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Influence of dopants and carbon nanotubes on polypyrrole electropolymerization and capacitive behavior

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ABSTRACT

In this work we demonstrate the feasibility of electropolymerization of polypyrrole (PPy) films on stainless steel substrates using alizarin red (AR) and anthraquinone-2-sulfonic acid sodium salt (AQ) as anionic dopants. The results indicate that AR offers the advantage of reduced electropolymerization potential. The comparison of experimental data for AR and AQ provides an insight into the influence of the dopant molecular structure on electropolymerization of PPy. The chelating properties of AR allow the fabrication of adherent films. Moreover, the use of AR allows the dispersion and charging of multiwalled carbon nanotubes (MWCNT) and their electrochemical incorporation into the PPy films during electropolymerization. Scanning electron microscopy observations show the formation of porous films, containing MWCNT, coated with PPy. The composite PPy-MWCNT films offer advantages, compared to pure PPy films, for application in electrodes of electrochemical supercapacitors (ES), due to higher specific capacitance (SC), improved SC retention with increasing film mass and lower impedance.

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1. Introduction

The interest in PPy for electrodes of ES is attributed to high SC, electrical conductivity and low cost of this material [1,2]. Electropolymerization is widely used for the fabrication of PPy films [3–5]. The selection of anionic dopants for the electropolymerization of PPy is important for the fabrication of adherent and conductive PPy films with high SC. However, the influence of the dopant molecular structure on the electropolymerization process and properties of PPy films is not well understood. It was found that PPy films electrodeposited in the presence of aromatic sulfonate dopants exhibit good electronic conductivity [5,6]. Aromatic dopants promoted orientation of the pyrrole rings parallel to the electrode surface and such orientation resulted in higher conductivity [7]. Large counterions have a restricted mobility, which offers benefits of improved stability of film properties [7]. However, low mobility during film growth results in restricted doping and lower electrical conductivity [7]. AQ and AR are aromatic sulfonate molecules, which are promising for application as dopants for the deposition of PPy films by electropolymerization. Recently PPy films with high conductivity were prepared by chemical polymerization using AQ as a dopant [8].

The goal of this investigation was the fabrication of PPy films on stainless steel substrates by electropolymerization using AQ

and AR dopants. The comparison of experimental data for the dopants provided an insight on the influence of the dopant molecular structure on PPy electropolymerization and film adhesion. The use of AR allowed the fabrication of composite PPy-MWCNT films, which showed improved capacitive behavior, compared to pure PPy films.

2. Experimental procedures

Pyrrole, AQ and AR (Aldrich) and MWCNT (Arkema) were used as starting materials. Electropolymerization was performed galvanostatically on stainless steel substrates from aqueous 0.1 M pyrrole solutions containing 5 mM AQ or AR. The electro-deposition cell included a substrate and Pt counter electrode. The microstructure of the films was investigated using a JEOL JSM-7000F scanning electron microscope (SEM). The measurements of film adhesion were performed according to the ASTM D3359 standard.

Electrochemical studies were performed using a potentiostat (PARSTAT 2273, Princeton Applied Research). Surface area of the working electrode was 1 cm². The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE). Capacitive behavior and electrochemical impedance of the films were investigated in 0.5 M Na₂SO₄ aqueous solutions. Cyclic voltammetry (CV) studies were performed within a potential range from −0.5 to +0.4 V versus SCE at scan rates of 2–100 mV s^{−1}. The specific capacitance $SC = Q/\Delta V$, was

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calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the film mass (M) and width of the potential window (ΔV).

The measurements of complex impedance $Z = Z' - iZ''$ were conducted in the frequency range between 10 mHz and 100 kHz with AC signal amplitude of 5 mV. The complex AC capacitance $C^* = C' - iC''$ was calculated from the impedance data according to Ref. [9], where $C' = Z''/w|Z|^2$, $C'' = Z'/w|Z|^2$.

3. Results and discussion

Fig. 1 shows potential versus time curves for the galvanostatic deposition of PPy on stainless steel substrates from the 0.1 M pyrrole solutions containing 5 mM AQ or AR. The results indicated that there is no induction time for the electropolymerisation of PPy on the stainless steel substrates. In contrast, deposition of PPy on stainless steel from the solutions containing oxalic acid revealed the presence of an induction period, related to the anodic dissolution of the substrates and formation of a passive layer [10]. The formation of the non-conductive and non-capacitive passive layer must be avoided, because it results in increasing charge transfer resistance and reduced capacitance.

At the beginning of the electropolymerization process, the potential difference between the working and reference electrode increased and then decreased. The deposition potential of PPy from the solutions, containing AR, was significantly lower than that for AQ. The reduced deposition potential is beneficial for suppressing anodic oxidation of the substrate.

The comparison of the chemical structures of AQ and AR (Fig. 1) indicated that OH groups of AR were beneficial for the application of this material as a dopant for the electropolymerization of PPy. Similar to other aromatic molecules from the catechol family, the structure of AR includes two OH groups bonded to the adjacent carbon atoms of the aromatic ring. It is known that materials from catechol family exhibit strong adhesion to various inorganic materials [11,12]. The chemisorption mechanism involves the deprotonation of the phenolic hydroxyl groups of the catechol and chelation of metal ions on the material surface. It is important to note that catecholate bonding facilitated charge transfer between inorganic and organic materials [5,13]. Therefore, the difference in experimental data for AQ and AR can be attributed to chelation of metal ions by OH groups of AR, which facilitated charge transfer and reduced the electropolymerization potential. The measurements of film adhesion for AR doped films according to the ASTM D3359 standard showed

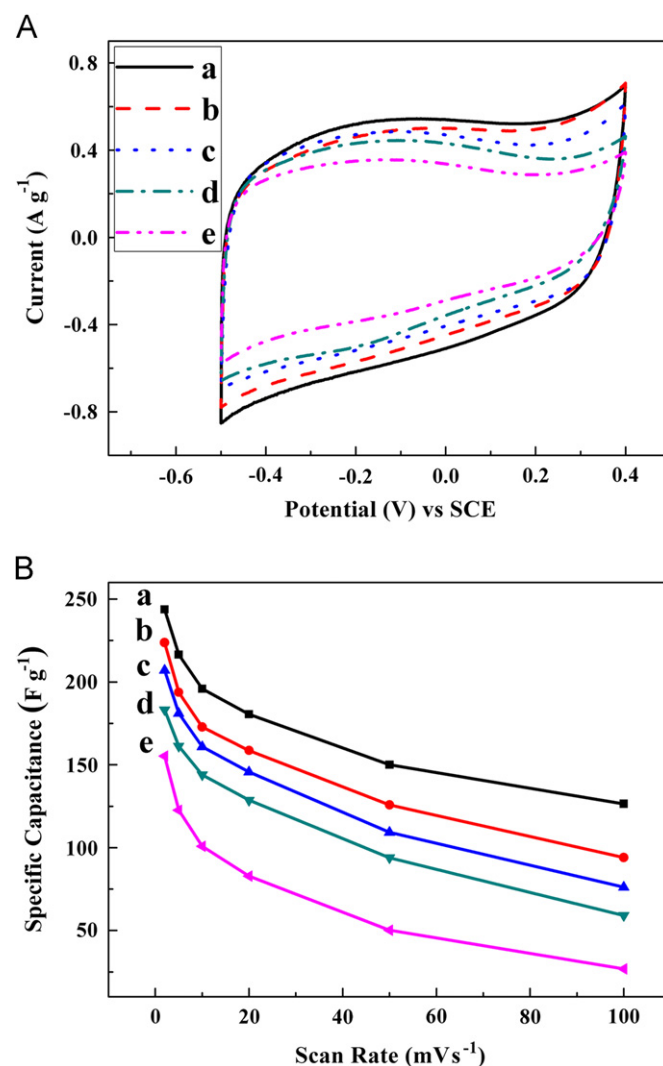
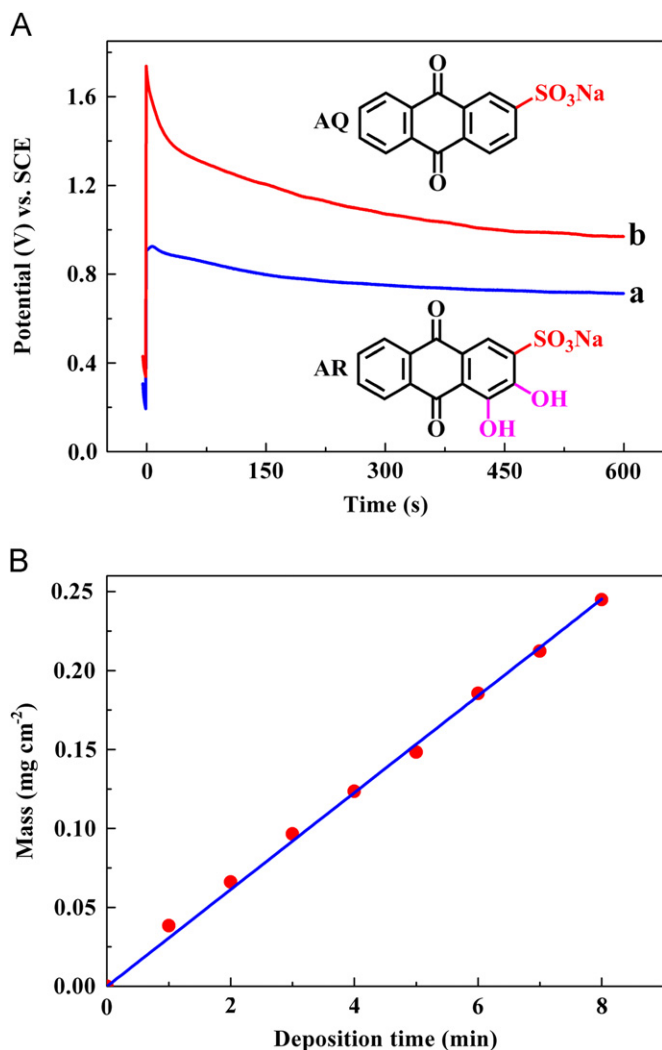


Fig. 1. (A) Chemical structures of AQ and AR and potential versus time curves for galvanostatic deposition of PPy from 0.1 M pyrrole solution containing (a) 5 mM AR and (b) 5 mM AQ at a current density of 1 mA cm⁻², (B) film mass versus time for PPy films prepared at a current density of 1 mA cm⁻² from 0.1 M pyrrole solution containing 5 mM AR.

Fig. 2. (A) CVs at a scan rate of 2 mV s⁻¹ and (B) SCs versus scan rate for films of different mass: (a) 0.13, (b) 0.18, (c) 0.23, (d) 0.32 and (e) 0.52 mg cm⁻², prepared from 0.1 M pyrrole solutions containing 5 mM AR.

that adhesion strength corresponded to the 4B classification. Turning again to the results of investigation of strong adhesion of catecholates to inorganic surfaces [11,12], it can be suggested that chelating properties of AR promoted film adhesion. Due to the advantages of AR as a dopant material, further investigations were focused on the AR doped films. The film mass increased linearly with increasing deposition time at a constant current density, indicating the possibility of deposition of films with different mass (Fig. 1B).

The PPy films showed capacitive behavior, as indicated by nearly box shape CVs, shown in Fig. 2A. The SC, calculated from the CV data decreased with increasing scan rate and film mass (Fig. 2B). Further improvement in capacitive properties was achieved by the use of MWCNT additives. It was found that AR allowed dispersion of MWCNT in aqueous solutions. The anionic AR molecules adsorbed on MWCNT and provided electrostatic stabilization of MWCNT and electric charge for electrodeposition. SEM data confirmed the formation of composite PPy-MWCNT films. Fig. 3(A,B) compares the SEM images of pure PPy and composite PPy-MWCNT films. Pure PPy films (Fig. 3A) were porous, the typical size of PPy particles was 100–200 nm. The film porosity and small particle size are beneficial for application of such films in ES, because they allow improved electrolyte access to the active material. Fig. 3B shows that MWCNT were co-deposited with PPy. Moreover the SEM image indicates that MWCNT were coated with PPy.

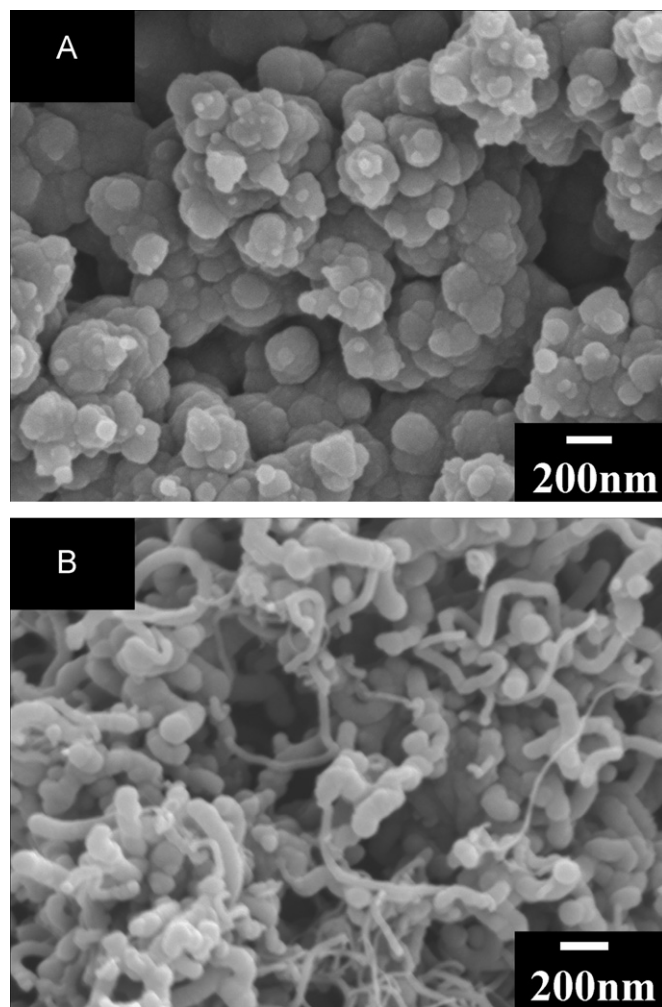


Fig. 3. SEM images for films prepared from 0.1 M pyrrole solutions, containing 5 mM AR and (A) 0 and (B) 0.3 g L^{-1} MWCNT.

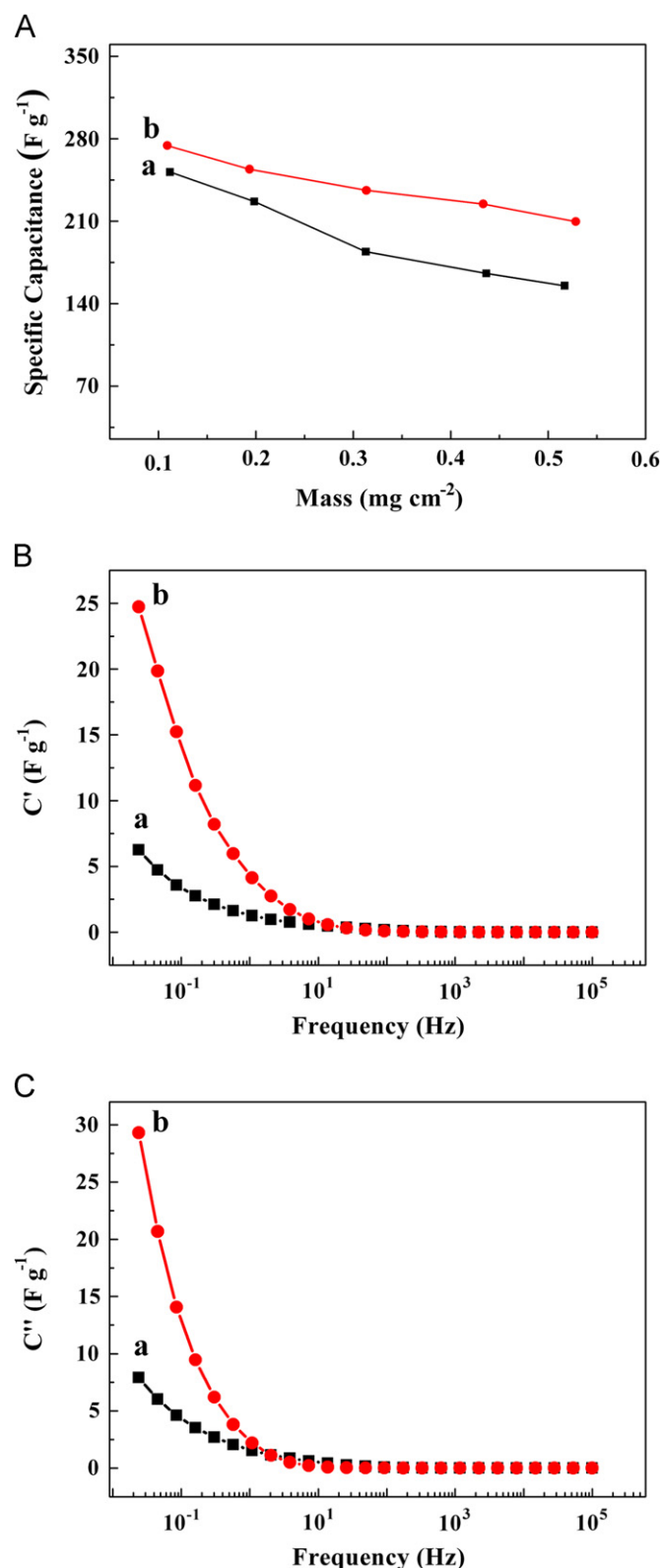


Fig. 4. (A) SC calculated from CV data versus film mass, (B) C' , and (C) C'' components of complex capacitance, calculated from AC impedance data, versus frequency for films prepared from 0.1 M pyrrole solutions, containing 5 mM AR and (a) 0 and (b) 0.3 g L^{-1} MWCNT.

Fig. 4A compares SC calculated from the CV data in a voltage window of 0.9 V for pure PPy and PPy-MWCNT films. The composite films showed higher capacitance, compared to pure PPy films. The results indicated improved SC retention of

PPy-MWCNT films with increasing film mass, compared to pure PPy films. The highest SC of 274 F g^{-1} was achieved for PPy-MWCNT films. The beneficial effect of MWCNT was also confirmed by measurements of AC capacitance. Fig. 4B showed significantly higher C' for PPy-MWCNT films. The C' decreased with increasing frequency. The corresponding data for C'' showed significantly higher C'' values for PPy-MWCNT films. This is attributed to lower impedance $|Z|$ of the composite films. Therefore, the incorporation of MWCNT into the PPy films allowed reduced impedance and improved capacitive behavior. The PPy-MWCNT films, prepared by electropolymerization using AR dopant, are promising electrode materials for ES.

4. Conclusions

PPy films were prepared by electropolymerization on stainless steel substrates using AR and AQ as anionic dopants. The comparison of the experimental data for AR and AQ and chemical structures of the organic molecules revealed the importance of OH groups of AR, which provided chelation of metal ions on substrate surface and allowed the formation of adherent films at reduced electropolymerization potential. The use of AR allowed dispersion, charging and anodic deposition of MWCNT. Anodic electropolymerization of PPy and electrodeposition of MWCNT were combined for the fabrication of composite films. The composite PPy-MWCNT films showed higher SC and improved SC retention with increasing film mass, compared to pure PPy films. The highest SC of 274 F g^{-1} was achieved for PPy-MWCNT films at a scan rate of 2 mV s^{-1} . The SC was higher than that reported for galvanostatically deposited PPy films (227 F g^{-1} [1] and 240 F g^{-1} [3]), tested in metal salt electrolytes. The films prepared in this investigation are promising for applications in electrodes of ES.

Acknowledgments

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