Specific capacitance and impedance of electrodeposited polyaniline, polypyrrole and polyaniline/polypyrrole composite films

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Abstract. The aim of this work was to prepare polyaniline, polypyrrole and polyaniline/polypyrrole composite films using electrodeposition techniques. Films were examined using a Fourier transform infrared spectrometer, which confirmed the formation of the single polymers and their composite. Morphological analysis was carried out using a scanning electron microscope and showed the flat and highly compact deposit of polypyrrole/polyaniline composites, whose morphological characteristics varied from those of the single polymers, which had porous deposits. Electrochemical properties of the materials were evaluated using cyclic voltammetry and electrochemical impedance spectroscopy techniques. Impedance values showed that polyaniline had the best charge transfer and the polyaniline/polypyrrole composite had the highest specific capacitance value, which was 530.96 F/g. This result indicates that the electrodeposited films can find application for electrode in capacitive deionization systems.

1. Introduction
Polyaniline is a relatively cheap conductive polymer with high electrical conductivity [1] and good mechanical properties [2]. It has the potential to be used in various fields and applications [3,4]. Nevertheless, polyaniline has been shown to be sensitive to the pH of its environment. At pH levels greater than 5, the conductivity of polyaniline is reduced due to the loss of proton bonds in its structure, especially when it reaches a neutral pH [5,6]. The stability of polyaniline could be improved by compositing it with other conductive polymers, such as polypyrrole, which have good electrochemical properties, easy surface modification, high conductivity and stability over a wide pH range [7]. Several previous studies have been successful in synthesising polyaniline and polypyrrole using oxidative polymerisation methods [8] and electropolymerisation [9].

In addition to conductivity and stability, other important properties in the synthesis of conductive polymers include impedance and capacitance, as these are directly related to the performance of materials in many applications, such as capacitive deionisation [10] and the construction of supercapacitors [11]. The performance of the device increases in materials with high capacitance. Impedance values are expected to be low, especially for materials used as supercapacitor electrodes [12,13]. These properties are related to the process of the intercalation and deintercalation of charge on
the surface of the film and indicate a low resistance value. Lower resistance values indicate an efficient charge exchange process [14]. Using oxidative polymerisation methods, polyaniline, polypyrrole and their composite have been synthesised with specific capacitance values of 149 F/g, 100 F/g and 346 F/g, respectively [15]. However, when an electropolymerisation method is used instead of an oxidative polymerisation method, polypyrrole with different structures and higher specific capacitance values can be produced. For example, researchers have successfully synthesised clustered polypyrrole nanobelts, nanobricks and nanosheets with capacitances of 296 F/g, 357 F/g and 584 F/g, respectively [14]. In the synthesis of conductive polymers, electropolymersisation methods are believed to produce better electrochemical characteristics than oxidative polymerisation methods. Therefore, in this study, polyaniline, polypyrrole and a polyaniline/polypyrrole composite were synthesised using electropolymerisation techniques. Morphological characteristics, specific capacitance and material impedance values have been reported.

2. Methods
Polyaniline, polypyrrole and their composite were synthesised using an electrodeposition method that utilised a three-electrode cell. A platina wire and Ag/AgCl electrodes were used as the counter and reference electrode, respectively. Plates of stainless steel 304 comprised the working electrode. Sample preparation was carried out at a potential of 900 mV vs Ag/AgCl with a deposition time of 5 min. Electrodeposition was controlled using an EDAQ potentiostat (EA 163) in electrolytes containing 0.5 M aniline or 0.5 M pyrrole prepared with an acid solution of 0.5 M H2SO4. For composite preparation, electrolytes were 0.5 M aniline or 0.5 M pyrrole in 0.5 M H2SO4. All chemicals used in this work were pure analytical grade and supplied by Merck. After deposition, each deposit was rinsed with distilled water and dried at room temperature. Samples were examined with a Fourier transform infrared (FTIR) spectrometer. Spectra of films formed by the polyaniline, polypyrrole and composite were obtained using FTIR spectrometer (Shimadzu IR Prestige-21) at wavenumbers ranging from 400 to 4000 cm⁻¹. Micrographs of samples were taken using a scanning electron microscope (JEOL JSM-6510LA). Electrochemical behaviour was examined using electrochemical impedance spectroscopy and cyclic voltammetry techniques with electrolytes containing 0.5 M KCl.

3. Results and discussion
In Figure 1, the FTIR spectra of polyaniline, polypyrrole and polyaniline/polypyrrole have been shown. The spectrum for polyaniline (Figure 1a) shows a peak at 1622 cm⁻¹, which is a typical peak of the strain interaction C=N quinoid [16]. Peaks at 1498 cm⁻¹ and 1400 cm⁻¹ indicated strain interactions of the C=C benzoid [17]. Other typical peaks of polyaniline included those at 1251 cm⁻¹, 1134 cm⁻¹, 1033 cm⁻¹, 792 cm⁻¹, 725 cm⁻¹ and 619 cm⁻¹. These showed the CN benzoid strain, N=Q=N (where Q represents the quinoid), Q=NH+-B (where B represents the benzoid), the bending vibration of CH and the deformation of CN, respectively. From the polypyrrole FTIR (Figure 1b), absorption peaks at 3427 cm⁻¹, 2918 cm⁻¹ and 2808 cm⁻¹ were identified, which confirmed the presence of NH strains from polypyrrole [14, 18, 19]. Peaks at 1035 cm⁻¹ and 960 cm⁻¹ indicated the presence of an N-H deformation and C-C out-of-plane deformation, respectively, which are typically found in polypyrrole. A peak observed at 821 cm⁻¹ corresponded to the out-of-plane bending of C-H. Other peaks observed at 667 cm⁻¹, 613 cm⁻¹ and 555 cm⁻¹ were identified as C-C and the out-of-plane bending of C-H, respectively [20, 21]. The FTIR spectrum of polyaniline/polypyrrole composite (Figure 1c) showed the presence absorption peaks typically found in polyaniline and polypyrrole. Some absorption peaks shifted slightly due to the interaction of simple alloys in the composite of the two polymers. The formation of polyaniline/polypyrrole composite was confirmed by the presence of absorption peaks at 920 cm⁻¹ and 786 cm⁻¹, which were associated with an interaction between CH structures from benzene and out-of-plane bending vibrations of C-H in polyaniline, which were assumed to interact with polypyrrole in the composite [22, 23].
Figure 1. FTIR Spectra of Polyaniline (a), Polypyrrole (b) and Composite Polyaniline/Polypyrrole (c).

Figure 2 shows the morphology of polyaniline, polypyrrole and their composite, polyaniline/polypyrrole. The micrograph in Figure 2a shows that polyaniline had a very fine and porous morphology. This porosity was similar to that found in the polypyrrole sample, despite the granular morphology of its deposit, as shown in Figure 2b. A very different morphology was observed in the polyaniline/polypyrrole composite (Figure 2c). The micrograph shows that the composite was composed of particles forming a dense and compact film with a relatively flat surface.

Specific capacitance values, determined using cyclic voltammetry with a scan rate of 250 mV/s, for polyaniline, polypyrrole and their composite have been shown in Figure 3. Compared to the single materials, the polyaniline/polypyrrole composite had the highest specific capacitance value, which was 530.96 F/g. This can be attributed to the contribution of the constituent materials, in this case, the ability of polyaniline to control the material’s structure and the role of polypyrrole in increasing charge transfer kinetics [23]. The high capacitance value of the composite was also possible due to a decrease in internal resistance and an increase in the electrolyte ion rate [15].
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Figure 3. Specific capacitance values determined using the cyclic voltammetry technique.

Values obtained using electrochemical impedance spectroscopy have been shown in a Nyquist plot (Figure 4). In the Nyquist plot, the semicircle produced was in the high frequency region. This semicircle shows the charge-transfer process in the double layer. The Nyquist plot shows that Rs values for polyaniline, polypyrrole and their composite were 6,574, 15,971 Ω and 6.2196 Ω, respectively. The low Rs value of the composite is due to its structural stability, as reported in previous studies [15]. The Rct values of polypyrrole and composite polyaniline were 21,947 Ω; 197,256 Ω and 312,166 Ω. Polyaniline had the lowest Rct value, suggesting it had good intercalation and deintercalation of charge due to the low resistance of the material [16]. This also suggested that polyaniline had a highly efficient ion adsorption process. In contrast, polypyrrole and the composite had higher Rct values, so they could be assumed to have a lower ion adsorption efficiency than polyaniline.

Figure 4. Nyquist Plot of Polyaniline (a), Polypyrrole (b) and Composite Polyaniline/Polypyrrole (c).

4. Conclusion
Thin films of polyaniline, polypyrrole and their composite were synthesised using an electrodeposition technique. Deposits of all electrodeposited polymers showed different morphological characteristics. Polyaniline and polypyrrole formed very porous deposits, while their composite formed a dense deposit with a relatively flat surface morphology. Electrochemical impedance analysis showed that polyaniline had better charge-transfer ability compared to polypyrrole and the composite. However, a high capacitance specific value can be obtained by compositing polyaniline with polypyrrole.
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