POLYANILINE FILM GROWTH AND CHARGE PROPAGATION DYNAMICS AT MICRODIMENSIONAL ELECTRODES

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Since conducting polymers were discovered they have immediately gained recognition as fascinating and promising materials not only in the field of electrochemistry but in various branches of industry and applied sciences. They are applicable in many areas of technology including energy storage (batteries and supercapacitors), electronic devices, electrocatalysis, electrochromic displays, corrosion protection and analytical sensors although the redox processes they undergo are complex and still not fully understood. Such properties as an ease of electropolymerization and good adhesion to various surfaces, including metals, make them extremely useful in the preparation of functionalised modified electrodes. Considering a diversity of popular conducting polymers polyaniline (PANI) exemplifies a model system in respect to mixed electronic and ionic conductivity, satisfactory stability in acidic media, clear generating procedure, good adhesion to metal surfaces, etc. PANI has been already broadly studied with respect to methods of preparation and dynamics of electrosynthesis as well as its redox behavior and kinetics of charge transport. Our present work aims at further exploration of PANI films and is oriented mainly towards introducing microelectrodes into these studies. Microdimensional electrodes are of great utility for both fundamental and applied studies. Such features like high current density, substantially diminished ohmic drop and charging current, almost ideal independence of response to hydrodynamics, etc. explain their usefulness in electroanalysis, especially in many demanding situations. The same features allow one to study more thoroughly the already known but still challenging materials - like PANI.

We developed general means of fabrication of microdimensional PANI and described its growth and redox properties under different conditions (various microelectrode radii, various acid solutions). Owing to their small dimensions and the ability to reduce ohmic drop, microelectrodes seem to be a useful tool for characterization of charge transport properties within PANI films. We demonstrated that the PANI layer thickness had a profound effect on the overall kinetics of the systems charge propagation as it occurred to be possible to generate a polymer coating of a considerable thickness in relation to the microelectrode dimensions. We also found that PANI films were electrodeposited as hemispheres on platinum microdisk electrodes, and the size of PANI microdeposits largely exceeds the size of Pt microdisks. Consequently, it is likely that the apparent surface area of the electrode is effectively larger than the geometrical one of the Pt microdisk.

An important feature of microdimensional PANI films is that they are characterized by the increasing dynamics of charge transport with the increasing loadings of PANI. The explanation is complex but the effect may originate from changes in the morphology (porosity) of PANI microdeposits, in addition to apparent changes in the effective surface area of microdisc electrodes.