results presented in this paper indicate that the chemical nature of the Cl and N species in the composite electrode are not altered by polarization in Ar atmosphere. However, when the composite electrode is polarized under the same electrochemical conditions in an O₂ atmosphere, there is a clear enhancement of the covalent $-Cl$ species. This result suggests that the orr leads to an increase in the concentration of OH⁻ inside the composite electrode which in turn explains the charge transport in PPy at negative potentials.

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