

Polypyrrole and composite electrodes for electrochemical supercapacitors.

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Polypyrrole is an attractive material for the fabrication of electrodes for electrochemical supercapacitors (ES) due to its high specific capacitance (SC) and good electrical conductivity. Polypyrrole (PPy) films for ES can be prepared by anodic electropolymerization from aqueous monomer solutions containing anionic additives or by chemical polymerization. The deposition of PPy on non-noble substrates presents difficulties related to anodic oxidation and dissolution of the substrates. It is known that the chemical and electrochemical passivation of the substrates for electropolymerization of PPy usually results in the formation of insulating films with low capacitance. The formation of such films results in a reduced total capacitance of the electrodes.

The problem of anodic deposition of PPy on stainless steel and Ni substrates was addressed by the use of advanced polyaromatic additives. The role of the additives is multifunctional. The anionic additives provided charge compensation of PPy during electropolymerization. Moreover, the additives reduced the electropolymerization potential and enabled the fabrication of uniform and adherent films. The results indicated that adsorbed additives, containing conjugated double bonds, provided wiring between the substrate and the growing PPy films and promoted charge transfer during electropolymerization.

The adhesion of the films, prepared using different anionic additives, was investigated using ASTM D3359 tape test. The deposition yield has been studied as a function of the additive concentration and pyrrole concentration in solutions. The results indicated that there is no induction time for the electropolymerization of PPy on the stainless steel and Ni substrates and the galvanostatic deposition yield and film thickness can be controlled.

New anionic additives were used for the fabrication of PPy nanoparticles with particle size of 50-100 nm. Fibrous PPy particles were prepared by chemical polymerization in the presence of new oxidants and dopants. The use of porous Ni plaque current collectors allowed the fabrication of electrodes with materials loading in the range of 10-35 mg cm⁻². Galvanostatic and pulse electropolymerization were used for the impregnation of current collectors. In another strategy, the impregnation of the current collectors was achieved using slurries, containing well dispersed PPy nanoparticles.

The PPy electrodes showed specific capacitance of 5.4 F cm⁻² and excellent cycling stability. Moreover good capacitance retention was achieved at scan rates of 2-100 mV s⁻¹.

Further progress was achieved by the use of multifunctional anionic dopants for the fabrication of composites, based on PPy. The new anionic dopants showed strong adhesion to the inorganic surfaces due to their ability to form interfacial chemisorption complexes. The results obtained for the anionic molecules with COO⁻, SO₃⁻ groups and different number of OH groups were analyzed. The adsorption mechanism was studied using Fourier transform infrared spectroscopy. The adsorption mechanisms involved the interaction of surface metal atoms and their complexation with adjacent OH groups or adjacent COOH and OH groups of the organic molecules. The polyaromatic dopant molecules showed strong adsorption on carbon nanotubes and graphene and allowed their efficient dispersion and charging. The adsorption mechanism is attributed to π - π interactions. The increase in the number of OH groups of the molecules resulted in improved suspension stability. The influence of dopant molecule size, structure and nature of functional groups on dispersion efficiency was investigated. The results allowed the use of new additives for the co-dispersion of different materials such as PPy, MnO₂, carbon nanotubes and graphene.

The PPy and composite films were prepared and investigated by electron microscopy. The investigation confirmed the formation of composite films. The incorporation of MWCNTs into the polypyrrole during electropolymerization resulted in the formation of porous films.

The composite polypyrrole-MWCNT and PPy-MnO₂ films showed improved capacitive behaviour compared to that of the pure PPy films. The capacitive behaviour was investigated as a function of deposition conditions, such as bath composition and anodic current density. The capacitive behaviour of the films prepared using different additives was compared. A highest SC of 410 F g⁻¹ (6.7 F cm⁻²) was obtained at a scan rate of 2 mV s⁻¹ for the composite films. The composite films showed good capacitive behavior at scan rates in the range 2-500 mV s⁻¹. The PPy films containing MWCNTs showed significant improvement in capacitive behaviour at high scan rates, compared to pure PPy and PPy-MnO₂ films. Impedance spectroscopy studies showed that the incorporation of MWCNTs into the PPy films resulted in reduced resistance. The composite films showed excellent cycling stability. The PPy and composite materials prepared using multifunctional anionic dopants are promising materials for ES.