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Influence of current collector on capacitive behavior and cycling stability of Tiron doped polypyrrole electrodes

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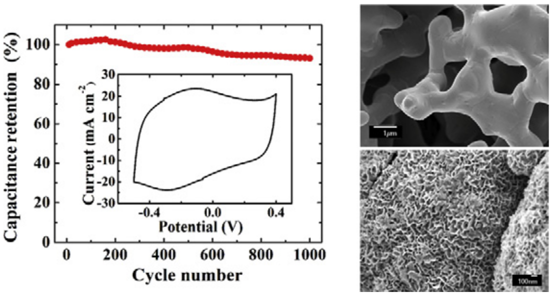
HIGHLIGHTS

- Polypyrrole electrodes for supercapacitors were prepared by electropolymerization.
- Tiron was used as an anionic dopant for deposition on Ni foils and plaques.
- The use of Tiron allowed the fabrication of adherent films.
- Ni plaque based electrodes allowed higher capacitance and good capacitance retention.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we demonstrate the feasibility of electrodeposition of adherent polypyrrole (PPy) films on Ni substrates using Tiron as an anionic dopant. Compared to other aromatic sulfonate dopants, Tiron offers the advantages of higher charge to mass ratio and chelating properties, which are beneficial for the efficient charge transfer during electropolymerization and fabrication of adherent films. The use of Ni plaque current collectors allows higher capacitance and higher PPy loading compared to Ni foil current collectors. Moreover, the use of Ni plaques allows significant improvement in capacitance retention at high scan rates. The problem of poor cycling stability of PPy films on Ni foil current collectors is successfully addressed by the use of Ni plaques. The electron microscopy studies and impedance spectroscopy measurements during cycling provide an insight into the factors, controlling capacitance retention. The results indicate that for pure PPy electrodes the mass normalized specific capacitance of 339–451 F g^{-1} and area normalized specific capacitance of 0.4–0.95 F cm^{-2} can be achieved for material loadings of 0.84–2.80 mg cm^{-2}. The PPy electrodes formed on Ni plaque current collectors are promising for applications in electrochemical supercapacitors.

1. Introduction

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 [1,2]. Many investigations have been conducted with the objective to utilize high specific capacitance [2,3] of PPy in ES. The capacitive behavior of PPy with theoretical capacitance of 620 F g^{-1} results from redox reactions, which allow charge storage in the bulk of the electrode material. The specific capacitance of PPy is lower than that of other active materials for ES, such as MnO_2 [4,5]. However, the fabrication of MnO_2 electrodes requires the use of conductive additives (15–30%) and binders (5–10%) [6–9], which reduce the specific capacitance of the composite material. The use of conductive additives and binders can be

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avoided in pure PPy electrodes due to high conductivity, binding and film forming properties 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 [2,10]. Many studies were focused on the development of advanced anionic dopants for PPy electropolymerization. Relatively high electrical conductivity and thermal stability of PPy films was achieved using aromatic anionic dopants [11–14]. It was shown that with the variation of the dopant anion, the conductivity of the PPy thin films can differ by three orders of magnitude [15]. The investigation of aromatic dopants, containing sulfonic anionic groups, showed that the conductivity of PPy films increased with increasing charge/mass ratio of the dopant molecules [12]. These studies generated significant interest in the use of 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron), which has higher charge/mass ratio, compared to that of toluenesulfonate, naphthalene sulfonate, naphthalene disulfonate and other aromatic sulfonate molecules used as anionic dopants for PPy electropolymerization [12]. The investigations of electropolymerization of PPy on Al alloy substrates in the presence of Tiron resulted in a discovery of its important properties [16]. It was shown that Tiron allowed the formation of continuous films and promoted charge transfer during electropolymerization. Compared to *p*-toluene sulfonic acid sodium salt [16], Tiron reduced deposition potential by 0.5 V, preventing Al alloy corrosion during electropolymerization. Moreover, the films prepared using Tiron as an anionic dopant and charge transfer mediator showed improved conductivity and adhesion. The use of Tiron allowed the formation of adherent PPy films on stainless steel substrates by electropolymerization from aqueous pyrrole solutions [17]. The films were investigated for application in ES [17]. These results also indicated that Tiron strongly adsorbed on the Al alloy and stainless steel surfaces [16,17]. It is in this regard that Tiron is a strong complexing agent [18–20], which belongs to the catechol family of aromatic materials. Recent investigations showed that materials from catechol family exhibit strong adhesion to various inorganic materials [21–24]. The chelating properties of Tiron and other catecholates are related to hydroxyl groups bonded to adjacent carbon atoms of the aromatic ring. The proposed chemisorption mechanism involved the deprotonation of the phenolic hydroxyl groups of the catechol and chelation of metal ions on the inorganic surface [21,22]. It is important to note that catecholate bonding facilitated charge transfer between inorganic and organic materials [25]. The strong adhesion of catecholates to various surfaces in the solutions of high ionic strength is especially attractive for the development of polymer film electrodes for electrochemical devices, containing aqueous electrolytes.

The goal of this investigation was the electropolymerization of PPy on Ni substrates, using Tiron as an anionic dopant, for the fabrication of electrodes of ES. The important finding was the possibility of electropolymerization of Tiron-doped PPy on commercial Ni plaque current collectors with high surface area, which allowed improved contact with active material. The results presented below indicated that high capacitance, good capacitance retention at high scan rates and good cycling stability can be achieved in pure PPy electrodes with relatively high materials loading. The analysis of the electrochemical impedance of PPy electrodes during cycling and corresponding SEM data provided an insight into the mechanism of capacitance decrease during cycling and paved a way for the fabrication of PPy electrodes with good cycling stability. The comparison of the experimental data for Ni foils and Ni plaque substrates showed that the use of Ni plaques offers benefits of significantly higher capacitance and materials loading, good capacitance retention at high charge–discharge rates and good cycling stability.

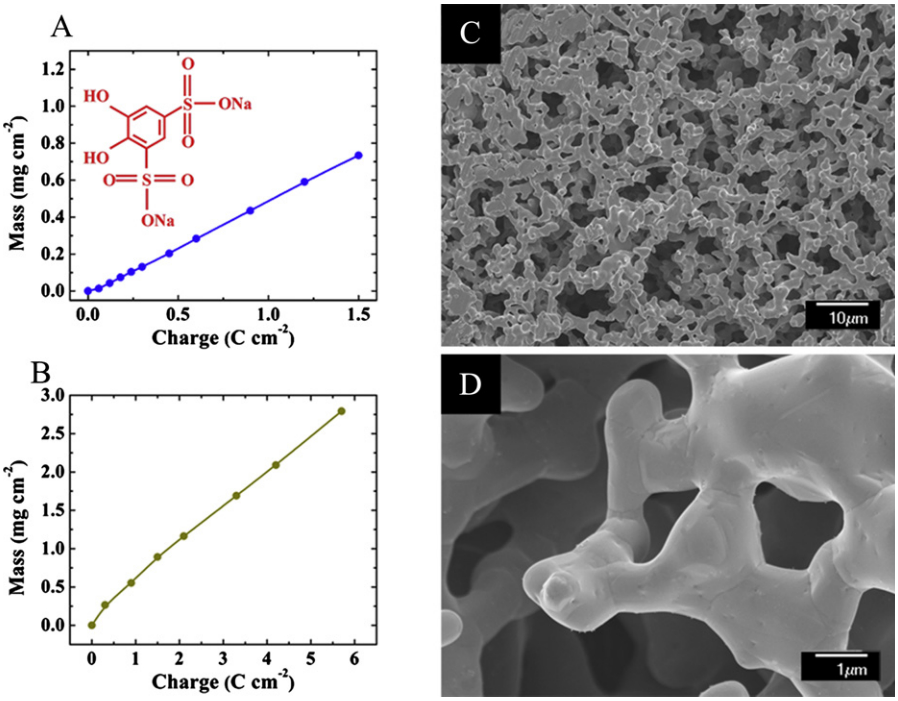

Fig. 1. (A, B) Deposit mass versus charge passed for deposition on (A) Ni foil (inset shows a chemical structure of Tiron dopant) and on (B) Ni plaque substrates and (C, D) SEM images of Ni plaques at different magnifications.