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EXAFS IN DISPERSIVE MODE, A NEW TOOL FOR STUDYING IN SITU KINETICS: EXAMPLE OF ELECTROCHEMICAL INCLUSION OF COPPER SPECIES IN AN ORGANIC CONDUCTOR

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Abstract

The mechanisms and the kinetics for the electrochemical inclusion of copper species inside poly 3methylthiophene (an organic conducting polymer) have been studied in situ by dispersive x-ray absorption spectroscopy. The EXAFS results complement the three chemical steps previously deduced from XANES and the nature of chemical bonds formed during the inclusions processes are then precised:

- a fast $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$ reduction where the $\text{Cu}^{1+}$ ions are complexed by the O atoms coming from the dopant used during the polymer synthesis ($\text{SO}_3\text{CF}_3$)$^-$

- Fixation of the new synthetized $\text{Cu}^{1+}$ions on the S atoms of poly 3methylthiophene

- Growing of (111) metallic copper platelets.

Introduction

Organic conducting polymers represent a new class of material whose conductivity can vary continuously between an insulator–semiconducting state to a conducting state upon doping. Among all these compounds,
polythiophene and derivatives\(^{(1)}\) appear to be the most promising, due to their high stability against oxygen and moisture both in their doped and dedoped forms. Thus practical applications in the fields of organic batteries, display devices or photovoltaic systems have been tested. Moreover we have shown \(^{(2)}\) that small metallic particles can be electrochemically included in poly 3 methylthiophene PMeT which leads to new interesting catalytic properties. However these characteristics depend strongly on the chemical nature and the sizes of the particles.

A first set of XANES experiments\(^{(3)}\) on a cathodically polarized PMeT film immersed in an aqueous Cu Cl\(_2\) solution has been recorded in situ using the dispersive x-ray absorption spectroscopy. It has revealed the existence of three chemical reactions:

- i) a fast partial Cu\(^{2+}\) \(\rightarrow\) Cu\(^{1+}\) transformation (time constant = 27s) just when the polarization is applied.
- ii) A second kinetic increasing the Cu\(^{2+}\) content but with a slower time constant (~600 s).
- iii) The appearance of metallic copper clusters whose size increases according to the polarization time.

These electrochemical processes have been easily detected because:

- i) an x-ray absorption spectrum can be recorded in a time as short as 8ms with the dispersive scheme and
- ii) the XANES features of each Cu\(^{2+}\)-Cu\(^{1+}\) and Cu\(^{2+}\) species are well defined and mostly related to their ionic charge and their characteristic multiple scattering oscillations. Thus the evolution of concentration with the electrochemical treatment for each species have been determined. However, several parameters were not precisely known and were connected with:
  - i) the nature of the interactions between the dopant and the polymer,
  - ii) the local environment of the three copper species and
  - iii) the sites of complexation for Cu\(^{1+}\) and Cu\(^{2+}\).

We report in this work an in situ dispersive EXAFS study performed in the same conditions that the previous XANES investigations when PMeT is cathodically polarized in a Cu Cl\(_2\) aqueous solution. The data unambiguously show that:

- i) the first synthetized Cu\(^{1+}\) ions are complexed by the oxygen coming from the SO\(_4\)CF\(_3\)\(^{-}\) dopant
- ii) the second chemical step corresponds to the fixation of the Cu\(^{1+}\)ions on the sulfur atoms of PMeT and
- iii) the first metallic copper clusters grow with a (111) platelet like structure.

II Sample preparation and experiment

PMeT is electrochemically grafted on a Pt wire in CH\(_3\)CN-5 \(10^{-1}\)M N(Bu)\(_4\) SO\(_3\)CF\(_3\) - 5 \(10^{-1}\)M 3methylthiophene electrolytic medium. The Pt electrode is anodically polarized at 1.35 V/SCE (saturated calomel electrode) to obtain the doped conducting polymer where the oxidized polymeric chains are associated with the SO\(_3\)CF\(_3\)\(^{-}\) ions; in these conditions, the doping level of
PMeT lies in the range 25-30%. This modified electrode is rinsed, dried and put in a 3 mm thick electrochemical cell composed of a teflon ring covered by two kapton windows. A copper chloride solution (H2O-50 mM CuCl₂, PH=6) is then poured into the cell. A two electrodes configuration is used to perform the copper inclusions: the grafted electrode and a Pt wire.

The focussed x-ray beam is adjusted to pass through the polymer close to the Pt wire. Since the sample attenuates the x-ray beam by a factor of about 80, 340 ms were chosen to complete a single spectrum with about 10⁸ photons. In fact, each spectrum is the addition of 8 consecutive accumulations and the acquisition was repeated each 3.8s.

Comparing the jump of the absorption edge of the 3 mm thick cell filled with the CuCl₂ aqueous solution with and without the polymer, we know that at most 64% of the investigated volume is filled with the solution, while the polymer fibers take the remaining 36% of the volume.

The EXAFS spectra have been recorded using the dispersive EXAFS line at DCI. These experiments have been done using a triangular shaped Si (111) crystal bent in order to vary continuously the glancing angle of the incident x rays. According to the curvature and the average Bragg angle related to the energy of the edge of interest the 23 cm long crystal can reflect a bandwidth large enough to collect a full EXAFS spectrum. At the copper K-edge a 800 eV-wide band pass is achieved when the bending radius is about 7 meters. The selected beam converges and forms a 800 μ-wide focal spot. The electrochemical cell is inserted at this focus point. The transmitted beam is detected by a photodiode array made of 1024 sensing elements 25μ-wide each which is capable of measuring the high X-ray flux supplied by the synchrotron radiation source (10¹⁰-10¹¹ cps after the crystal). The energy resolution of this detector is determined by the sizes of the pixel and focal spot and the distance between them, and is computed to be 2.5 eV for the Si(111) (Fig.1). There is sufficient fast memory so that we are able to collect 60 spectra of 1024 data of 16 bit-long words at a time. In addition, a LOG-ROM table allows rapid computation and display of the 60 absorption spectra.

Results and discussion

XANES

The evolution of the XANES features with the polarization time reproduced exactly those already obtained during the first set of experiments. The three most characteristics spectra are displayed in Fig.1. The Cu²⁺ spectrum is shifted by 8.5 eV from the Cu⁺ edge and shows an important white line due to the octaedral symmetry of the six water molecules which complex the Cu²⁺ ion. The Cu²⁺-O bond length is the regular one 1.95 Å. During the electrochemical treatment, a bump appears on the low energy side with a decrease of the white line intensity relevant to the formation of Cu¹⁺ ions. For longer polarization time, metallic Cu particles are synthetized, characterized by the typical oscillations close to the edge.
EXAFS

A selected set of the $k^3$-weighted Fourier transforms using a 350 eV-wide window are shown in Fig. 2. One can observe as a first evolution (2a→2b) a shift of the principal peak towards the short distances, as well as a broadening ($\Delta t=160s$). After 168s this peak is splitted into two components (2c) whose intensity ratio inverts with the polarization time. The fast evolution of the system is illustrated in Fig. 3 which corresponds to two consecutive spectra separated by only 8 sec. If the electro chemical treatment is pursued, a shoulder appears at long distance on the main peak which becomes more and more pronounced. After 280 sec, a unique peak is observed which shifts continuously towards longer distances.

At this stage, the intensity of the FT peak increases, indicating that the atoms of the first shell have either a longer backscattering amplitude, or that their number increases. At the end of the process, the characteristic FT of metallic copper is obtained (2c), with in addition a remaining little peak at short distances. Fig. 4 abcd shows the filtered back transformed spectra of the first shell. These curves are characterized by a continuous decrease of the amplitude of the oscillations with the appearance of a beat node at about 250 eV (fig.4c) directly related to the splitting of the Fourier transform. This beat node clearly shows that two different atoms with a $\pi$ difference in their phase shifts contribute to the EXAFS oscillations. The only possibility to explain it involves O and S elements in the first coordination shell.

This hypotheses is reinforced by the EXAFS characteristics of Cu$_2$O and Cu$_2$S taken as references which exhibit a $\pi$ differences in their phase shifts (fig.5).

Thus the first chemical step corresponds to the formation of Cu$^{1+}$ ions complexed by O atoms coming from the (SO$_3$CF$_3$)$^-$ dopant used during the polymer synthesis.

The second step is clearly identified as the fixation of new synthetized Cu$^{1+}$ ions by the S atom of the polymer itself. Finally metallic copper clusters are formed. In order to precise the amounts of each copper species inside the polymeric matrix, we have calculated theoretical Fourier transforms using the Cu$_2$O, Cu$_2$S and Cu$^+$ amplitude and phase shift values.

Several conclusions can be pushed out:

i) the broadening of the peak observed after ~80 sec results from the presence of Cu$^{2+}-$0, Cu$^{1+}-$0 and Cu$^{1+}-$S species, ii) the splitting of the peak is reproduced when only Cu$^{1+}$-0 and Cu$^{1+}$-S are considered which excludes the presence of Cu$^{2+}$ atoms, iii) the further evolution of the FT for longer polarization time are relevant to the formation of metallic copper clusters in the matrix iv) finally the intensity ratio for the 3$^{th}$ and 4$^{th}$ shell is inverted when compared to the bulk cfc metallic copper : this implies that the early stages of metallic clustering involves a (111) platelet growth since
fig 4

fig 5
the distances inside the (111) planes are preferentially observed to the distances between planes.

However one must point out that two problems remain unsolved:

i) the discrepancy detected in the evolutions of the XANES and EXAFS characteristics for this experiment.

ii) the difference in the amplitude value of the TF obtained theoretically and experimentally which lies in the range of 25-30%. This last point should come from the chemical nature of the compounds taken as references. It's obvious that the different copper environment included in the polymer may be different of the crystallized materials.

The overall number of neighbours is probably different in the polymer from it is in the standards, even if the ionic bond lengths must be kept without major changes. An ab-initio fitting of the EXAFS data will give a more definite answer providing phase-shifts and amplitude can be extracted from suited samples.

**Conclusion**

The dispersive x ray absorption spectroscopy during the in situ electrochemical copper inclusion processes inside PMeT allowed us to precise all the chemical steps which lead to the formation of metallic copper aggregates:

- a rapid Cu$^{2+}$ $\rightarrow$ Cu$^{1+}$ transformation where the Cu$^{1+}$ ions are complexed by the oxygen atom coming from the SO$_3$CF$_3$ dopant.

- a second kinetic domain where the new synthetized Cu$^{1+}$ ions are fixed on the sulfur atoms of PMeT.

- the first metallic copper clusters grow with a (111) platelet like structure.

The dispersive absorption spectroscopy is well adapted to follow kinetic studies of chemical reactions and structural modifications. The good signal noise ratio gives the possibility of studying dilute systems.

Further developments of the present study deal with the initiation and the early stages of copper clustering.

Using isomorphous polyselenophene polymers and other dopants will give us new systems to check the ideas developed in this paper.

**References**

1) G. Tourillon "Handbook on conjugated electrically conducting polymers" Ed. T. Skotheim, Marcel Dekker 1 chap. 9 p. 294 (1986)
5) This is twice as much as we obtained with a 7cm long crystal. This aberration effect should be reduced by using an appropriate shape of the crystal in order to allow a bending close to the ideal elliptical profile.

Figure captions
- 1) Evolution of the copper XANES spectra versus polarization time:
  a) 0 sec, b) 160 sec, c) 168 sec, d) 200 sec, e) 460 sec.
- 2) Principal steps of evolutions of the $k^3$ Fourier transforms versus polarization time. Same steps as in fig. 1
- 3) $k^3$ Fourier transforms of two consecutive spectra separated by 8 sec. Note the inversion of the intensity ratio for the two peaks of the first shell.
- 4) Fourier backtransformed copper spectra. Same steps as in fig. 2.
- 5) Fourier backtransformed spectra of standards:
  a) aqueous CuCl$_2$ solution, b) Cu$_2$O, c) Cu$_2$S, d) metallic copper foil