

Investigation of Electrochemical Coating of Polypyrrole in The Presence of Sodium Molybdate and Sodium Tungstate

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ABSTRACT

Polymer composites are considered alternative material because they combine the advantages of all their components. Furthermore, polymer composites can exhibit unique electrochemical and physical properties, enabling their use in applications where metals may not be suitable. Polypyrrole, as a conductive polymer, is a promising candidate for synthesizing new composite materials due to its high electroactivity and ease of processing. Incorporating certain organic and inorganic species into polypyrrole matrices can enhance its electrochemical and physical properties. In the study, polypyrrole films were electrochemically coated in the presence of varying concentrations of sodium molybdate and sodium tungstate. The effects of these metal oxides on the growth of polypyrrole were analyzed, and the electrochemical properties of the resulting composite films were examined in monomer-free solutions. The findings indicate that molybdate and tungstate reduce film's electroactivity, alter redox peaks, and lead to the formation of a new electrochemical film. The maximum anodic peak charge density for polypyrrole, polypyrrole/WO₃ and polypyrrole/MoO₄ films was 12.4 mC cm⁻², 3.57 mC cm⁻² and 3.14 mC cm⁻², respectively. Additionally, the results demonstrated that an optimal amount of sodium tungstate enhances charge transfer while maintaining reversibility in redox reactions.

Keywords: Polypyrrole, Sodium tungstate, Sodium molybdate, Electrochemical deposition.

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Introduction

Conductive polymers are interesting materials because, unlike metals, their conductivity and insulating properties can be reversibly modified. In other words, while their neutral state is insulating, they can easily be converted into conductive materials through electrochemical or chemical doping [1]. Due to these unique properties, conductive polymers are widely used in energy storage devices [2–4], corrosion protection [5,6], and various sensors, gas, chemical, and biosensors [1,7]. Additionally, conductive polymers exhibit color changes in response to changes in conductivity, making them suitable for use in electrochromic devices [1,8,9]. Polyaniline [10–12], polypyrrole [13,14] and polythiophene [15,16] are the most common conductive polymers [1]. Polypyrrole stands out for its high electroactivity, strong environmental stability, and facile synthesis, which does not require acidic or basic media [17]. It is synthesized from pyrrole monomer in an appropriate electrolyte solution through chemical or electrochemical methods [18]. The electrochemical method is often preferred for producing polymer and polymer composite films, as it allows for precise control of film thickness and electrochemical properties [18]. Polypyrrole has been utilized various fields, including controlled drug release systems [19], corrosion prevention [13] and optical devices [20,21].

In recent decades, the fabrication of polymer composite films has gained significant attention,

especially when incorporating certain types of species, such as organic monomers, carbon nanotubes, graphene, or inorganic species. These species can improve the chemical and physical properties of the polymer films [22]. For example, studies have shown that chemically copolymerizing pyrrole and aniline results in a crystal structure distinct from their individual homopolymers and demonstrates selective ammonia-sensing capabilities [23,24]. Additionally, Khan *et al.* reported that a polyaniline/NiO composite exhibits improved conductivity and thermal stability compared to pure polyaniline [22]. In other words, polymer composites offer a great opportunity to produce new polymer films with enhanced electrochemical properties.

Transition metal oxides like molybdate and tungstate are promising candidates for synthesizing polymer composite materials due to their high specific energy capacity, low operating voltage, multiple reversible redox states, abundant availability, environmental friendliness, and strong physical chemical stability [16,25–29]. In the present study, the electrochemical deposition of polypyrrole was investigated in the presence of various concentrations of sodium tungstate and sodium molybdate. The resulting polymer composite films were analyzed for their electrochemical properties.

Experimental Work

Chemicals and Reagents

Pyrrole was purchased from Sigma-Aldrich and used without distillation. Other reagents, including potassium nitrate (KNO_3) from Sigma Aldrich, and sodium tungstate ($\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$, 99.5%) and sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) from Carlo Erba, were also purchased. All solutions were prepared with deionized water.

Instrumentation

Cyclic voltammetry (CV) experiments were conducted using a Gamry Instruments Interface 1000E. A glassy carbon electrode (0.07 cm^2) served as the working electrode, a platinum flag electrode (0.06 cm^2) as the counter electrode and an Ag/AgCl electrode was used as the reference electrode.

Preparation and Characterization of Polymer Composite Films

Polypyrrole and its composites were synthesized by cyclic voltammetry using pyrrole monomer in 0.1 M KNO_3 . Initially, a pure polypyrrole film was synthesized from a solution containing 0.1 M pyrrole and 0.1 M KNO_3 at a scan rate of 10 mV s^{-1} for 10 cycles. Subsequently, polymer composites were synthesized in the presence of various concentrations of sodium molybdate and sodium tungstate (0.05 M, 0.1 M, 0.2 M, 0.3 M). Electrochemical coating of the polymer and polymer composites was carried out at a scan rate of 10 mV s^{-1} over several cycles. Characterization was performed in 0.1 M KNO_3 monomer-free solutions at a scan rate of 50 mV s^{-1} over multiple cycles.

Results and Discussions

Deposition of Polymer and Polymer Composites

The electrochemical behavior of a polymer-modified electrode depends on the type of conductive polymer the nature of electrode and electrolyte, and the applied voltage during the polymerization [30]. The coating of polypyrrole and polypyrrole composite films was carried out under identical conditions to specifically compare the effects of metal oxides, $\text{NaWO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$.

Figure 1a shows the electrochemical coating of polypyrrole formed from 0.1 M pyrrole and 0.1 M KNO_3 at a scan rate of 10 mV s^{-1} over 10 cycles. The increase in current density with each cycles indicates an increase in electroactive sites within the film. Polypyrrole exhibits a broad anodic peak between -0.36 V and 0.48 V , and a broad cathodic peak between -0.74 V and 0.63 V , along with an irreversible peak at 0.8 V , consistent with previous reports [14]. After deposition, an insoluble black polypyrrole film forms on the electrode surface, imparting unique electroactive properties to the modified electrode.

Figure 1b shows CV curve of the polypyrrole film in a monomer-free 0.1 M KNO_3 solution at a scan rate of 50 mV s^{-1} over 10 cycles. The anodic peak appears between

0.45 V and 0.75 V with a peak current density of 6.28 mA cm^{-2} , while the cathodic peak occurs between -0.76 V and 0.76 V with a peak current density of -5 mA cm^{-2} . The anodic and cathodic charge densities of the polymer film were determined to be 12.4 mC cm^{-2} and 10.6 mC cm^{-2} . When oxidized, the polypyrrole film becomes conductive and upon reduction, it returns to an insulating state.

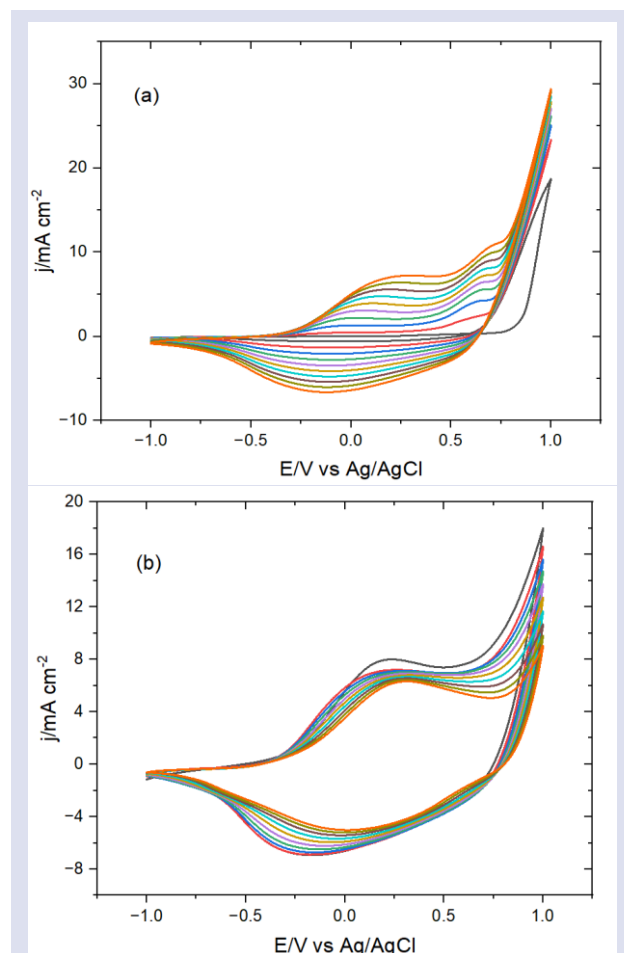


Figure 1. (a) Electrochemical coating of polypyrrole film from 0.1 M pyrrole and 0.1 M KNO_3 (b) CV curve of the polypyrrole film in monomer-free 0.1 M KNO_3 at a scan rate of 50 mV s^{-1}

For the synthesis of the PPy/ WO_3 polymer composite, electrochemical coating of polypyrrole was applied at a scan rate of 10 mV s^{-1} in the presence of varying concentrations of sodium tungstate (0.05 M, 0.1 M, 0.2, 0.3 M), with the resulting CV curves shown in Figure 2. In the pure polypyrrole growth curve, the oxidation and reduction peak current densities are approximately 7.14 mA cm^{-2} , with an irreversible peak current density of 28.6 mA cm^{-2} . For the polypyrrole/ WO_3 composites, the irreversible peak current density was greatly reduced, and the redox peaks almost disappeared, except in the case of polypyrrole/ WO_3 (0.05M). This indicates that higher concentrations of sodium tungstate block the electroactive sites within the polymer matrix. Conversely, a low concentration (0.05 M) does not substantially affect the oxidation and reduction peak positions.

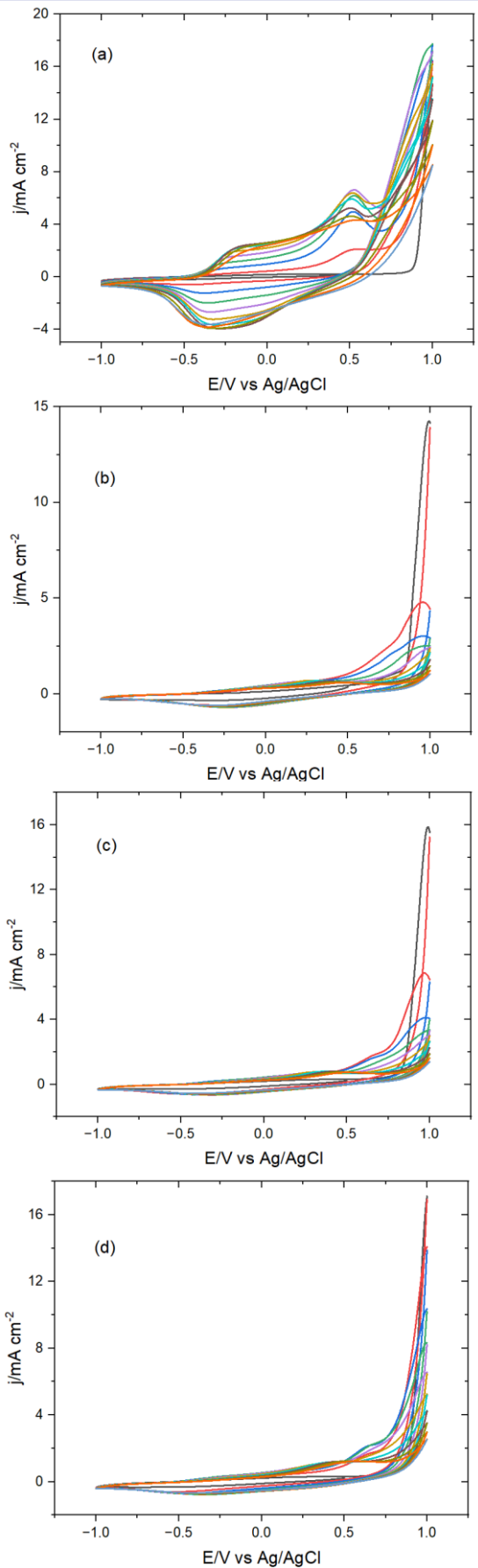


Figure 2. Electrochemical coating of polypyrrole was applied at a scan rate of 10 mV s^{-1} in the presence of various concentrations of sodium tungstate (a) 0.05 M (b) 0.1 M (c) 0.2 M and (d) 0.3 M

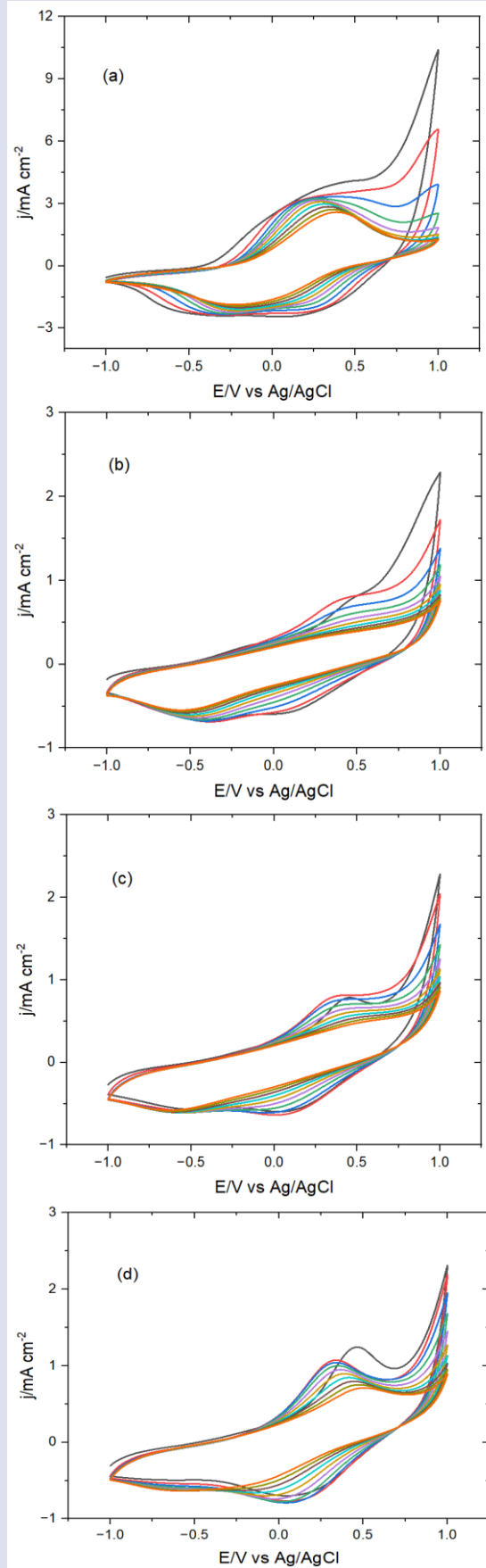


Figure 3. CV curves of polypyrrole/ WO_3 composite films in 0.1 M KNO_3 monomer-free solutions at a scan rate of 50 mV s^{-1} (a) polypyrrole/ $\text{WO}_3(0.05)$ (b) polypyrrole/ $\text{WO}_3(0.1)$ (c) polypyrrole/ $\text{WO}_3(0.2)$ (d) polypyrrole/ $\text{WO}_3(0.3)$

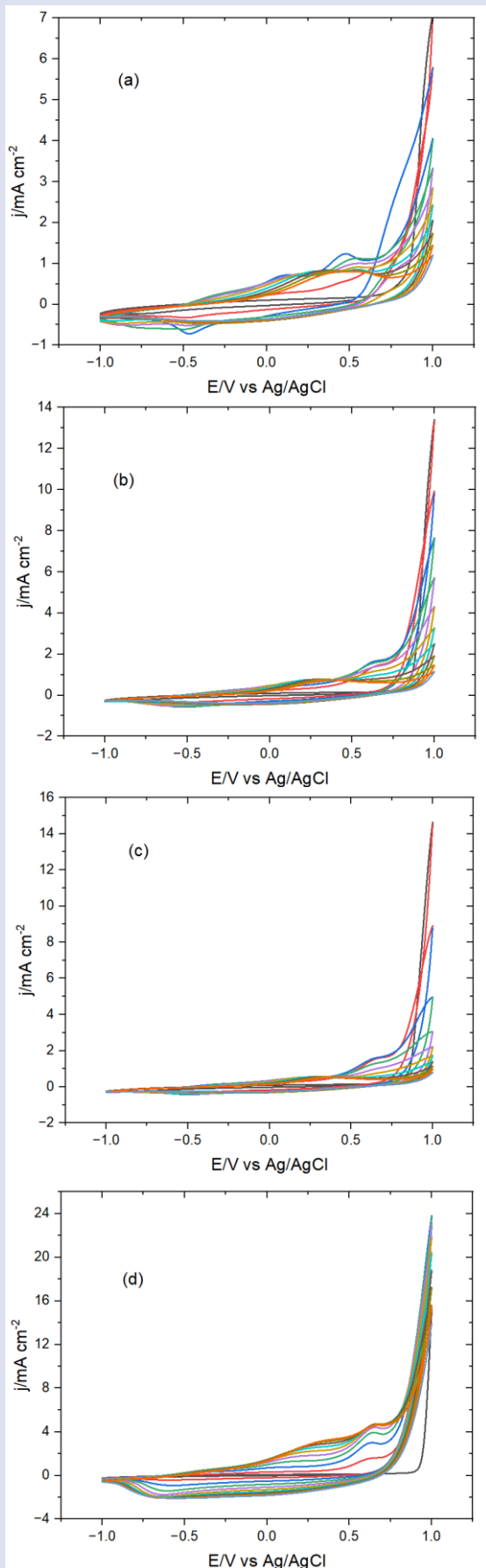


Figure 4. Electrochemical coating of polypyrrole was applied at a scan rate of 10 mV s^{-1} in the presence of various concentrations of sodium molybdate (a) 0.05 M (b) 0.1 M (c) 0.2 M and (d) 0.3 M

The electroactivity of the resulting composite films was characterized in a monomer-free 0.1 M KNO_3 solutions at a scan rate of 50 mV s^{-1} , as illustrated in Figure 3. Figure 3a indicates that the existence of sodium tungstate imparts more reversible behavior to the film compared to pure polypyrrole (see Figure 1b). Adding 0.05 M sodium tungstate does not alter the redox characteristics of the polypyrrole film, but the anodic charge density decreases from 12.4 mC cm^{-2} to 3.57 mC cm^{-2} . While this is a significant reduction, the addition of sodium tungstate introduces reversible behavior. However, with continuous cycling, the film's behavior becomes unstable, suggesting that tungstate ions block the electroactive sites. Increasing the concentration of sodium tungstate in polymer matrix further reduces the electroactivity of the polypyrrole and shifts the anodic peak potential to more positive values. These findings show that tungstate ions block electroactive sites, as evidenced by disappearance of redox peaks after several cycles. Thus, the presence of sodium tungstate makes polypyrrole a recyclable but low-electroactive composite

The electrochemical coating of polypyrrole was also studied in the presence of sodium molybdate, with the growth curves shown in Figure 4. The results are similar to those Figure 2, as both the current density values decrease, and the redox peaks disappear with higher concentrations of sodium molybdate. Interestingly, however, the highest concentration of sodium molybdate (0.3 M) produces broad peaks and an increase in current density values.

The electrochemical properties of the polypyrrole/ MoO_4 composite film were examined in 0.1 M KNO_3 at a scan rate of 50 mV s^{-1} , with the resulting cyclic voltammograms shown in Figure 5. In the presence of higher concentration of sodium molybdate, the oxidation peak of the polypyrrole composite films shifted to more positive potentials, and their electroactivity became unstable and decreased with continued cycling. However, a high concentration of sodium molybdate (0.3 M) provided a more stable and reversible behavior. The anodic peak charge density of this composite film was 3.14 mC cm^{-2} , matching that pure polypyrrole, but with the added advantage of improved reversibility.

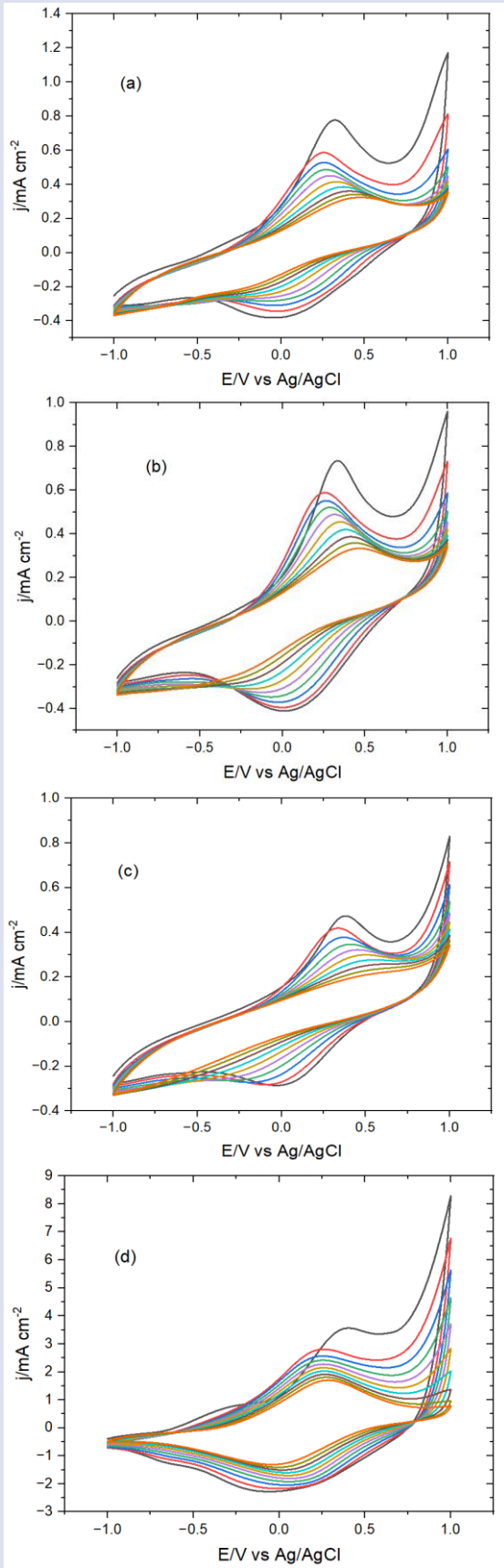


Figure 5. CV curves of polypyrrole/MoO₄ composite films in 0.1 M KNO₃ monomer free solutions at a scan rate of 50 mV s⁻¹ (a) polypyrrole/MoO₄(0.05) (b) polypyrrole/MoO₄(0.1) (c) polypyrrole/MoO₄(0.2) (d) polypyrrole/MoO₄(0.3)

Table 1. shows the charge density values passing through oxidation and reduction redox, and as can be seen, the charge densities values for composite films decrease, but it is also noteworthy that composite films gain reversible properties.

Table 1. Charge density values of polypyrrole and its composites during redox reactions.

<i>Polymer Composite Film</i>	<i>Anodic Peak Charge Density (mC cm⁻²)</i>	<i>Cathodic Peak Charge Density (mC cm⁻²)</i>
Polypyrrole	12.4	10.6
Polypyrrole/WO ₃ (0.05)	3.57	3.57
Polypyrrole/WO ₃ (0.1)	0.86	1.00
Polypyrrole/WO ₃ (0.2)	1.00	1.14
Polypyrrole/WO ₃ (0.3)	1.28	1.28
Polypyrrole/MoO ₄ (0.05)	0.57	0.57
Polypyrrole/MoO ₄ (0.1)	0.57	0.57
Polypyrrole/MoO ₄ (0.2)	0.43	0.43
Polypyrrole/MoO ₄ (0.3)	3.14	2.43

Conclusion

In this study, various polypyrrole composite films were synthesized in the existence of NaWO₃.2H₂O and Na₂MoO₄.2H₂O. The results indicate that while both sodium tungstate and sodium molybdate provide polypyrrole with reversible redox properties, they influence the polymer matrix differently depending on their concentrations. At a lower concentrations of sodium tungstate (0.05 M), the anodic charge density is 3.57 mC cm⁻², which is lower than that of pure polypyrrole but exhibits excellent redox reversibility. However, higher concentrations of sodium tungstate block the electroactive sites in polypyrrole, leading to decreased current density and a shift in peak potential to more positive values. In contrast, for sodium molybdate, the highest concentration (0.3 M) results in significantly higher anodic current density, while lower concentrations have minimal impact on the polypyrrole film. The anodic charge density of the optimized polypyrrole/MoO₄ composite film is 0.22 mC cm⁻², which is lower than that pure polypyrrole (0.87 mC) but offers improved reversibility in redox reactions. Overall, both composite films allow for the synthesis of polypyrrole films with enhanced redox reversibility, although their electrochemical stability is limited. Further studies could focus on creating electroactive, reversible chemical sensors for various applications by increasing the thickness of polypyrrole through different coating techniques.

Conflict of interest

There is no conflict of interest in this work.

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