

## XANES AND EXAFS STUDIES OF Pt-DOPED POLYMERS

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A new application of noble metals dispersed in polymer matrices as heterogeneous catalysts has been developed in recent years. In the present work we have examined Pt ions incorporated in electroactive polymers namely polyaniline (PANI), poly(o-toluidine) (POT), poly(o-methoxyaniline) (POM), polypyrrole (PPY) and Pt ions incorporated in electro-inactive polymer poly(4-vinylpyridine) (PVP) by using x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) methods.

Polymers were doped with platinum at room temperature using appropriate precursor solutions of Pt<sup>+4</sup> or Pt<sup>+2</sup> compounds. The X-ray absorption spectra near the Pt L<sub>3</sub> and Pt L<sub>2</sub> absorption edges for Pt-doped polymers and several Pt compounds like (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub>, PtO<sub>2</sub> and H<sub>2</sub>[Pt(OH)<sub>6</sub>] were measured in transmission mode at room temperature at the station A1 in HASYLAB.

For all the spectra, the background was fitted below the edge, extrapolated by a linear function above the edge and subtracted. Then the spectra were normalized by means of a linear function fitted in the EXAFS region and extrapolated to the edge.

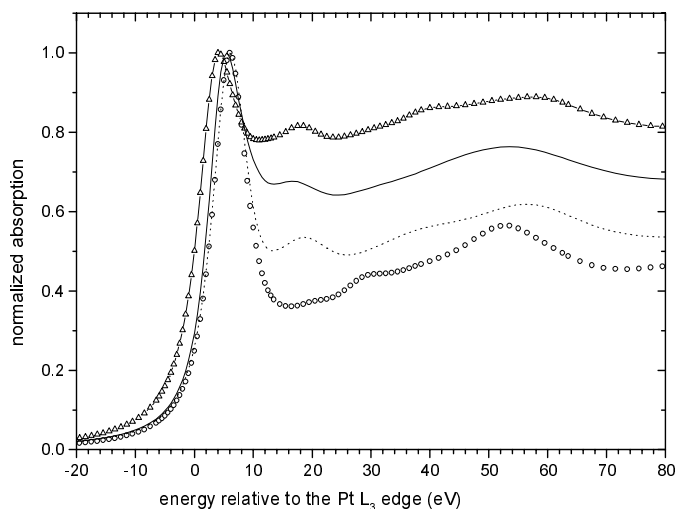
The XANES spectra at the Pt L<sub>3</sub> and Pt L<sub>2</sub> absorption edges contain information on the density of unoccupied

5d electron states around Pt ion. The height of the white line (WL) depends on valency of Pt ion and bond ionicity, as well. For given type of anions, WL of Pt<sup>+4</sup> ions is stronger than that one of Pt<sup>+2</sup> ions. From the other hand, WL of Pt<sup>+4</sup> ions bonded to oxygen ions is stronger than that one of Pt<sup>+4</sup> ions bonded to chlorine ions. The energy positions of the absorption edge and WL depend on the valency of Pt ion. The absorption edge and WL of Pt<sup>+4</sup> ions are shifted to higher photon energy in comparison to those of Pt<sup>+2</sup> ions.

A few examples of XANES spectra at the Pt L<sub>3</sub> edge are presented in Figure 1, in which the spectra were renormalized to the maximum of WL in order to illustrate chemical shifts of the edge. WL position of Pt/PVP sample is identical to that of PtO<sub>2</sub>, while WL position of Pt/PANI sample is shifted to lower energy and is placed between curves for (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> and PtO<sub>2</sub>. The small peak at about 18 eV above the edge is caused by hybridization of Pt 5d electron states with Cl electron states [1]. This peak is characteristic for Pt-Cl bond and its height depends on number of Cl ligands around Pt ion. It was found out that the Pt<sup>+4</sup> ions were partially reduced by electroactive polymers studied (PANI, POT, POM and PPY). In contrast, the Pt<sup>+4</sup> ions doped in electro-inactive polymer PVP have not been reduced.

Figure 1.

XANES spectra at the L<sub>3</sub> Pt edge for (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> (triangles), Pt/PANI (solid line), Pt/PVP (dotted line) and PtO<sub>2</sub> (circles).



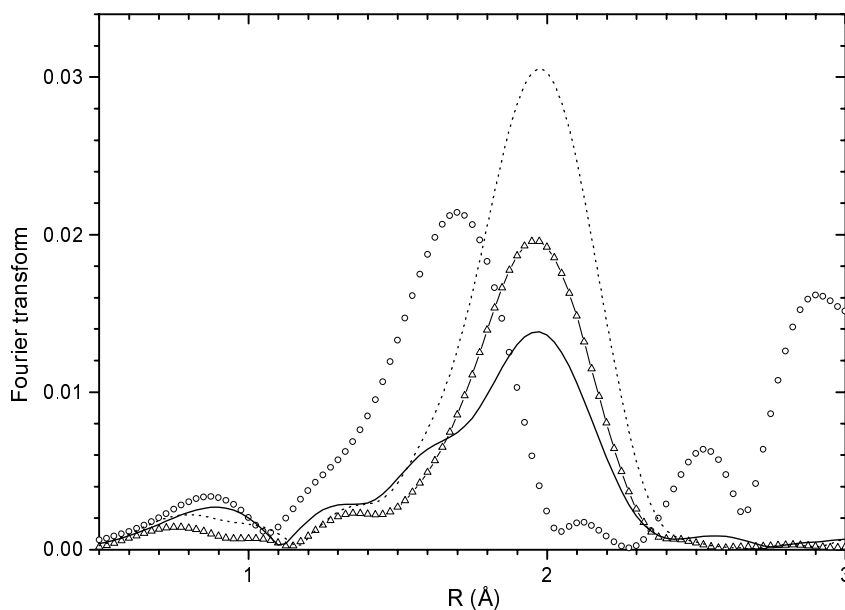


Figure 2. Fourier transforms of EXAFS spectra  $\chi^2 k^2$  for  $(\text{NH}_4)_2\text{PtCl}_4$  (triangles), Pt/PANI (solid line), Pt/PVP (dotted line) and  $\text{PtO}_2$  (circles).

In Fourier transforms (FT) shown in Figure 2, the peak at  $R = 2 \text{ \AA}$  originates from Pt-Cl bond. For the PANI sample an additional peak at  $R = 1.7 \text{ \AA}$  originating from Pt-O and/or Pt-N bonds is present. Unfortunately, it is difficult to distinguish O and N neighbours in such a case. The strong amplitude of Pt-Cl bond in case of Pt/PVP sample is evidence that the  $\text{Pt}^{+4}$  ion is surrounded by 6 chlorine ions. In contrast, the small amplitude of Pt-Cl bond in case of Pt/PANI can be interpreted that aqueous ligands and/or active groups of the polymer chain have replaced chlorine ligands.

Our studies showed that mainly Cl ligands were present around Pt ions in polymers. However the number of Cl neighbours strongly depends on polymer and on preparation procedure. Additionally, aqueous or oxygen

ligands could appear around Pt ions in part of samples depending on preparation procedure and individual properties of polymers.

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#### Reference

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