In situ XAS characterization of the electrochemical insertion of copper in polypyrrole films

M. C. M. Alves,[a] N. Watanabe,[a,b] A. Y. Ramos[a,c] and H. C. N. Tolentino[a]

[a]Laboratório Nacional de Luz Síncrotron - PO Box 6192 - CEP 13083-970, Campinas, SP, Brasil, [b]Universidade Estadual de Campinas – Cidade Universitária Zeferino Vaz, Campinas, SP/Brazil, [c]Laboratoire de Minéralogie et Cristallographie, CNRS-Paris VI, France. Email: maria@lnls.br

We report the electrochemical insertion of copper in polypyrrole films followed by XAS spectroscopy. Depending on the applied potential the copper remains as an ionic form like Cu^{+n}-$(OSO_3^-)_n$. For more reductive potentials metal particles are synthesized. Small particles with an estimated average diameter of 20 Å were obtained.

Keywords: electrochemistry, metal cluster, polypyrrole, XANES&EXAFS.

Introduction

Nanostructured systems have been extensively studied due to their large technological improvements in several areas as semiconductors, catalysts or magnetic materials (Schmidt & Weinheim, 1994). The electrochemical insertion of metals in different conductive polymers such as polypyrrole, polythiophene and polyaniline has been performed aiming nanometric particle production ((Laborde et al., 1994); (Tourillon et al., 1984); (Tourillon et al., 1986); and (Hepel, 1998)).

In this work the electrochemical insertion of Cu in polypyrrole was followed by in-situ XAS spectroscopy. Thin polymeric films were grown and the copper insertion was carried out at selected potentials chosen from the electrochemical response of the system. An electrochemical cell was specially designed and developed for these experiments (Watanabe & Alves, 1999).

1. Materials and methods

The electrochemical cell was filled with a solution composed by pyrrole (2x 10^{-2} M), H_2SO_4 (0.1M), $CuSO_4$ (10^{-2} M) and SDS ($CH_3(CH_2)_{11}OSO_3^-Na^+$) ($10^{-2}$ M). The reference was a Ag/AgCl electrode, the counter electrode was a Pt wire and the working electrode was a carbon disk.

A polypyrrole film of about 1.7 μm in thickness was obtained by holding the working electrode at 900mV vs Ag/AgCl for 500 seconds. The copper reduction was carried out in different reductive potentials (400, 220, 200, 150 mV vs Ag/AgCl) during 600 seconds. These potentials were kept constant during the spectra acquisitions.

SEM measurements were performed at the JSM-5900LV/LME at the LNLS. Results obtained for the polymer polarized at 150 mV showed the formation of large Cu clusters having an average diameter of 1000Å approximately. As this technique is sensitive to large particles, this value might be an overestimation of the real average diameter of the particles.

XAS measurements were performed at the Cu K edge and room temperature in the LNLS XAS beam line (Tolentino et al., 1998). The X-ray beam was collimated by slits and monochromatized with a “channel cut” Si(111) crystal. Vertical slits of 0.5 mm placed before the monochromator gave an experimental resolution at the Cu K edge (8979 eV) of 2.2 eV. The beam divergence and the intrinsic width of the Si(111) reflection are 1.8 and 1.2 eV respectively. The core hole life time broadening is 1.55 eV. The total energy resolution on the beam line was 2.7 eV.

The spectra were recorded with the incident beam at 10^o with respect to the substrate. A NaI scintillator placed on the top of the cell was used to monitor the fluorescence signal.

The XANES&EXAFS spectra were analysed using the WINXAS program (Ressler, 1997). A background subtraction was done by means of a polynomial function normalised to the height of the absorption edge step. For EXAFS spectra the various neighboring shells were obtained by a Fourier transform of the EXAFS signal from 3 to 11 $Å^{-1}$ using a Kaiser window with a coefficient of 2.5. By an inverse Fourier transform into *k* space, the EXAFS oscillations corresponding to one or two neighbor shell were extracted. Structural parameters were obtained from least squares fitting using experimental phase and amplitude functions deduced from a model compound ($CuSO_4$ or Cu metal). Three variables were used in the one-shell fits: mean coordination number (N), mean interatomic distance (R) and mean square relative displacements between the atoms (σ^2). Six variables were used in the two-shell fits: N (Cu-O and Cu-Cu), R(Cu-O and Cu-Cu) and σ^2 (Cu-O and Cu-Cu). The energy shifts ΔE_0 of the photoelectron energy zero were fixed to 0 eV. In any case the number of free parameters did not exceed the number of independent data points given by the Nyquist theorem (Koningsberger, 2000).

2. Results and discussion

The cyclic voltammogram of copper in the polypyrrole (Figure 1) shows well defined peaks that correspond to the electrochemical reduction and oxidation of copper in the film.

XAS spectra at the Cu K edge (figure 2) were taken at the potentials indicated by the arrows in Figure 1. The position and the shape of the Cu K edge features depend on the chemical species present in the solution and in the polymer. The aqueous solution $CuSO_4$ spectrum has a sharp edge (feature A) that corresponds to the 1s →4p transition consistent with the presence of Cu^{+2} species in an octahedral environment. Feature B is related to the oxygen neighboring atoms around copper. For Cu metal the 1s →4p

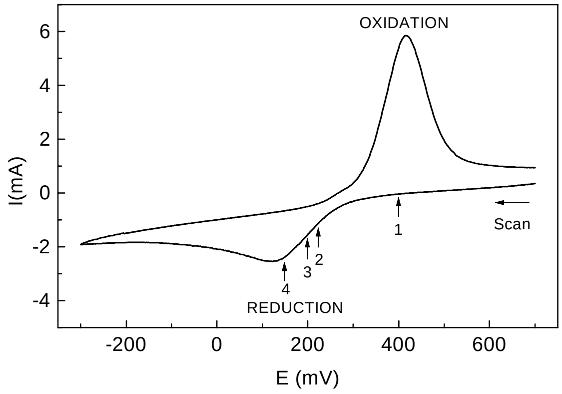


Figure 1 – Cyclic voltammogram of copper.

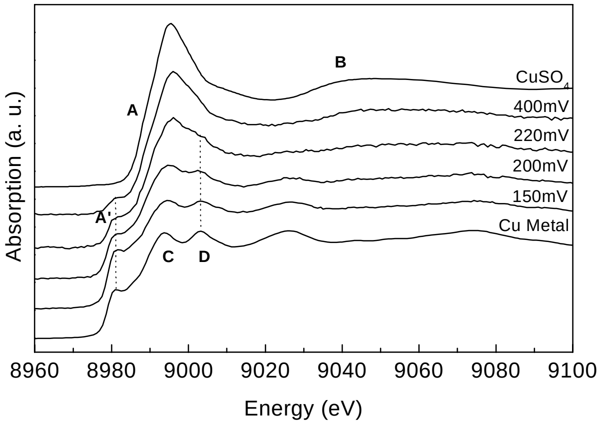


Figure 2 – XANES spectra.

transition appears at lower energy (A’). Features C and D are characteristic of fcc copper.

Strong modifications are observed at the near edge region as a function of the applied potentials. At 400 mV the appearing of a small pre-edge (A´) followed by the decrease in the intensity of the main edge is indicative of the beginning of Cu reduction in the matrix, nevertheless the majority of the Cu ions are in an oxidized state (Cu^{+n}). A linear combination of the XANES spectra of $CuSO_4$ and Cu metal indicated that the spectrum obtained at 400 mV is composed by the contribution of 80% of Cu^{2+} and 20% of Cu^0. It is important to point out that 15% of the Cu^{2+} signal comes from the solution, so the remaining 65% of Cu^{+n} ions are inserted in the polymer.

At 220 mV the increase of feature A´ and the clear split of the main edge with appearance of D feature indicates the further reduction of the copper atoms in the film. At 150 mV only the Cu metal features are observed. These findings evidence the inclusion of copper particles inside the polypyrrole film.

The EXAFS (Fig. 3) are in agreement with the XANES evolution. At 220 mV the oscillations present a dominant low frequency that corresponds to the oxygen shell around copper. The arrows show a small beat pattern that indicates the presence of another contributing shell as evidenced by the corresponding XANES spectrum.

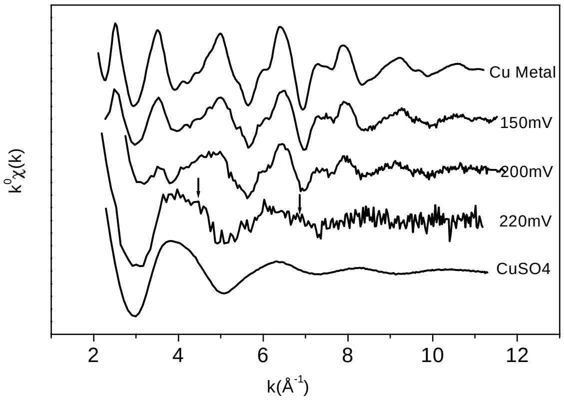


Figure 3 – EXAFS signal.

The Fourier Transform (FT) of the EXAFS oscillations (Fig 4) has initially (at 400 mV) only one peak centered at approximately 1.5 Å, uncorrected from the phase shift, due to the Cu-O correlation. The gradual vanishing of Cu-O and formation of Cu-Cu distances going from higher to lower potentials starts at 220 mV. At 150 mV only Cu-Cu distances are present. The appearance of next nearest neighbors shows the existence of medium order range.

The reduction in the FT height suggests the formation of small metallic particles (Greegor & Lytle, 1980).

A quantitative analysis of the FT first peak is presented at Table 1. The good quality of the fits can be seen in Fig 5.

At 220 mV only oxygen neighbors (N=5.2) at 1.93 Å with small disorder are found. These values are in between the Cu-O bond length in $CuSO_4$ and CuO and can be related to the existence of $Cu^{+n}(OSO_3^-)_n$ links in the polypyrrole film (Tourillon et al., 1986).

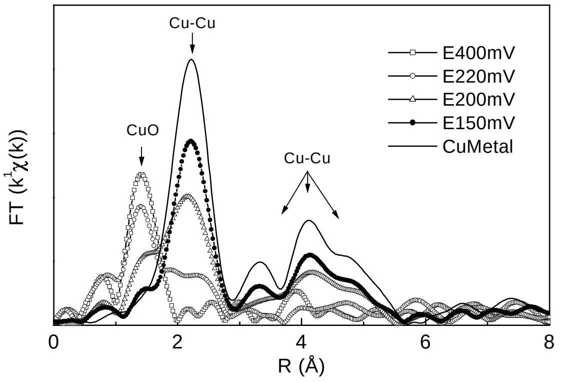
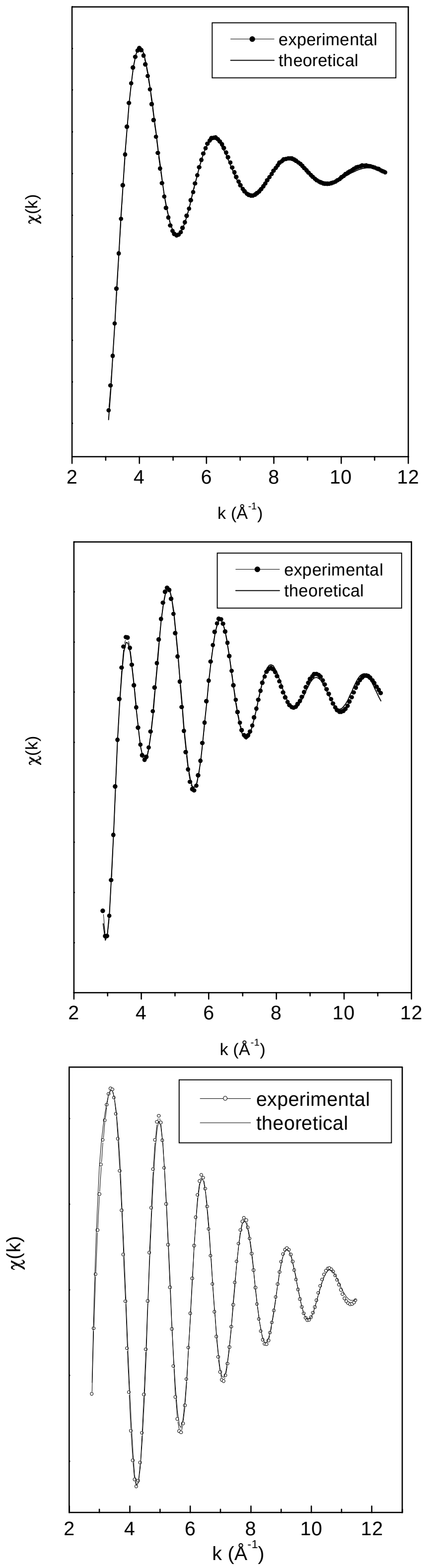


Figure 4 – Fourier transform of the EXAFS signal

Table 1 – Neighbors number (N), distance (R) and disorder (σ^2).

Sample	**N** Cu-O	R_{Cu-O} **(Å)**	$\sigma^2.10^3$ **(Å^2)**	**N** Cu-Cu	R_{Cu-Cu} **(Å)**	$\sigma^2.10^3$ **(Å^2)**
220mV	5.2 ±0.5	1.93 ±0.002	-2.9 ±0.6	-	-	-
200mV	2.7 ±0.5	1.98 ±0.002	-1.1 ±0.2	5.3 ±1	2.56 ±0.004	-1.6 ±0.3
150mV	-	-	-	7.3 ±.0.7	2.55 ±0.002	-1.4 ±0.3
Cu metal	-	-	-	12	2.56	-
Cu_2O	2	1.85	-	-	-	-
CuO	4	1.96				
$CuSO_4$	6	1.88	-	-	-	-

Figure 5 – Fitting at (a) 220, (b) 200 and (c) 150 mV.



At 200 mV, the significant reduction in the number of oxygen atoms and appearance of Cu-Cu bonds evidence a partial reduction of the oxide initially formed. At 150 mV the N value obtained (N=7.3) is smaller than the one found for bulk copper indicating the synthesis of small Cu clusters (Greegor & Lytle, 1980). Assuming the formation of spherical clusters the corresponding diameter of the Cu particles obtained at this potential is around 20 Å (Borowski, 1997).

3. Conclusions

XANES and EXAFS results evidenced the copper inclusion in polypyrrole in an ionic form, probably like $Cu^{+n}(OSO_3^-)_n$. The later reductive potential yielded metallic clusters. The reduction in the N value suggested the production of metallic particles with diameter around 20 Å.

The authors are indebted to LNLS staff and wish to acknowledge the financial support to this work by Brazilian agencies CNPq and FAPESP. Thanks to the help of Dr. Daniel Ugarte and Paulo C. Silva from LME/LNLS. FAPESP Proc. n^o 97/06967-6, 99/07872-4 and 95/06439-4, LNLS XAS proposal n^o 581/99.

References

Borowski M. (1997). *J. de Physique IV Coll.* ***7*** , Coll 2, Suppl. JPIII, 4, C2 259-260.

Greegor, R.B., Lytle, F.W. (1980). *J. Catal*. 63, 476-486.

Hepel, M. *(*1998). *J. Electrochem. Soc*. 145 (1), 124-34.

Koningsberger, D.C., Mojet, B.L., van Dorssen, G.E., Ramaker, D.E. (2000) *Topics in Catalysis* 10, 143-155.

Laborde, H., Leger,J-M., Lamy C. (1994). *J. of Applied Electrochemistry* 24, 1019-1027.

Ressler, T. (1997). Winxas: A New software package not only for the analysis of energy-dispersive XAS data. *J. Phys. IV France 7*, C2 269-270.

Tolentino,. H., Cezar, J. C., Cruz, D.Z., Compagnon-Caillol, V., Tamura, E., Martins Alves M.C. (1998). *J. Synchrotron Rad*. 5, 521-523.

Tourillon, G., et al. (1984). J. Electroanal. Chem. 178, 357-67.

Tourillon, G., Dartyge, E., Fontaine, A., Jucha, A. (1986). *Physical Review Letters* 57(5), 603-606.

Watanabe, N. and Alves, M.C.M. (1999), IX RAU, LNLS, Campinas, 77.

Received 31 July 2000 • Accepted 8 November 2000