Sakarya University Journal of Science

ISSN : 2147-835X
Publisher : Sakarya University

Vol. 28, No. 5, 1031-1039, 2024
DOI: https://doi.org/10.16984/saufenbilder.1499385

Research Article

Analysis of Electrochemical Deposition of Polyaniline and Polyaniline Composites in Sodium Tungstate and Sodium Molybdate Solutions

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ARTICLE INFO

Keywords:
Polyaniline
$Na_2WO_4.2H_2O$
$Na_2MoO_4.2H_2O$
Electrochemical deposition
Polymer composits

Article History:
Received: 11.06.2024
Accepted: 17.09.2024
Online Available: 18.10.2024

ABSTRACT

Although polyaniline has a high electroactivity in environments below pH 5, it loses its electroactivity in neutral and basic environments. In addition, polyaniline film does not give physically stable film when it becomes thick. For these reasons, polyaniline has been synthesized in the presence of other monomers or inorganic/organic species, leading to the obtaining of composite polymers with some new electrochemical and physical properties. In this study, novel composite polymer films of polyaniline were synthesized electrochemically in the presence of different concentrations of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$, and these composite polymer films were examined in monomer-free solutions for electrochemical investigation. As a result, the cathodic charge of polyaniline increased from 0.25 mC to 1.50 mC in the presence of 0.05 M $Na_2MoO_4.2H_2O$. Also, the polyaniline/WO_3 composite achieved a charge transfer of 0.42 mC in the presence of 0.25 M $NiSO_4.2H_2O$, 0.05 M $NiCl_2.6H_2O$, Na_2WO_4, $Na_2MoO_4.2H_2O$, 0.4 M $Na_3C_6H_5O_7.2H_2O$ and 0.05 $Na_2WO_4.2H_2O$ as a metal source. These prove the better charge transfer during the redox reaction of the polyaniline composite film.

1. Introduction

Studies on the synthesis, characterization and applications of conductive polymers are still being studied extensively due to their high conductivity and cost-effectiveness [1-3]. Moreover, this interest in conductive polymers has increased with the discovery of polymer composites (or polymer hybrids) because these compounds provide new application areas for polymers by revealing new and improved chemical and physical properties. A wide range of studies have been conducted with composite films in energy storage device, biosensors, and corrosion protection [4-7]. These studies also prove that composites are generally better than their components in terms of electrochemical and physical aspects [3].

Polyaniline is the most preferred conductive polymer due to its high electroactivity, its remarkable stability and processibility in exposure to air and moisture, for both conducting and as well, as insulating forms [8-11]. It also provides a good network for the distribution of other species (monomer, organic, or inorganic). In other words, its easy integration with other species makes polyaniline advantageous for the synthesis of polymer composites [12-16].

Polyaniline can be prepared by chemical or electrochemical techniques [8-9, 17] but cannot be prepared or even used without acid. The pH of the medium must be above 5, otherwise polyaniline will not be synthesized and cannot exhibit electroactive behavior [3, 18]. This is an important limitation of polyaniline. It is possible to eliminate this problem with polyaniline composite syntheses. According to some studies, polyaniline composites show new electrochemical properties and can also show electroactivity at high pH values [19-22]. Hao *et*

Cite as: A. Ünal (2024). Analysis of Electrochemical Deposition of Polyaniline and Polyaniline Composites in Sodium Tungstate and Sodium Molybdate Solutions, *Sakarya University Journal of Science*, 28(5), 1031-1039. https://doi.org/10.16984/saufenbilder.1499385

al. reported that polyaniline/boron-doped graphene exhibits a dramatic increase in electrochemical specific capacitance in an alkaline medium [13]. Another study reports that a polyaniline-based nickel molybdate composite could be used as a cation exchanger by the sol-gel method [23].

According to the literature, tungstate and molybdate can be promising alternatives for energy storage devices [24-26]. A few studies have explored their polymer composites but often do not provide detailed explanations of their effects on polymer matrices [27-30]. This study aims to understand these effects and describe the resulting film properties.

In this work, the electrochemical deposition of polyaniline was studied in the different ratios of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ under optimal conditions with or without the presence of nickel sulfate, nickel chloride and sodium citrate (as complexing agent). The resultant polymer composites were examined in terms of electrochemical properties by cyclic voltammetry.

2. Experimental Work

2.1. Chemicals and reagents

Aniline and HCl were purchased from Sigma Aldrich. Reagents for the synthesis of polyaniline composites including $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ were purchased from Carla Erba while nickel sulfate $NiSO_4.6H_2O$, nickel chloride $NiCl_2.6H_2O$ and sodium citrate ($Na_3C_6H_5O_7$) were purchased from Sigma Aldrich.

2.2. Instrumentation

Gamry Instruments Interface – 1000E was used to conduct cyclic voltammetry experiments. Electrochemical experiments of electrode materials were carried out using a three-electrode system, in which a glassy carbon electrode was the working electrode (0.018 cm^2), platinum flag as counter electrode (0.25 cm^2) and Ag/AgCl electrode was preferred as reference electrode.

2.3. Sysnthesis of polymer composites

Polyaniline and polyaniline composite polymers were deposited on the working electrode (glassy carbon electrode) by electrochemical method. Electrochemical deposition of polyaniline was performed from a solution containing 0.1 M aniline monomer and 0.1 M HCl solutions at 10 mVs^{-1} for several cycles. Electrochemical deposition of polyaniline composite polymer films was obtained from 0.1 M aniline and 0.1 M HCl and different ratios of $Na_2MoO_4.2H_2O$ (or $Na_2WO_4.2H_2O$) at 10 mVs^{-1}. The obtained polyaniline polymer film and polyaniline composite films were examined by cyclic voltammetry in 1 M monomer-free HCl solutions at 50 mVs^{-1} for several cycles. At this stage, the reason for choosing a solution containing 1 M HCl that polyaniline-based films show high electroactivity when acidity increases. In this way, the electroactivity of the resulting film can be tested easily.

On the other hand, the reason for using 0.1 M HCl during the electrochemical deposition of the polyaniline is the tendency of inorganic species to precipitate in the presence of 1 M HCl. Using 0.1 M HCl prevented this the film during deposition. If the test solution is in 1 M HCl, polyaniline composite films in which inorganic species have already been incorporated can be easily tested. Similarly, polyaniline composites were obtained from $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ in the presence of nickel sulfate, nickel chloride and sodium citrate to make nickel/Mo and nickel/W alloy in polymer matrices. For this, the solution containing 0.25 M $NiSO_4.2H_2O$, 0.05 M $NiCl_2.6H_2O$, Na_2WO_4, $Na_2MoO_4.2H_2O$ as metal sources (with 0.05 M W and/or 0.05 M Mo) and 0.4 M $Na_3C_6H_5O_7.2H_2O$ as complexing agent was prepared.

3. Results and Discussions

3.1. Electrochemical deposition of polyaniline and its electrochemical properties

Initially, monomer solutions of aniline were prepared in the presence of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$, but since $Na_2WO_4.2H_2O$ was insoluble in hydrochloric acid according to

Equation 1 and it gives a tungstic acid, which is amorphous yellow powder. Therefore, the synthesis and electrochemical properties of polyaniline/MoO_4 were only discussed in the first part of the study. The other part of the study is related to the synthesis of both $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ polymer composite films in a solution consisting of nickel sulfate, nickel chloride and sodium citrate.

$$Na_2WO_4 + 2HCl \longrightarrow H_2WO_4 + 2NaCl \quad (1)$$

Figure 1 shows the electrochemical deposition of polyaniline from a solution containing 0.1 M aniline and 0.1 M HCl at 10 mVs^{-1}. The current of the anodic and cathodic peaks increases with continuing cycling, and three redox peaks were observed throughout the redox reaction, with an irreversible peak at 0.80 V. While the anodic peaks occur at 0.25 V, 0.50 V and 0.75 V, the cathodic peaks occur around 0.1 V, 0.45 V and 0.70 V, and these are consistent with the literature [31-33]. The first redox pair of polyaniline can corresponds to the transformations between leucoemeraldine state and emeraldine states of polyaniline and the second pair of redox peaks is attributed to the trasnformatiıon between emeraldine state and perninganiline states [31]. When it was cycled in monomer-free 1 M HCl solution, as shown in Figure 1b, the next peaks at 0.25 V and 0.63 V are more prominent, unlike the growth voltammogram. The anodic charge and cathodic charge passing during the redox reaction are determined as 0.25 mC and 0.25 mC.

As seen in Figure 1, electrochemical deposition of polyaniline is carried out in 0.1 M HCl, and it is reported in the literature that more concentrated acids contribute to the formation of electroactive polyaniline. On the other hand, electrochemical deposition of polyaniline can be implemented at lower acid concentrations, which facilitates the integration of other species into polymer matrices. Therefore, the synthesis of polyaniline composite polymer films was carried out in 0.1 M HCl under identical conditions.

Figure 2a and Figure 3a reveal the electrochemical precipitation of polyaniline into the composite polymer film from a solution containing 0.1 M aniline, 0.1 M HCl, and 0.05 M /0.1 M $Na_2MoO_4.2H_2O$ at 10 mVs^{-1} for 20 cycles. As seen in Figure 2a and Figure 3a, the excessive increase in the amount of $Na_2MoO_4.2H_2O$ resulted in the formation of a graph that gave only two specific redox pairs. In other words, the other redox pairs seen in Figure 2a have disappeared. However, when the current of the redox peaks in Figure 2a and Figure 3a is compared, it is seen that the current of the peaks in Figure 3a also becomes lower. This can be explained as the addition of $Na_2MoO_4.2H_2O$ in high amounts blocks some electroactive sites in the polymer matrices.

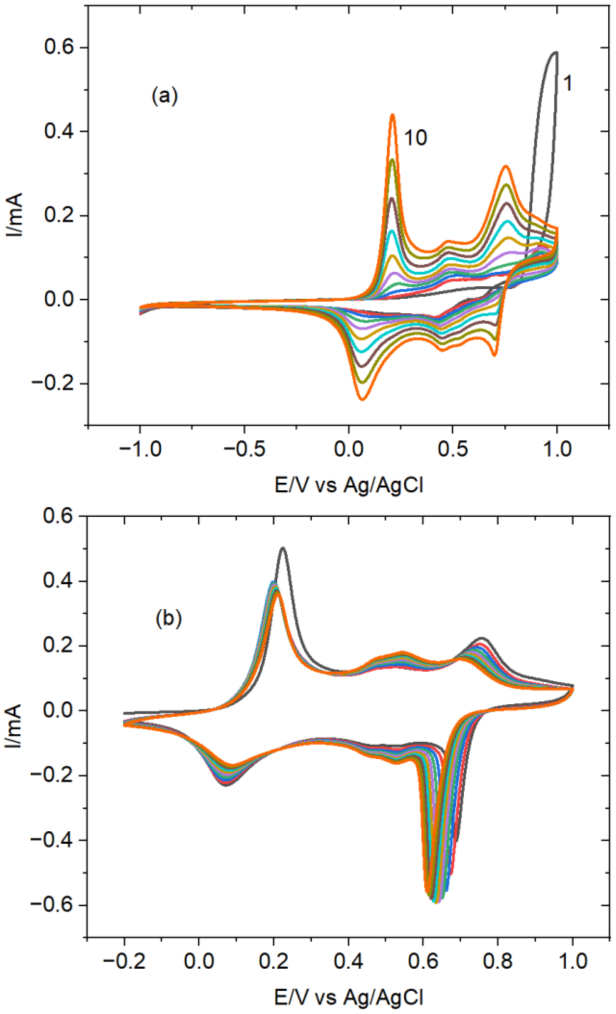

Figure 1. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl at 10 mVs^{-1} over 10 cycles (b) Cycling of polyaniline film in 1 M HCl monomer free solution

Additionally, a closer look at Figure 2a shows that the current is 0.25 mA for the 10th scan, which is higher than the current of the 10th peak of polyaniline obtained from 0.1 M HCl. This also proves that a low amount of $Na_2MoO_4.2H_2O$

contributes the stability and electroactivity while giving reversible redox reactions.

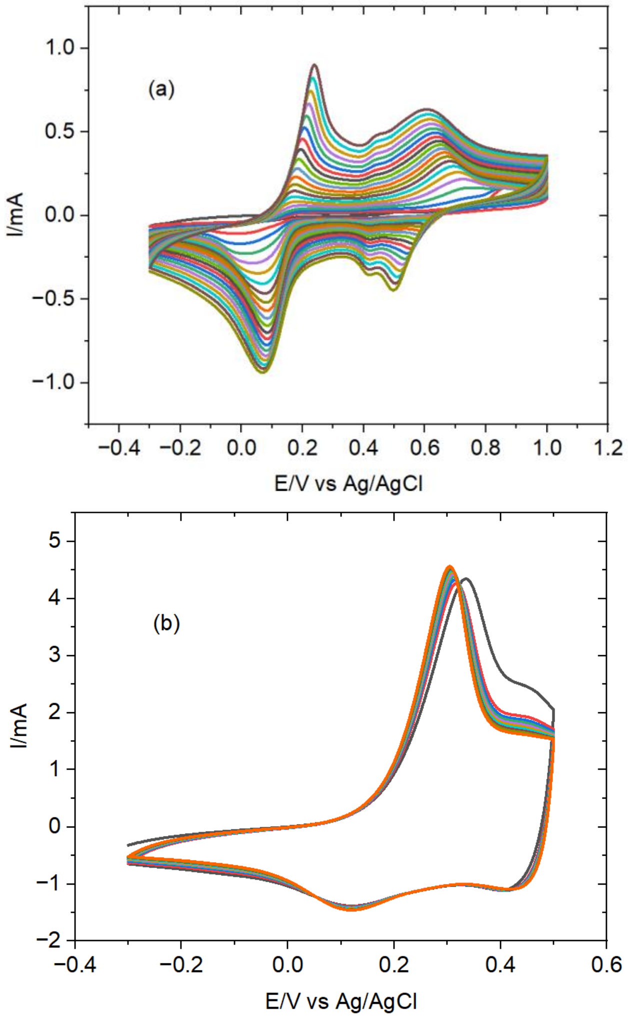

Figure 2. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.05 M $Na_2MoO_4.2H_2O$ at 10 mVs^{-1} over 20 cycles (b) Cycling of polyaniline/$Na_2MO_4.2H_2O$ in 1 M HCl at 50 mVs^{-1}

The electroactivity of these polyaniline composite polymer films was examined at 50 mVs^{-1} in monomer-free 1 M HCl solutions and their cyclic voltammograms are given in Figure 2b and Figure 3b.

As seen in the Figures 2b and 3b, polyaniline/MoO_4 (0.05 M) shows high electroactivity with stable cycling. On the other hand, polyaniline/MoO_4 (0.1 M) started to give peaks at lower currents (0.15 mA) as the cycle continued to increase, indicating the unstable behavior of the film. The anodic load in Figure 2b and Figure 3b was determined as ***1.57 mC and 1.50 mC***, and the cathodic load was determined as ***0.18 mC and 0.20 mC***. As a result, it can be said that the optimum amount of $Na_2MoO_4.2H_2O$ in the polymer matrices increases the electroactivity, while its excess amount blocks the electroactive regions of the polyaniline film.

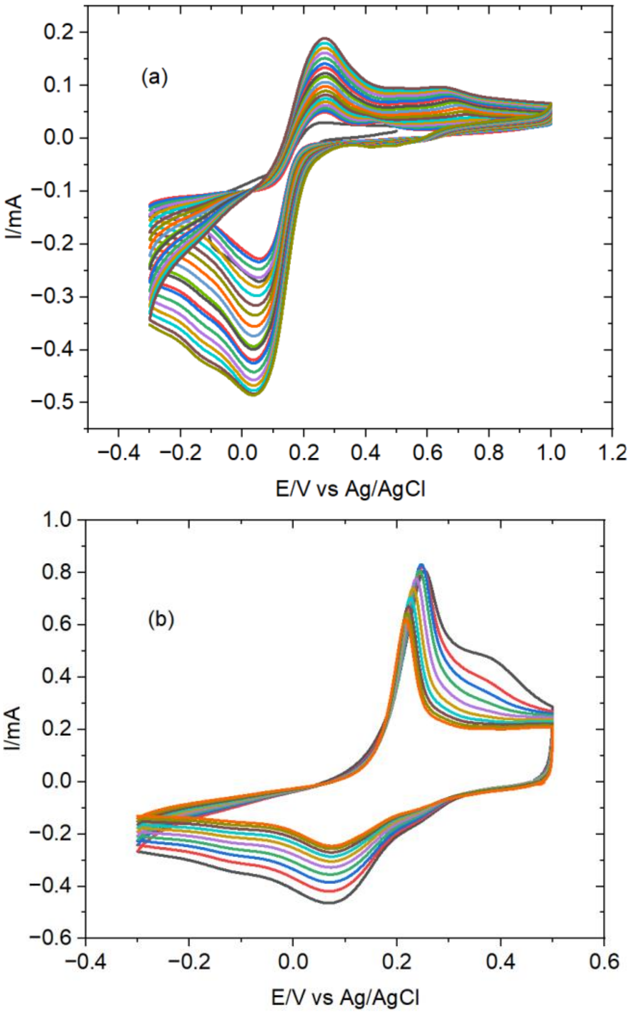

Figure 3. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.1 M $Na_2MoO_4.2H_2O$ at 10 mVs^{-1} over 20 cycles (b) Cycling of polyaniline/$Na_2MoO_4.2H_2O$ in 1 M HCl at 50 mVs^{-1}

Electrochemical deposition of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ was also carried out from 0.1 M aniline and 0.1 M HCl in the existence of 0.25 M $NiSO_4.2H_2O$, 0.05 M $NiCl_2.6H_2O$, Na_2WO_4, $Na_2MoO_4.2H_2O$ as metal sources (with 0.05 M W and/or Mo) and 0.4 M $Na_3C_6H_5O_7.2H_2O$ as previously mentioned. Figure 4 shows this electrochemical deposition of polyaniline without $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ [34]. Sodium citrate forms stable complexes for electroplating metal or alloys such as NiMoW [34].

The cyclic voltammogram of this polyaniline is quite different from the pure polyaniline film, which has given three anodic peaks and three cathodic peaks (see Figure 1). Here, a board anodic peak and two cathodic peaks were observed. Additionally, the current of an anodic peak is 0.07 mA, which is quite low compared to the peak current values of pure polyaniline. This solution appears to result in the synthesis of low electroactive polyaniline. On the other hand, when the resulting film is cycled in a monomer-free 1 HCl solution, it gives a voltammogram similar to the pure polyaniline voltammogram (Figure 1b) with low electroactivity. The anodic and cathodic loads determined from cyclic voltammograms are 0.18 mC and 0.17 mC.

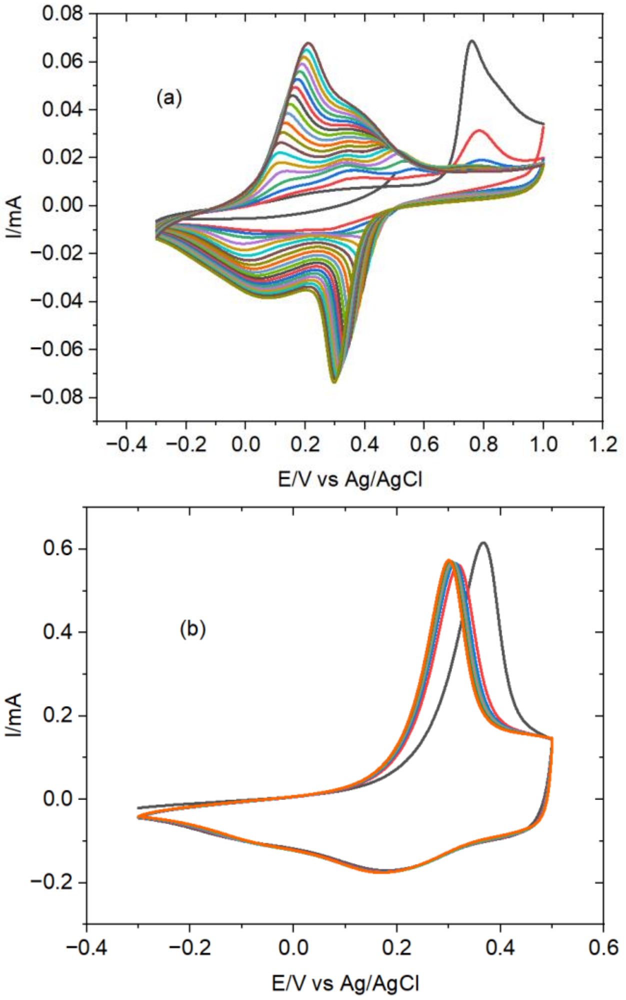

Figure 4. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.25 M $NiSO_4.6H_2O$, 0.05 M $NiCl_2.6H_2O$ and 0.4 M $Na_3C_6H_5O_7$ at 10 mVs^{-1} (b) Cycling of polyaniline composite polymer film in 1 M HCl monomer free solution

Figure 5 presents the electrochemical co-deposition of polyaniline in the presence of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ in addition to $NiSO_4.6H_2O$, $NiCl_26H_2O$ and $Na_3C_6H_5O_7$. The participation of $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ did not affect the electroactive properties of polyaniline much, and the anodic and cathodic charge transfer was found to be lower, at 0.15 mC and 0.14 mC. Afterward, $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ were added into the solution separately and the polymer composites were obtained under identical conditions.

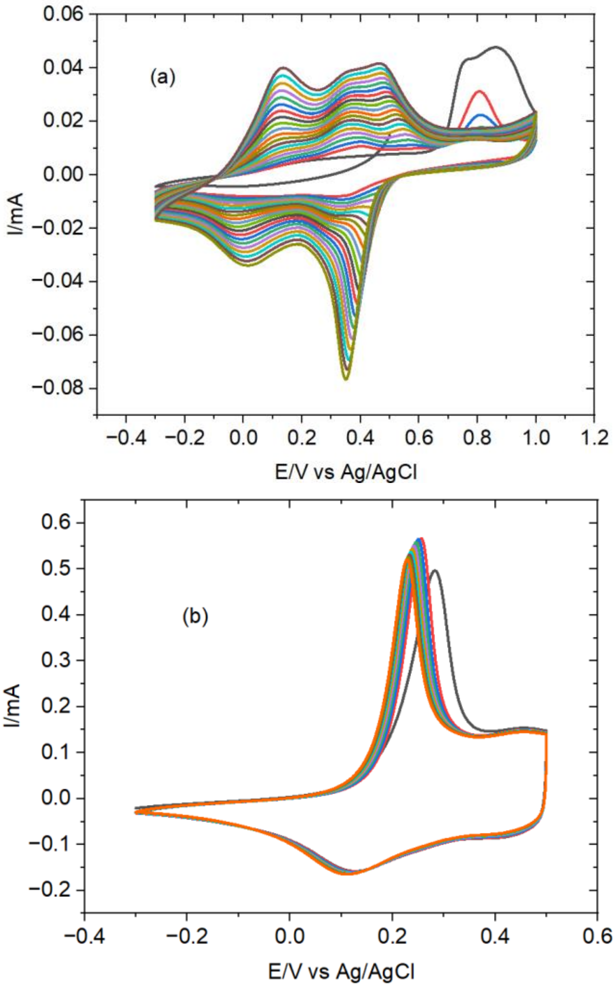

Figure 5. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.25 M $NiSO_4.6H_2O$, 0.05 M $NiCl_2.6H_2O$ and 0.4 M $Na_3C_6H_5O_7$ with 0.05 M $Na_2MoO_4.2H_2O$ and 0.05 M $Na_2WO_4.2H_2O$ at 10 mVs^{-1} (b) Cycling of polyaniline composite polymer film in 1 M HCl monomer free solution

Figure 6 shows the electrochemical deposition of polyaniline/WO_4 in the presence of $NiSO_4.6H_2O$, $NiCl_26H_2O$ and $Na_3C_6H_5O_7$. The first thing worth noting is that the peak current is increased by the addition of $Na_2WO_4.2H_2O$ without changing the voltammogram of pure polyaniline. On the other hand, the incorporation of $Na_2WO_4.2H_2O$ electroactive properties of the resulting film because its current is still between 0.04 mA and 0.06 mA. This suggests that $Na_2WO_4.2H_2O$ contributes to the increase of electroactive sites in polymer matrices.

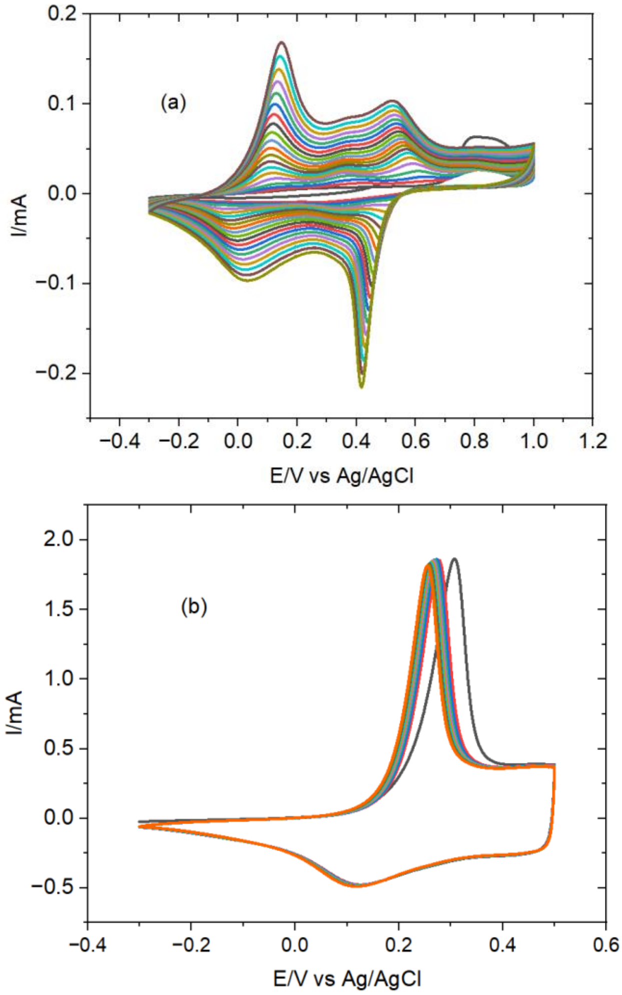

Figure 6. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.25 M $NiSO_{4.}6H_2O$, 0.05 M $NiCl_{2.}6H_2O$ and 0.4 M $Na_3C_6H_5O_7$ with 0.05 M $Na_2WO_4.2H_2O$ at 10 mVs^{-1} (b) Cycling of polyaniline composite polymer film in 1 M HCl monomer free solution

Figure 7 displays the electrochemical deposition of polyaniline/MoO_4 in the presence of $NiSO_4.6H_2O$, $NiCl_26H_2O$ and $Na_3C_6H_5O_7$. The addition of $Na_2MoO_4.2H_2O$ affects the size of the anodic peaks without significantly impacting the cathodic peaks. The current values are lower comapred to the growth of polyaniline/WO_4, as seen in Figure 6. The characterization of the resuting film also supports that polyaniline/WO_4 is more electroactive than the polyaniline/MoO_4 composite film. The anodic peak and cathodic peak charge for polyaniline/WO_4 were found to be 0.43 mC and 0.42 mC, while polyaniline/MoO_4 was 0.20 mC and 0.18 mC.

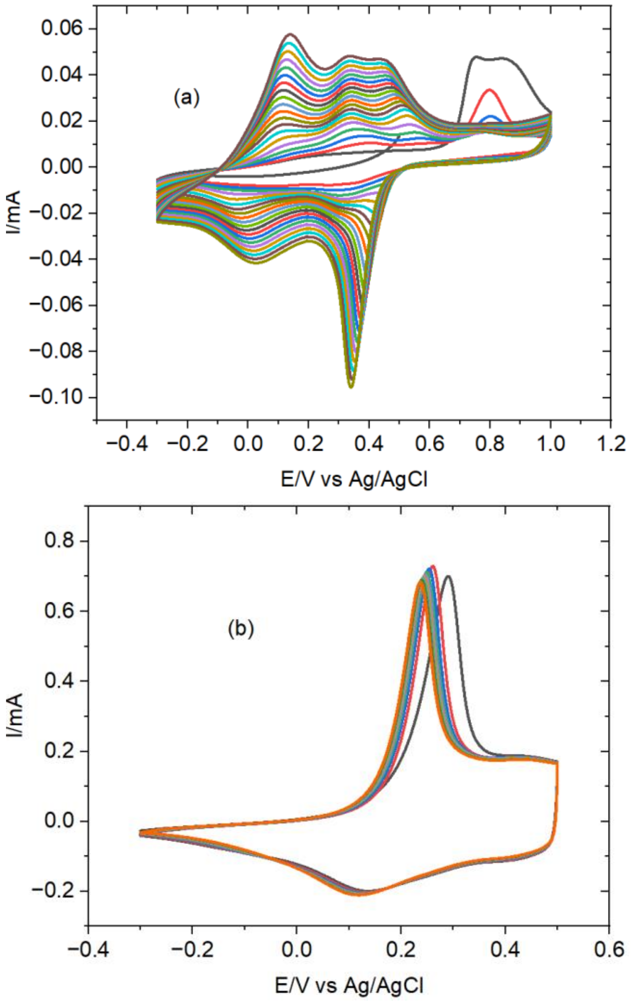

Figure 7. (a) Electrochemical deposition of polyaniline from 0.1 M aniline and 0.1 M HCl in the presence of 0.25 M $NiSO_{4.}6H_2O$, 0.05 M $NiCl_{2.}6H_2O$ and 0.4 M $Na_3C_6H_5O_7$ with 0.05 M $Na_2MoO_4.2H_2O$ at 10 mVs^{-1} (b) Cycling of polyaniline composite polymer film in 1 M HCl monomer free solution

4. Conclusion

In the current study, the electrochemical deposition of polyaniline with $Na_2MoO_4.2H_2O$ and $Na_2WO_4.2H_2O$ in the presence or absence of $NiSO_4.6H_2O$, $NiCl_26H_2O$ and $Na_3C_6H_5O_7$ was investigated. The fact that the cathodic charge of polyaniline/MoO_4 composites increased from 0.25 mC to 1.50 mC shows that $Na_2MoO_4.2H_2O$ improves the properties of pure polyaniline. Polyaniline/MoO_4 composite also shows a charge value of 0.18 mC when synthesized in the presence of 0.1 aniline monomers, 0.1 M HCl and $NiSO_4.6H_2O$, $NiCl_26H_2O$ and $Na_3C_6H_5O_7$. This shows that MoO_4 does not have a significant effect on this solution. On the other hand, polyaniline/WO_4 composites show that 0.42 mC cathodic load passes after reduction. This proves that WO_4^{2-} doping into polyaniline matrices increases the electroactive sites of polyaniline, enabling fast, reversible redox reactions. Well distrubitıon of WO_4^{2-} in polymer matrices can be used to increase the synergic effect between two components with other techniques such as spin coating and can be examined for energy storage devices in further studies.

According to the literature, the chemical synthesis of polyaniline with zinc tungstate and copper tungstate demonstrates that a PANI/$CuWO_4$ modified electrode can selectively detect quercetin [29], while PANI/$ZnWO_4$ enhances conductivity [28]. Additionally, the electrosynthesis of PANI/MoO_4 in oxalic acid on steel reveals the corrosion protection properties of polyaniline [27]. In light of these, the reversible behavior of PANI/WO_4 and PANI/WO_4 suggests its potential use in chemical and biosensors.

Article Information Form

Acknowledgments

The author are thankful to Prof. Dr. Abdullah Yıldız and Yıldız Research Group for useful discussions and providing support.

Funding

The author (s) has no received any financial support for the research, authorship or publication of this study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

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