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STUDIES OF INTERACTIONS BETWEEN CONDUCTING POLYMER AND ORGANIC VAPORS, APPLICATIONS TO CHEMICAL SENSING

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In order to understand the physicochemical mechanism involved in the organic semiconductor charge-transfer processes occurring upon doping of the films with vapor molecules different experimental approaches much be taken. The effect of vapor diffusion into the electrochemically deposited poly(pyrrole), PP and poly(N-vinylcarbazole), PNVCz, films was investigated by monitoring the mass change of the exposed polymer, absorbance changes in the absorption spectra, and the work function change due to the modulation of the Fermi level in the material. An important step in that investigation was to establish the link between the distribution of the active dopant within the surface and the bulk of the material (1).

The most straightforward strategy is the characterization of the responses due to variation of the oxidation state of the conducting polymer and the solubility related phenomena caused by sorption of the gaseous dopant in various conducting matrixes by steady-state and in-situ measurements. Those investigations require characterization of the polymer film during its prepatation. From the correlation between the theoretically predicted electronic transitions (2) and the experimentally obtained optical absorption spectra it has been possible to characterize the oxidized and reduced state of the synthesized polypyrrole films. The collected spectra show the existence of the polaron and bipolaron defect structure induced by the dopant anions and by the electrochemically applied positive or negative polarization potential . From the basic study of the polymer properties, the electron affinity was experimentally determined and the relative changes in the concentration of the redox active centers (polaron, bipolaron), due to the applied ionization potential, were evaluated. Incorporation of foreign molecules into the film also provides morphological changes which influence the mechanical properties of the material.

Combined electrochemical and microgravimetric measurements have been used to study the influence of the electropolymerization processes on deposition of N-vinylcarbazole (3) and pyrrole (4). By comparing the charge consumed in the deposition process and the total mass loading at the working electrode, the occurrence of the termination reactions could be seen (3). Furthermore, the quantitative EQCM study of the polymerization processe allows us to identify the properties which can be correlated with the sensitivity response of the conducting sample. The investigation of the PNVCz films applied as sensitive material indicates that the deposition mode affects the electroactivity of that layers. The is different behavior during vapor exposure dependent on the conditions of deposition, namly on the different concentration of water in the acetonitrile solution containing lithium perchlorate as an electrolyte salt . The results show that in the electrolyte with 2 Vol.% of H_2O a highly cross-linked, porous film is formed. The doping level of this film is much higher than that of the films grown from solutions with water content higher than 10 Vol.%. The study of the redox switching properties of these films in background electrolyte proves that both anions and cations participate in the charge compensation process. Furthermore, the microgravimetric data show that upon overoxidation, delamination from the substrate of the films grown from 2 Vol.% water occurs. The experimentally obtained information about he nature of the polymerized PNVCz films was used to characterize the film behavior upon the exposure to propylamine vapor. A comparison of the results was used for comprehensive improvement of reproducibility in adsorption and desorption process of the films .

Doping of conducting polymers during exposure to various vapors in a thermodynamically reversible manner indicates the formation of a charge transfer complex between the organic semiconductor and the electrically neutral guest molecule by the work function difference measurement (Kelvin Probe technique) and by the transmission optical spectra (5). From the simultaneously applied spectrophotometric and work function measurement it was possible to evaluate the changes in the distribution of electronic active state within the band gap energy of the organic semiconductors upon the chemical doping process (4). A careful analysis of the data obtained from the quartz microbalance measurements during exposure of the conducting polymer to different vapors shows a dependence between the film thickness and the mass response. From the existing relation between the sorbent coating and the amount of the vapor being absorbed a partition coefficient can be calculated. The deviations from linearity of that parameter are attributed to the changes of the permeability of the sorbent coating (6). For thicker films the interaction results in the diffusion process which occurs rapidly so that the adsorption appears to be the rate limiting process. As the result, the rate constants of mass transients for the absorption and desorption processes are found to increase with the amount of the vapor in the film (7).

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