

Electrochemical Charging of Hybrid Organic-Inorganic Films Composed of Poly(3,4-Ethylenedioxythiophene)/PEDOT and Tungsten Oxide

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Over the last several years, there has been growing interest in conducting and redox polymer films on electrodes due to the prospects of their applications in various microtechnological systems that include charge storage devices (e.g. redox supercapacitors). Out of many conducting polymers, poly(3,4-ethylenedioxythiophene) or PEDOT has recently been of interest as a particularly stable, highly-conductive and electroactive organic polymer. For example, PEDOT has been used as an anti-static coating, a conductive electrode in light emitting diodes, and as a material for electrochromic devices. It is commonly accepted that PEDOT is very stable in its doped state and reaches conductivity as high as 200 S cm^{-1} . Although the latter parameter is dependent on the film morphology, the overall conductivity of the polymer in the oxidized state is high. The exact nature of electrochemical processes occurring in PEDOT films is fairly complex, and the system is believed to undergo several overlapping fast redox transitions characterized by high diffusion coefficients for charge propagation, namely on the level of 10^{-7} or $10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The above properties make PEDOT attractive as a potential material for fabrication of composite matrices with immobilized metals, functionalized dopants, redox and reactive centers.

PEDOT can be synthesized both chemically and electrochemically through oxidation of the corresponding monomer from mostly organic nonaqueous and sometimes aqueous solutions. In the latter case, application of water as a solvent is somewhat limited due to the low solubility of a thiophene monomer. The possibility of use of an aqueous anionic micellar

medium containing sodium dodecyl sulfate to electrosynthesize robust and conducting PEDOT films on inert electrode substrates have recently been explored. The fact of the observed improvement of the electrosynthesis and physicochemical properties of PEDOT by application of anionic surfactants in aqueous including acid media has prompted us to consider electrodeposition of PEDOT using tungstate/sulfuric acid micellar aqueous medium. The approach resulted in the fabrication of a robust electroactive organic-inorganic composite (hybrid) film in which within the PEDOT matrix inorganic metal oxide (WO_{3-x}) is immobilized. Among various metal oxides, WO_{3-x} has found application in electrochromic devices, semiconductor gas sensors, catalysis including electrocatalysis and photocatalysis. Our composite (hybrid) organic/inorganic systems can be fabricated as thin and moderately thick (μm level) films on electrode surfaces. During electrodeposition by potential cycling composite microstructures of PEDOT and nonstoichiometric tungsten oxide (WO_{3-x}) are produced. Due to the existence of electrostatic attraction between negatively charged WO_4^{2-} structural units of tungsten oxide and positively charged (oxidized) conducting polymer (PEDOT), the composite material cannot be considered as a simple mixture of inorganic and organic components. It comes from scanning electron microscopic studies that the morphology of the composite film is granular, but its structure is fairly dense. The fact, that the reversible and fast redox reactions of tungsten oxide lie in the potential range where PEDOT is conductive, allows the system to operate reversibly and reproducibly in acid electrolytes. Our hybrid system is characterized by very rapid redox reactions, high effective diffusion coefficient for charge propagation and excellent stability. The whole concept may lead to the fabrication of composite (hybrid) films having very promising properties for effective accumulation of charge and showing high current densities at electrochemical interfaces particularly to the construction of high density charge storage redox capacitors.