

## Dispersive X-Ray Spectroscopy for Time-Resolved *In Situ* Observation of Electrochemical Inclusion of Metallic Clusters within a Conducting Polymer

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Electrochemically synthesized polythiophene is a very promising conducting polymer able to support tiny metallic particles which could be useful in various applications (e.g., conducting leads, catalysis, . . .). Time-resolved *in situ* investigation of the process of the inclusion of metallic aggregates has been achieved by dispersive x-ray absorption spectroscopy. The unique capability of this new structural tool comes from the association of the properties of synchrotron radiation with a photodiode array used as a position-sensitive detector.

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Conducting polymers represent an important class of materials in the fields of catalysis and energy storage, from both a fundamental and technological point of view. Moreover, the electrical properties of these metal-loaded polymers make them attractive as candidates for electrical leads in microelectronic circuits. Recently Tourillon *et al.*<sup>1</sup> and Tourillon and Garnier<sup>2</sup> reported catalytic properties of poly-3-methylthiophene (PMeT) loaded with Cu and Pt aggregates. The size of the aggregates and the polymer-cluster interactions are obviously important for control of the catalytic efficiency. An appealing feature of polythiophene is its good stability against moisture and oxygen.<sup>3</sup> Furthermore, it is of very high purity since it is synthesized electrochemically without any catalyst.

X-ray absorption spectroscopy is an attractive method to characterize the growth and interaction of polymer-supported metal clusters since information on oxidation states, coordination geometry, and bonding angles can be determined by extended x-ray absorption fine structure (EXAFS), and/or extracted from the x-ray absorption near-edge structure (XANES).<sup>4</sup> Furthermore, dispersive x-ray absorption spectroscopy<sup>5</sup> offers the possibility of *in situ* investigations of growth mechanisms and kinetics. This Letter reports the *in situ* observation of the electrochemical inclusion of copper into PMeT using specifically (i) the small size of the x-ray beam to probe spatially the PMeT grafted on a Pt wire, and (ii) fast data acquisition to follow the time-dependent evolution of the copper clusters in the polymer. Information on the copper electronic structure is contained in the near-edge photoabsorption spectra as is shown in Fig. 1 for  $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ , and metallic copper.

In interpretation of XANES for any element beyond the first row, the  $1s$  orbital is essentially a hydrogenic wave function which is nearly a delta function centered at the origin. The energy position of the edge is an indication of the effective charge density on the ab-

sorber, reflecting the tendency for an electron-deficient atom to bind the remaining electrons more tightly. In addition, because of the dipole selection rule, the shape of the edge carries information concerning both the type and symmetry of the ligands. The strength or weakness of low-energy peaks can indicate that certain  $1s$ -to-bound-state transitions are either allowed or disallowed, according to the local geometry. Moreover, it has been proven with use of scattering theory to describe the final state, that multiple scattering by neighbors must be invoked to explain the particular shape of edges.

As an example, the discernible shoulder just in the middle of the rise of the absorption cross section of metallic copper appears clearly when multiple-scattering calculations include the 24 atoms belonging to the third shell. This feature, as well as the first oscillations separated by 9 eV and the following one at 42 eV are completed when the fourth shell is taken into account.<sup>6</sup> The  $\text{Cu}^{2+}$  edge shape is related to the classical chemical shift (8.5 eV) because of the double ionization of the copper. The strong bound molecular resonance gives rise to the white line which is centered 15 eV above the metallic-copper edge. The location of such a resonance changes according to the distance of first neighbors (oxygen in octahedral coordination in the present case), as demonstrated by Natoli, who suggested that  $(E_r - V)R^2$  is constant, where  $E_r - V$  is the energy position measured from an average potential  $V$  of the material under consideration.<sup>7</sup>

Interpretation of the edge features of the  $\text{Cu}^{1+}$   $K$  edge is more controversial. On the one hand, it is claimed that the linear coordination of  $\text{Cu}_2\text{O}$  is directly responsible for an excitonically enhanced spectral peak in the rise of the absorption cross section.<sup>8</sup> On the other hand, it has been proposed that the excited electron in the XANES energy region is multiply scattered by the surrounding oxygens, and resonance then occurs.<sup>9</sup> Within that framework, the shoulder is related

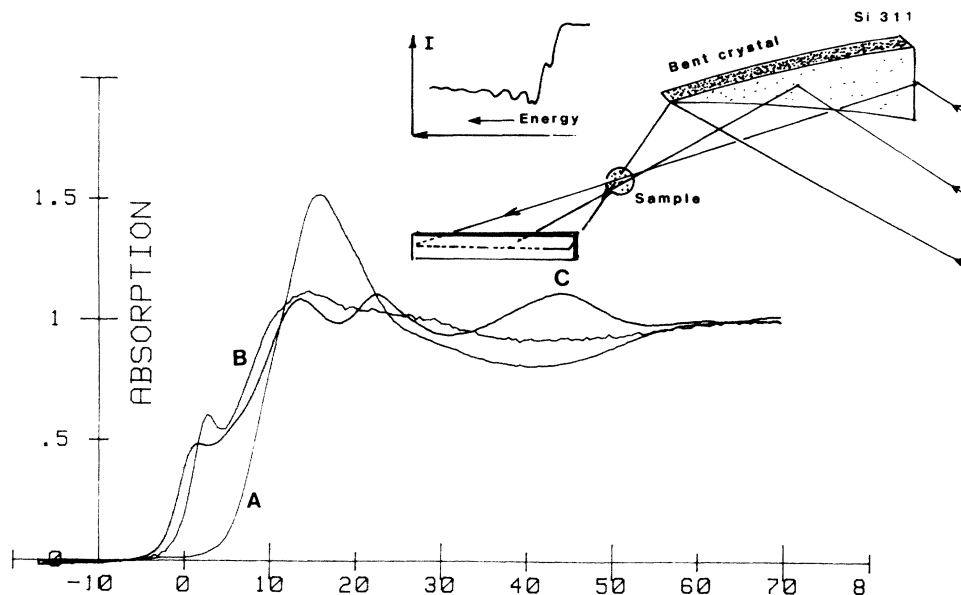


FIG. 1. Cu  $K$ -edge absorption spectra of three copper species obtained with a dispersive EXAFS using a Si(311) crystal: curve *A*, 50-mM aqueous  $\text{CuCl}_2$  solution; curve *B*,  $\text{Cu}^{1+}$ -bipyridine complex in acetonitrile; curve *C*, copper foil (photon energy 8978 eV is taken to be the reference energy 0). Data has been collected in 9600 ms for curve *A*, 300 ms for curve *B*, and 460 ms for curve *C*. Inset: Scheme of the dispersive EXAFS experiment.

to the linear O-Cu-O molecular cluster, which is stretched when the copper ion is deficient by one electron. This formalism works also for  $\text{Cu}^{1+}$ -bipyridine complex, since nitrogen sits in the first-neighbor position.

Two sets of spectra were taken to characterize the electrochemical steps which lead to (i) the complexing of  $\text{Cu}^{1+}$  ions by the polymer, and (ii) the formation of metallic-copper aggregates in PMeT.

First, before the start of the copper electrochemical inclusion, the aqueous  $\text{CuCl}_2$  solution, the polymer alone, and the polymer immersed in the solution were measured.

Second, the evolution of the copper  $K$ -edge spectrum was followed versus the cathodic polarization time. The kinetics of the inclusion processes were determined from the time dependence of  $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ , and  $\text{Cu}^0$  concentrations. These concentrations were obtained by deconvolution of the near-edge spectrum. Several independent sets of spectra were measured and analyzed independently and yielded similar results, as reported below.

These experiments have been achieved by use of a triangular-shaped Si(311) monochromator crystal bent in order to vary continuously the glancing angle of the incident x-ray photons, spread over 1 mrad. The diffracted beam converges and forms a 350- $\mu\text{m}$ -wide focal spot. Great care is taken to put the electrochemical cell just at the focal spot. Lateral adjustments are provided by remote-controlled translation stages. The transmitted beam is detected by the pho-

todiode array made of 1024 sensing elements that are able to measure the high x-ray flux supplied by the synchrotron radiation source ( $10^{10}$ – $10^{11}$  cps behind the crystal) (inset, Fig. 1). The Bragg angle-photon energy correlation of the curved crystal results in a pixel number–energy correlation in the detector. The energy resolution, estimated to be 1.5 eV (Fig. 1), is controlled by the size of the focal spot and the distance between it and the photodiode array. Data with very good signal to noise ratio may be collected at a very high rate, currently up to 3000 times faster than in the usual step-by-step scanning method. This dramatic gain opens new possibilities of achieving time-resolved spectra with a time scale down to 10 msec, depending on the concentration of the probed element.

The grafting of poly-3 methylthiophene (PMeT) on the Pt wire involves the oxidation of the monomer, 3-methylthiophene, 0.5 M in  $\text{CH}_3\text{CN}$  + 0.5 M  $\text{N}(\text{C}_4\text{H}_9)_4\text{SO}_3\text{CF}_3$  at +1.35 V/SCE (saturated calomel electrode). The polymer is formed directly in its doped conducting state, where the oxidized polymeric chains are associated with the  $\text{SO}_3\text{CF}_3^-$  ions; under these conditions the doping level of PMeT lies in the range 25%–30%, which is equal to the stoichiometry of the  $\text{SO}_3\text{CF}_3^-$  ions as determined by microanalysis. 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. An aqueous copper solution ( $\text{H}_2\text{O}$  + 50 mM  $\text{CuCl}_2$ ,  $\text{pH}=6$ ) is then added to the cell. Two electrodes are used to develop the copper inclusions (the grafted electrode and a Pt

wire).

The cell was aligned so that the focused x-ray beam passed through the polymer close to the Pt wire. Since the sample attenuates the x-ray beam by a factor of about 200, the collection time for each spectrum was chosen as 3.6 s, which corresponds to about  $2 \times 10^8$  photons/pixel. Comparing the jump of the absorption edge of the 3-mm-thick cell filled with the  $\text{CuCl}_2$  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.

We let electrolyte diffuse within the porous fiberlike structure of the polymer. The potential was applied as soon as the amount of copper  $\text{Cu}^{2+}$  ions became constant. The edge jump gives the initial amount of copper inserted in the polymer structure. Since the x-ray absorption of the dry polymer was measured, we were able to estimate that there are 10 monomers per  $\text{Cu}^{2+}$  ion.

Data acquisitions were spaced 7.19 s apart, twice the acquisition time of each spectrum. Figure 2 shows a series of spectra of the near-edge region of the Cu *K* edge. A rapid shift of the copper edge towards lower energy (by 8.5 eV) appears, in addition to a small bump in the rise of the absorption just at the edge. It clearly shows that the  $\text{Cu}^{2+}$  transforms into  $\text{Cu}^{1+}$  for

the first step of the reaction. This was checked by the formation of a red complex when the material was treated with a bipyridine solution. Conversely, a blue complex is observed with the  $\text{Cu}^{2+}$  ion. Since  $\text{Cu}^{1+}$  ions are unstable in aqueous solution, they must be stabilized by the polymer.

If the cathodic polarization is continuously applied, the changes in the XANES spectrum are consistent with the evolution of the system to a reduced species. The bump in the rise of the absorption is shifted slightly from a value consistent with  $\text{Cu}^{1+}$  to the  $\text{Cu}^0$  value. Also, the first two oscillations of the metallic spectrum which are separated by 9 eV emerge, and, fifteen or twenty minutes after starting polarization, characteristic oscillations of bulk metallic copper can be clearly seen (Fig. 2). These inclusion processes are fully reversible. Reversing the potential from -4 V to 1 V leads to  $\text{Cu}^0$  cluster dissolution into  $\text{Cu}^{1+}$  ions, followed by reappearance of  $\text{Cu}^{2+}$  ions on a similar time scale.

Then the overall electrochemical reactions proceed via several polarization time-dependent steps:  $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+} \rightarrow \text{Cu}^0$ . After this treatment, the conductivity of the polymer as measured *ex situ* increases by a factor of 3 ( $\sigma \approx 150 \Omega^{-1} \text{cm}^{-1}$ ). If it is completely undoped, the conductivity has a low value ( $\sigma \approx 10^{-8} \Omega^{-1} \text{cm}^{-1}$ ). According to just the  $\text{SO}_3\text{CF}_3^-$  ion con-

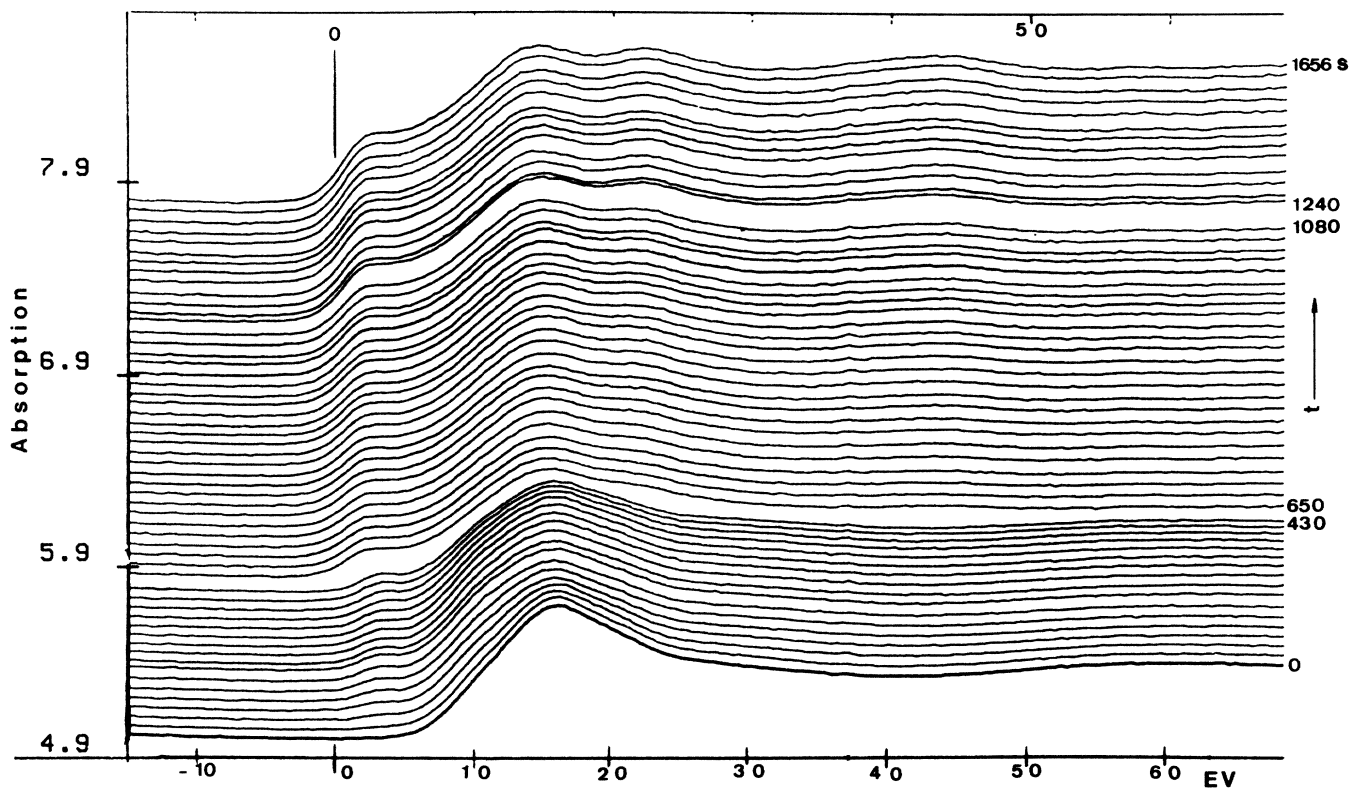


FIG. 2. *In situ* measurements of the evolution of the Cu *K* edge when PMeT is cathodically polarized in an  $\text{H}_2\text{O}-\text{CuCl}_2$  50-mM electrolytic medium.

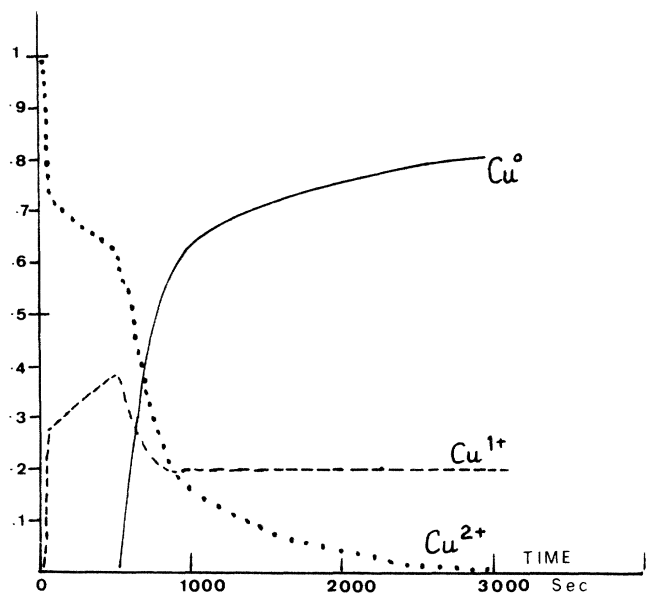


FIG. 3. Variations of the concentration of  $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ , and  $\text{Cu}^0$  inside the polymer vs the polarization time.

centration, a conductivity up to  $\sigma \approx 50 \Omega^{-1} \text{cm}^{-1}$  can be achieved.

The time-dependent concentration of species (Fig. 3) can be determined by a simple analysis in terms of a linear combination of the XANES spectra of  $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ , and metallic copper, as shown in Fig. 1. One has to stress that this linear combination is relevant to  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  species only. In that case, the environment of each species does not change during reduction. This is also true when copper clusters involve more than three shells, as demonstrated by Durham, Pendry, and Hodges.<sup>9</sup> It means that the very early stage of the time-dependent  $\text{Cu}^0$  content should begin more smoothly than is shown in Fig. 3.

Thus three different kinetic domains must be considered.

(1) The first is a fast  $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$  transformation where  $\text{Cu}^{1+}$  ions are stabilized by the polymer backbone and form complexes with the  $\text{SO}_3\text{CF}_3^-$  ions. assumption is consistent (i) with the well-known stabilization of  $\text{Cu}^{1+}\text{SO}_3\text{CF}_3^-$  by benzene<sup>10</sup> (giving rise to a crystallized compound), and (ii) with our EXAFS data, which show that  $\text{Cu}^{1+}$  ions are surrounded by oxygen which can come only from  $\text{SO}_3\text{CF}_3^-$ . This sulfur obviously comes from the PMeT since the binding with  $\text{SO}_3\text{CF}_3^-$  proceeds via O.<sup>11</sup> The time constant of this rapid fixation is 27 s. As mentioned earlier, the initial  $\text{Cu}^{2+}$  content is about ten monomers per cation. Since the  $\text{Cu}^{1+}$  concentration reaches 25% at the end of this first process, we infer that there is one  $\text{Cu}^{1+}$  for 40 monomers. If the Cu were only fixed on the

surface of the fiber whose diameter is 1500 Å, this ratio should be smaller, which implies that the whole fiber is involved in this process. This is also consistent with the increase of the diameter of the polymeric fibers only under the cathodic treatment (1500 Å  $\rightarrow$  3000 Å), as determined by scanning-electron microscopy. Conversely, if the fiber is just immersed in the copper solution without any polarization, the diameter does not change.

(2) The second kinetic domain is characterized by a longer time constant [600 s (Fig. 3)], where the  $\text{Cu}^{1+}$ -ion concentration increases from 25% to 40%. Since the doping level of PMeT is equal to 25%, no more  $\text{SO}_3\text{CF}_3^-$  ions are available for this process. Thus the newly synthesized  $\text{Cu}^{1+}$  ions should come from a direct interaction with the polymer backbone.

(3) The last step is dominated by the metallic-copper cluster formation. We assume that in the initial process, all the accessible sulfur sites of PMeT are saturated. Then, in the absence of a stabilizing agent in aqueous solution, the monovalent copper ions undergo disproportionation to produce  $\text{Cu}^{2+}$  ions and metallic copper. Additional  $\text{Cu}^{2+}$  is then drained from the solution, resulting in an increase in the absolute copper content, including all species, of the polymer 70% after 30 min of polarization as measured from the Cu absorption jump.

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