Electrodeposition of polypyrrole and composite electrodes for electrochemical supercapacitors

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Polypyrrole (PPY) is under intensive investigation as a promising electrode material for supercapacitors due to its high conductivity, light weight, large voltage window, low cost, and the ease of synthesis. PPY films can be fabricated on inert metals (e.g. noble metals). However, dissolution and oxidation of active metals (e.g. stainless steel) occur during the electropolymerization process. Therefore, electrodeposition of PPY films on active metals is an important area, consider its commercial application. In addition, the low cycling stability of such electrodes caused by swelling and degradation of PPY during the charge-discharge process is another subject, which needs further study.

In this work, multifunctional additives from catechol, salicylate and chromotropic acid families were considered to be added into PPY films, in order to improve the adhesion of such films fabricated on active metals. Meanwhile, two strategies to improve the capacitive behavior of PPY based electrodes have been proposed. One of them was fabrication of PPY-MWCNTs (multi-wall carbon nanotubes) composites, since the high surface area and high conductivity of MWCNTs was assumed to improve the charge-discharge efficiency of PPY based electrodes. But the low dispersibility of MWCNTs in water is a big problem need to be solved. Another option was using advanced current collectors (e.g. Ni plaques) as substrates. Those substrates have porous structures, which allow more space for ions to transfer in and out during the charge-discharge process and benefit the capacitive performance. Fabrication of PPY and composite films was developed using different electrodeposition methods.

The PPY and composite PPY-MWCNTs films were fabricated by electropolymerization and combined with electrophoretic deposition (EPD) on stainless steel and Ni plaque. The conditions of electrodeposition such as current density, deposition time and concentration of solutions were optimized in order to obtain uniform and adherent films. Multifunctional anodic additives were investigated to find their effect on adhesion of PPY films and dispersion of MWCNTs. The morphology and properties of PPY and composite films were characterized by SEM, adhesion test and electrochemical tests which including cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

According to the experimental data, it is proved that the dissolution and oxidation of metals have been minimized by adding those additives mentioned before, since no induction time exists during the electrodeposition process. The strong adhesion of PPY films is considered by bonding between additives and metals. Two OH groups lose two protons and form bonding to metal substrates during electropolymerization process. It is also found that those multifunctional additives are absorbed on the MWCNTs by π-π stacking and contribute to the homogeneous dispersion of MWCNTs by repulsing each other. In addition, negative charges required in EPD process also provided by those additives. The results also show that excellent cycling stability can be achieved using Ni plaque combined with pulse deposition. PPY films fabricated in this way kept their 91% capacitance after 1000 cycles. Meanwhile, the porous structure of Ni plaque also offers advantages of significantly higher materials loading and superior capacitive behavior compared to thin film electrodes formed on stainless steel. The specific capacitance of sample with high density of 2 mg/cm^2 can even reach 320 F/g.

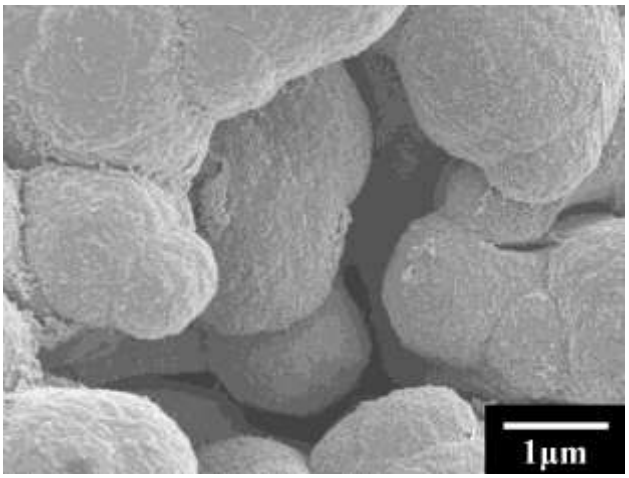

Fig.1 SEM picture of PPY films on Ni plaque by pulse method.