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Spontaneous and Electrochemical Reduction of Silver by Polypyrrole Deposits

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Abstract: Polypyrrole (ppy) coatings doped with p-toluene sulfonate sodium on stainless steel mesh (SSM) have been electrosynthesized in aqueous solution. The removal of Ag^+ ions from acidic solutions was investigated through spontaneous reduction (SR) and electrochemical reduction (ER) procedures using reduced composite ppy-SSM. Higher removal efficiencies and current efficiencies were obtained by ER process for ppy-SSM rather than SR process for ppy-SSM and ER process for SSM under comparable conditions. Due to its high efficiency and simplicity, ER was supposed to be an alternative advantageous method for the recovery of low-level silver concentration in industrial wastewater. Cyclic voltammetry was carried out to characterize the electrochemical behavior of ppy-SSM in acid solutions containing Ag^+. Metallic silver deposited on ppy-SSM has been evidenced by scanning electron microscopy (SEM) analysis.

Keywords: Electrochemical reduction, polypyrrole, silver, spontaneous reduction

INTRODUCTION

Silver is one of the most important precious heavy metals and has been widely used in many industrial processes, such as electroplating, metal finishing, electronics, mirror manufacture, etc. The discharge of wastes

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containing silver is strictly controlled due to its toxic effects. Although chemical precipitation is the most economical method for the treatment of silver-bearing effluents, the chemical reagents are consumed in the reaction process and cannot be recovered for reuse. In addition, the use of these reagents can produce a large volume of sludge, which causes secondary pollution. Many other methods like adsorption, coagulation, ion exchange, and reverse osmosis have been developed (1–5). One of the most effective ways is the electrochemical process. The electron is a clean reagent without the disadvantages of conventional treatment. However, this method is economically unfavorable and is not practically adopted on a large scale because of the low reaction rates and current efficiencies obtained. To solve this problem, the development of new technologies is economically and environmentally necessary.

Conducting polymers have aroused much interest and have been studied extensively for decades. In particular, ppy is one of the most frequently investigated polymers due to its high electric conductivity and good stability. More recently, it has been shown that conducting ppy films can be used to reduce heavy metals (6–15), opening up the possibility of a new environmental remediation technology. Wang et al. (11) have investigated the electrocatalytic reduction of Cr(VI) by ppy-modified glassy carbon electrodes. Pickup and co-workers (12) have studied the extraction of silver by ppy films upon a base-acid treatment. The recovery of gold cyanide using inherently conducting polymers has been conducted by Ding et al. (13).

Ppy can undergo good reversibility between the insulator and the conductive states. Freshly synthesized ppy is in its oxidative (conducting) state. It be can reduced at negative potential to reversibly transform to its neutral (insulating) state. Then, Ag^+ ions can be reduced by neutral ppy, ppy^0. Since the redox reaction between ppy^0 and Ag^+ occurs spontaneously, this reduction method can be called spontaneous reduction (SR) or open-circuit reduction. After reaction, the polymer becomes oxidized and can be reduced again for the next cycle. Although this process is effective, it has its own limitations which will be further demonstrated in this connection:

1. Operation steps are complicated.
2. Reuse of ppy films can cause conductivity decay and lose its reversibility.

Obviously, SR is not ideal, which makes the process inapplicable on an industrial scale. It is reported that the polymer film under open-circuit potential had the same effect of keeping it under very positive potentials where polymer degradation takes place (16). Therefore, we suppose another method called electrochemical reduction

(ER), which can avoid the disadvantages of SR. During the ER process, the continuous application of a negative potential to the film maintains the polymer stability. In order to evaluate this modified process, the efficiency and influencing parameters for silver reduction with reduced ppy deposits on SSM have been investigated in this study. Special attention was given to compare the effect between SR and ER, which can lead to a better understanding of redox property of ppy deposits for silver recovery.

EXPERIMENTAL

Pyrrole was distilled before use. Polypyrrole was potentiolstatically polymerized at 0.8 V on SSM from the solution with 0.15 M pyrrole and 0.20 M sodium p-toluene sulfonate in a three-electrode cell under nitrogen atmosphere. The consumed charge was controlled for 20 C. SSM used as a working electrode was 80 ppi (pores per inch) and 10 × 10 mm in dimensions. A stainless steel plate (15 × 15 mm) was used as a counterelectrode and both were rinsed in acetone and distilled water before use. A saturated calomel electrode (SCE) was used as the reference electrode throughout this study and all the potentials were measured against the SCE electrode. All the reagents were of analytical reagent grade, and deionized water was used for preparing all the solutions.

The freshly synthesized ppy was in its oxidized state and was reduced at −0.8 V in 0.1 M Na_2SO_4 solution for 24 min to ensure it in its reduced state. After being rinsed in distilled water, it was put in contact in 20 mL acidified $AgNO_3$ solution (with a concentration of 6.05×10^{-4} mol/L, pH of 2.0) for 24 min.

Electrochemical reduction was carried out at a constant potential of −0.8 V for 24 min in the same acidified $AgNO_3$ solution.

Unless otherwise stated, the temperature was controlled at $20 \pm 0.1\,^{\circ}C$ by immersing the whole cell in a water bath. Each experiment was duplicated under identical conditions.

Concentrations of silver in all samples were determined by a Perkin Atomic Adsorption Spectrophometer Model AA-646 (Hitachi, Japan).

Cyclic voltammetry was carried out in acid solution containing $AgNO_3$ with the same concentration mentioned above from −0.8 to 1.2 V at a scan rate of 100 mV/s.

All the electrochemical measurements were performed on a Potentialstat/Galvanostat Model 263 A (Princeton Applied Research, America). The scanning electron microscopy was performed on a Microscope Model JSM-5600 LV (Hitachi, Japan).

RESULTS AND DISCUSSION

Influencing Parameters on the Removal Efficiency of Silver Reduction

Effect of PH

Reduced ppy-SSM electrodes were immersed into Ag^+ solutions with different pH. Data described removal efficiency as a function of pH illustrates in Fig. 1. The curves for spontaneous and electrochemical processes present a different trend. The ER process has obtained higher removal efficiencies at different pH as compared to SR, which indicates that the electrochemical method is more effective for silver reduction. It is known that low pH generally leads to a higher removal efficiency for heavy metals reduction. The reduction of Ag^+ to Ag^0 is thermodynamically favored under acidic conditions due to an increase of its standard potential with proton concentration (17–19). But in the case of SR, when the pH is lower than 2 in this study, the deposited metallic silver is dissolved in the acid medium and causes the efficiency decrease. The overall reaction is:

$$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_2 \uparrow + H_2O \tag{1}$$

With this competing reaction, the removal efficiency for SR has a maximum at pH about 2.6. In this spontaneous process, after reaction

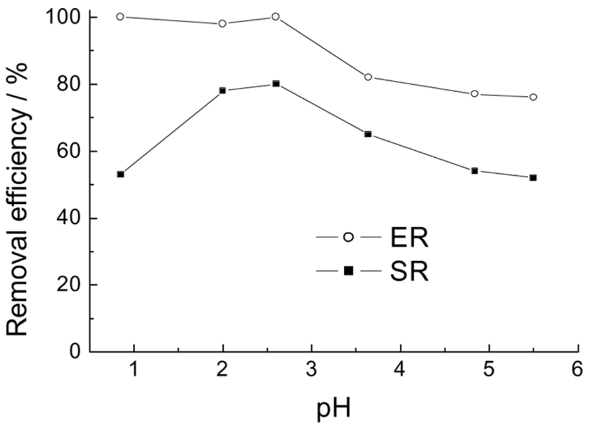


Figure 1. Variation of removal efficiency of silver by spontaneous and electrochemical reduction as a function of pH.

between ppy^0 and Ag$^+$, ppy is oxidized and it loses its redox property. But in the electrochemical process, the electrons transfer for silver reduction will continue throughout the whole process, since ppy is always in its reduced state. As a result, in the ER process, the removal efficiencies are much higher than those in the SR process. Additionally, even at lower pH, it still shows higher removal efficiencies.

It should be considered that the Ag$^+$ will ingress into the polymer to form a complex between the silver ions and the amine groups of ppy, but this silver species present in the +1 valence is quite limited compared to the silver species in the zero valence metallic state (20).

Effect of Temperature

Figure 2 displays the plot of silver reduction by spontaneous and electrochemical reduction versus temperature. Increasing temperature would increase the driving force of silver deposition process. But in the case of SR, when the temperature is higher than 80 °C, the removal efficiency drastically declines because the metallic silver is rapidly dissolved in a dilute acid medium (seen equation 1) at higher temperature. In contrast, in the case of the ER process, the evolution of silver reduction efficiency versus temperature is different from that in SR process. Namely, the efficiency of silver reduction is 100% with the temperature even higher than 80 °C. In this case, ppy is in a reduced state throughout the ER process, and the rate of silver reduction predominates over the silver oxidation.

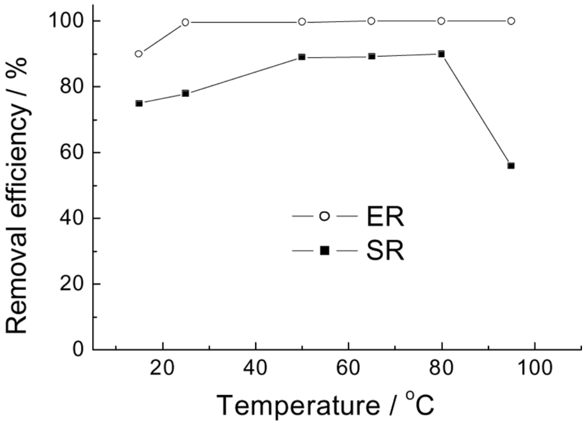


Figure 2. Variation of removal efficiency of silver by spontaneous and electrochemical reduction as a function of temperature.

Although it has been reported that a rapid degradation of ppy film occurs at elevated temperature (21), this effect is insignificant in this case, since silver reduction process is very fast. It should also be noted that under comparable conditions, a higher removal efficiency was achieved in the ER process.

Kinetics Investigation

Kinetics of reaction behavior between ppy^0-SSM and Ag^+ is shown in Fig. 3. The reduction efficiency is 55% for SR and 75% for ER at only 3 min, which indicates that the reaction of silver reduction is very fast. In the SR process, ppy is gradually oxidized and there is a loss in a part of its redox properties (22,23). However, in the ER process, ppy keeps in a reduced state and retains its good stability. Therefore, the ER process exhibits a higher rate and a high removal efficiency for silver reduction as compared to the SR process.

The Advantages of ER Process for Ppy-SSM Electrode

In order to show the advantages of ER process of ppy-SSM for silver reduction, removal efficiencies (RE) and current efficiencies (CE) recorded at −0.6 and −0.8 V are listed in Table 1. For comparison, data obtained for bare SSM under the same conditions is also included.

After polymerization, ppy is in an oxidative state. Before it was put in contact with Ag^+ ions, the ppy film has been reduced electrochemically to ensure it is in a reduced state. Although silver was reduced under an

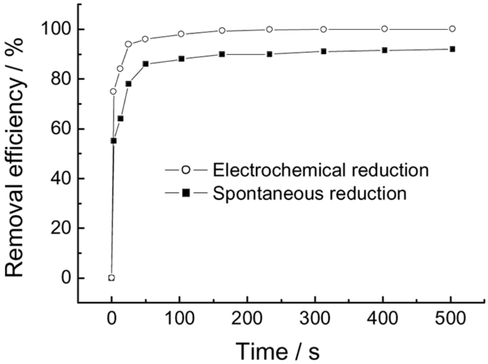


Figure 3. Variation of removal efficiency of silver as a function of contact time.

Table 1. RE and CE values obtained from ER for ppy-SSM, SR for ppy-SSM and ER for SSM electrodes

	SR for ppy-SSM		ER for ppy-SSM		ER for SSM	
Condition	RE (%)	CE (%)	RE (%)	CE (%)	RE (%)	CE (%)
−0.6 V	42	8	78	93	65	46
−0.8 V	78	17	94	92	83	32

open-circuit condition, the stored charge during the procedure of ppy reduction can be recorded for the calculation of current efficiency. The theoretical charge needed to reduce the Ag^+ ions with a concentration of 6.05×10^{-4} mol/L for 20 mL is 0.91 C if the removal efficiency is 78% under the condition of −0.8 V (seen Table 1). The practical charge recorded during the ppy reduction process is 5.4 C. Therefore, the current efficiency in this case is 17%.

Data in Table 1 show that higher RE and CE were obtained for the ER process at ppy-SSM electrode. Although ER could also be performed at SSM electrode without ppy coating and also show higher removal efficiencies; however, the current efficiencies are considerably low, as compared to the ER process for the ppy-SSM electrode. This is due to the competing side reaction of hydrogen evolution at −0.6 and −0.8 V on the surface of the bare SSM. For the ppy-modified electrode, the hydrogen evolution can be inhibited which is one of the important properties of the ppy film discovered in our lab and will be discussed in another article in detail. This result indicates that CE can be substantially improved by the deposition of ppy on SSM electrode for the practical application of silver reduction. The SR process shows the lowest removal efficiencies among the three processes, which demonstrates that the ppy film cannot be completely reduced in the indicated time intervals or partially oxidized before it is put into the solutions containing Ag^+.

Electrochemical Behavior of ppy-SSM Electrode

Figure 4 shows progressive voltammograms of freshly synthesized SSM-ppy and the naked SSM electrodes in acidified Ag^+ solution by repeated potential scanning within the range from −0.8 to 1.2 V. For SSM in the first cycle, the oxidation peak A at about 0.56 V is attributed to silver oxidation, while the reduction peak B at about 0 V is attributed to silver deposition. For ppy-SSM electrode, the current values are much higher

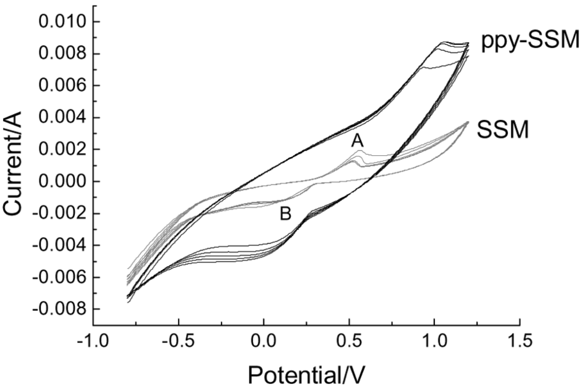


Figure 4. Progressive cyclic voltammograms for SSM-ppy electrode in acidified $AgNO_3$ solution (with concentration of 6.05×10^{-4} mol/L, pH of 2.0).

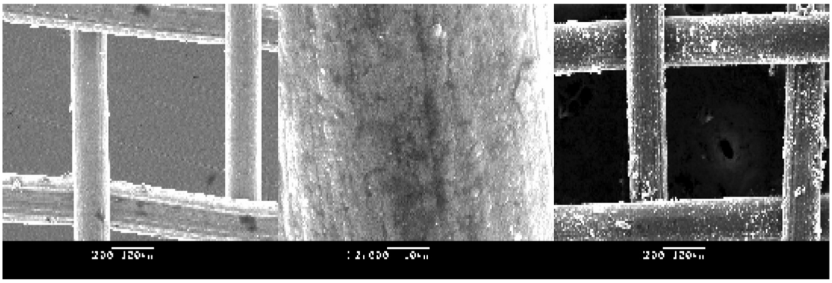
than that of SSM. If these values are considered as the measure of the electroactivity, it could be said that ppy-SSM have better catalytic efficiency with respect to bare SSM electrode.

With increasing cycles, more silver granules were deposited onto the film leading to the increase of the specific area, which is available for the access of more silver ions onto its surface. Thus, the current magnitude became bigger at the latter cycles.

Since the mobility of dopant anions, the pTS^- in ppy matrix is comparatively low, cations of Ag^+ would insert in the polymer for charge compensation when the ppy is reduced before it has been fully covered by silver deposits, which indicates that the silver species present at the oxidized state in the innermost of the polymer matrix (20). But the amount of this valence silver can be neglected. Most Ag^+ ions could be reduced to the zero valence metallic state on the surface of the polymer. In the voltammograms of ppy-SSM, the peaks due to the silver oxidation and reduction can be observed, but it is not as obvious as that for SSM. The redox peaks at around 0.9 and 0.35 V are associated with the oxidation and reduction of the polymer itself, which can be observed in the same acidified solution without the silver species.

Surface Morphology

Figure 5(a) and (b) are ppy modified SSM photographs which exhibit a three-dimensional structure with globular nucleus less than 1 μm in diameter. Figure 5(c) is the morphology of the ppy-SSM film after being in contact with Ag^+, and the white part in the picture are the silver deposits.



(a) (b) (c)

Figure 5. Surface morphology for (a) ppy-coated SSM(× 200), (b) ppy-coated SSM(× 2000) and (c)SSM-ppy after reaction with Ag^+(× 200).

CONCLUSIONS

ppy deposits were obtained on the substrate of SSM. The removal efficiency and its influencing parameters such as the pH and the temperature for silver recovery at reduced ppy-SSM electrodes through spontaneous and electrochemical processes were investigated. In electrochemical procedure, ppy retained as its neutral state and shows high reduction ability, while in spontaneous procedure, ppy is oxidized and loses redox property after being in contact with Ag^+. Therefore, a higher removal efficiency was achieved by the electrochemical reduction process. Furthermore, current efficiencies for ppy-SSM in ER process are much higher than that of ER for SSM and SR for ppy-SSM, which indicates that the ER process with ppy coating is an alternative promising method for silver reduction in practical application. Cyclic voltammograms of SSM-ppy and SSM show that ppy-SSM have better catalytic efficiency with respect to the bare SSM electrode.

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