Chemical and electrochemical fabrication of polypyrrole and composite electrodes for electrochemical supercapacitors using multifunctional anionic dopants.

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The growing interest in application of polypyrrole (PPy) for electrodes of electrochemical supercapacitors (ES) is attributed to high specific capacitance and electrical conductivity, low cost and chemical stability of PPy. Electropolymerization is an attractive method for the fabrication of PPy electrodes for ES. In this approach, anodic polymerization of PPy allows the pyrrole monomer, dissolved in a solvent, containing an anionic dopant, to be oxidized at the electrode surface by the applied anodic potential, forming a polymer film. PPY particles can be obtained by chemical polymerization from pyrrole solutions, containing anionic dopant and oxidant.

The goal of this investigation was the development and testing of PPy and nanocomposite materials and their application for charge storage in electrodes of ES. The new approach is based on the use of multifunctional anionic dopants and advanced current collectors.

The investigation of aromatic molecules from catechol, salicylic acid and chromotropic acid families resulted in a discovery of efficient anionic dopants, which provided high conductivity of PPy films, prevented substrate oxidation and dissolution during electropolymerization and reduced electropolymerization potential. Moreover, new anionic dopants provided improved adhesion by complexation of metal ions on substrate surface. The efficiency of anionic dopants from catechol, salicylic acid and chromotropic acid families were compared. The measurements of film adhesion according to the ASTM D3359 standard showed that adhesion strength corresponded to the 4B classification. New anonic dopants promoted charge transfer during electropolymerization. The size of PPY particles prepared by chemical polymerization was reduced by the use of new anionic dopants. Moreover, the polyaromatic anionic dopants, such as pyrocatechol violet allowed efficient dispersion of carbon nanotubes. It was found that carbon nanotubes can be electrophoretically deposited on various anodic substrates using anionic dopants as charging and dispersing agents. The electropolymerization of PPy and electrophoretic deposition of carbon nanotubes can be combined for the fabrication of composites. PPy-carbon nanotube composites were also prepared by a chemical polymerization method.

New electrochemical and chemical strategies were utilized for the fabrication of PPy and PPy – carbon nanotube electrodes for ES using non-noble substrates, such as stainless steel and Ni. The method allowed the fabrication of electrodes, using commercial Ni plaque current collectors, designed for high power battery applications and Ni foams. The problems related to the oxidation and dissolution of high surface area current collectors were avoided using new anionic dopants with chelating properties. The results obtained using stainless steel, Ni foil, Ni plaque and Ni foam current collectors were compared. The use of Ni plaque and Ni foam current collectors offered the advantage of high materials loading. The materials loading of 5 $mgcm^{-2}$ was achieved using Ni plaque current collectors. The material loading of 20 $mgcm^{-2}$ was achieved using Ni foams. Ni plaques were impregnated with PPy or composite PPy-carbon nanotube materials galvanostatically and by pulse deposition methods.

The specific capacitance (mass normalized C_m and area normalized C_s) were obtained from cyclic voltammetry and impedance spectroscopy data using Na_2SO_4 electrolyte. The C_m of 510 Fg^{-1} and C_s of 10 Fcm^{-2} were obtained. The use of Ni foams allowed 70% retention of C_s with increasing scan rate from 2 to 100 mVs^{-1}. The investigation of cycling stability showed capacitance retention of 95% after 1000 cycles.

The use of pulse deposition offered advantages of improved impregnation of current collectors, enhanced porosity and higher capacitance. The influence of dopant structure on film adhesion, size of PPY particles prepared by chemical synthesis method, C_s and C_m, cycling stability and capacitance retention at high scan rates was investigated. Polyaromatic anionic dopants from phenol family allowed improved dispersion of carbon nanotubes and their deposition at high deposition rates. The use of PPY –carbon nanotube composites allowed improved capacitance. The PPy and composite materials prepared using multifunctional anionic dopants are promising materials for ES.