

Mechanistic Study of the Poly(3,4 Ethylene Dioxythiophene) Redox Process

Riccardo Ruffo^a, Ayse Celik^b, Uwe Posset^b, Claudio M. Mari^a and G. Schottner^b

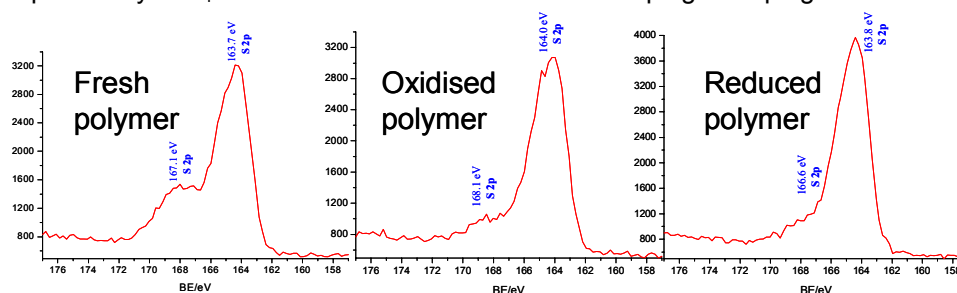
^aUniversity of Milano-Bicocca, Material Science Dept, Via Cozzi 53, 20135 Milano, Italy

^bFraunhofer Institut Silicatforschung (ISC) Neunerplatz, D-97082 Wuerzburg, Germany

riccardo.ruffo@mater.unimib.it

The polymers (PEDOTs) obtained from 3,4-ethylene dioxythiophene (EDOT) are interesting materials for application in electrochromic devices. For this reason the electrical, optical and spectro-electrochemical properties of PEDOTs were widely investigated in the last fifteen years,¹ while only little research work was devoted to understand the structure-morphology changes during the redox processes. In particular, some questions are still debated about the doping-undoping mechanism, responsible for colour change. Such electrochemical process is a redox reaction involving ion transport into and out of the polymer matrix to preserve its electroneutrality. The ion transport can simply be attributed to anions leaving and entering the polymer during the cathodic and anodic polarization, respectively. However, this mechanism might be more complicated also involving electrolyte cations. Aasmundtveit et al.², investigating (in-situ, by X-ray glazing incidence diffraction) the redox mechanism of PEDOT/tosylate films in lithium PF₆ solution, proposed both cations and anions of the electrolyte to be involved in the doping-undoping process and the tosylate anions to remain in the polymer.

To confirm this hypothesis, changes in the chemical composition (EDX and XPS) of chemically polymerized (by Fe³⁺/tosylate) PEDOT-tosylate films were investigated during the redox process in LiClO₄/propylene carbonate electrolyte. The binding energies for the sulphur atoms in PEDOT and in the tosylate ion are different as revealed by the S(2p) core-level XP spectra (164 and 167 eV respectively, see figure). Electrochemical and spectroelectrochemical properties as well as the morphology (SEM) of the layers were also studied. The experimental results do not confirm Aasmundtveit's suggestions, but highlight the partial substitution in the polymer matrix of the tosylate with the perchlorate ions during the redox cycles. The tosylate amount is reduced from around 17 % in the native polymer to about 7.5 % after cycling; this latter quantity might be correlated to the residual iron ion amount detected in all the samples. Only ClO₄⁻ anions should be involved in the doping-undoping mechanism.



[1]. L. B. Groenendaal, G. Zotti, P.-H. Aubert, S.M. Waybright, J. R. Reynolds, *Adv. Mater.* **2003**, *15*, 855.

[2] K.E. Aasmundtveit, E.J. Samuelsen, O. Ingnas, L.A.A. Pettersson, T. Johansson, S. Ferrer, *Synth. Met.* **2000**, *113*, 93.