

OC-40: Effects of High Frequency Ultrasound on Electroactivity and Doping Level of Conducting Polymers: Influence of OH· Radicals, Structure and Ions Mobility

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Materials such as conducting polymers (CPs), which combine polymer properties to good electrical conductivity, have been extensively investigated for the last 30 years. It led them to be used in many various applications like field effect transistors, light-emitting diodes, solar cells, protection of metals or biosensors to name a few. The easiness of preparation and the possibility to control experimental conditions by electrochemical technique make it the most employed way. Polypyrrole (PPy) stays one of the most studied CPs, particularly due to its easy deposition from aqueous and non-aqueous media, to its adherence to many types of substrates, its conductivity and stability. Chemical and physical properties of electrochemically deposited PPy have been shown to be strongly dependent on many parameters: the nature of solvent, the supporting electrolyte, the temperature, the deposition potential/current. Previous works showed that low frequency ultrasound (20 kHz) leads to denser, more resistant and conducting polymer films, with a thinner and more homogeneous surface structure. Much bigger compactness has also been reported by Atobe *et al.* for PPy films leading to very specific electrochemical behavior. Nevertheless, at low frequencies, cavitation phenomena can be very violent leading to partial destruction of the electrodeposited polymer film. At higher frequencies, the behavior of cavitation bubbles is more stable as described by Et Taouil *et al.*, and their destructive effect towards the polymer surface can be highly reduced.

1. Relation between structure and ions mobility in polypyrrole electrothesized under high frequency ultrasound irradiation

500 kHz ultrasound was shown to have very interesting effects on PPy elaborated with various counter-ions: perchlorate (ClO_4^-), p-toluenesulfonate (TS^-) and molybdate (MoO_4^{2-}). All these electroactive species move into the polymer film by diffusion, to ensure the electroneutrality. Many parameters may influence the global kinetics, driven by electronic transfer between the electrode substrate and the film as well as diffusion into the film. Mobility of ions within PPy films was then studied by electrochemical techniques, and it has been show that the ion size and charge are of first importance, but that the film compactness plays similarly a major role (Levi *et al.*, Raudsepp *et al.* and Kupila *et al.*). Specific electrochemical behavior was evidenced for sonicated PPy/ MoO_4^{2-} as well as unique ions repartition within the organic matrix, thanks to Glow Discharge Optical Emission Spectroscopy (GDOES).

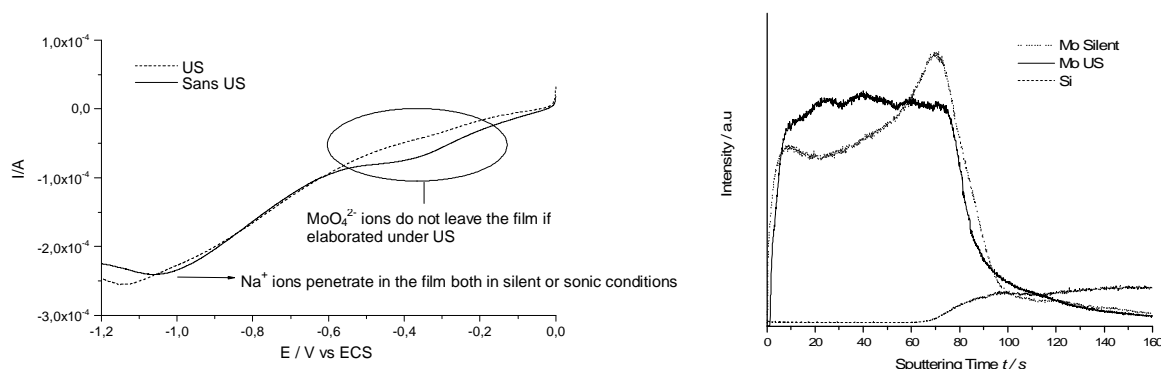


Figure 1: electrochemical and GDOES measurements of PPy films with molybdate counter-ions

This technique was used in original manner to study presence and repartition of doping ions in the film by Et Taouil *et al.* (2011). X-Ray Photoelectron Spectroscopy (XPS) analyses showed an increase in doping level for

sonicated PPy but electrical conductivity measurements let appear a decrease in conductivity for PPy elaborated under sonication.

Mass transfer enhancement has been evidenced by chronoamperometry. Since first stages of deposition, ultrasound leads to higher number of growth centers leading eventually to thinner and more homogeneous surface structure for thick deposits. Ultrasound is thus useful to control surface structure properties of such films. Changes in polymer growth for sonicated films were highlighted by Atomic Force Microscopy (AFM) while Scanning Electron Microscopy (SEM) showed thinner and more homogeneous surface structure for PPy elaborated under ultrasound. Much more compact structure for sonicated films is likely to be the cause of change in rate-determining steps during PPy reduction process. Very interesting ion-sieving behavior was attributed for PPy/MoO₄²⁻ films elaborated under ultrasound. Unique electrochemical properties and ions repartition within polymer matrix were assigned to these films, thanks to very dense structure.

2. Influence of OH· radicals generated by high frequency ultrasound on electroactivity and doping level of conducting polymers

Another interesting phenomenon, observed for low and high frequencies, is an increase in doping level for irradiated polymers. However, the reasons of such increase were still very ambiguous. Moreover, in spite of formation of OH· radicals by ultrasound propagation, no negative effect is seen on irradiated polymers' electroactivity while these radicals have been proved to be highly destructive towards redox properties of such organic films. Indeed, their high oxidative power can lead to irreversible film overoxidation which is characterized by two main phenomena:

reduction of charged polaron and bipolaron structures to neutral ones (film dedoping). Expulsion of counterions occurs to ensure electroneutrality

incorporation of carbonyl groups on β position of the aromatic ring breaking chain electronic conjugation.

This contribution means to clarify this point and also investigate the origin of the increase in doping level for conducting polymers synthesized under ultrasound, especially by investigating chemical effects of sonication.

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