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ORIGINAL PAPER

Comparative investigation on electroreduction of Cu(II) using polypyrrole electrode and stainless steel electrode

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Abstract The electroreduction of Cu(II) by polypyrrole (ppy)-modified electrode and stainless steel (SS) electrode under potentiostatic and potentiodynamic conditions was studied. Compared with SS electrode, ppy-modified electrode presented higher Cu(II) removal ability since it acted as electrocatalyst during reduction process. Extremely high current efficiency was achieved on ppy-modified electrode due to the inhibition effect on the side-reaction of hydrogen evolution, exhibiting important advantage over other electrode materials for heavy metal treatment. Conductivities of ppy films after different treatments were detected to evaluate the stability of the polymer.

Keywords Polypyrrole · Potentiodynamic reduction · Potentiostatic reduction · Stainless steel · Cu(II)

1 Introduction

Copper-containing materials are widely used in variety of industrial applications. Wastewater, containing copper ions, is produced from many processes, such as metal finishing, mining, electroplating, and electronic industry. Many methods have been put forward to treat this wastewater, including chemical precipitation, ion exchange, filtration, reverse osmosis, etc. The frequently acceptable method for Cu(II) treatment is chemical precipitation. However, this process is found to generate secondary polluted byproducts and be ineffective at low pH or low concentrations [1, 2]. Therefore, emphasis should be placed on further developments of sustainable technologies for Cu(II)-containing wastewater treatment.

Electrodeposition is a clean and effective technology due to its recovery of heavy metals through redox reactions without the disadvantages of conventional chemical precipitation. However, electrodeposition has not been widely used in practical wastewater treatment because of the relatively large capital investment and the need for expensive electricity supply [3]. In order to make this technology more competitive and develop its practical applications, one of the biggest challenges is to choose proper electrode materials that provide low concentration polarization and high current efficiency.

Recently, it has been shown that conductive polypyrrole (ppy) films can undergo good reversibility between its conducting and insulating states. This ability of conductive polymers suggests its potential application as an effective electrode material in electrodeposition process for heavy metal treatment. Reduction of chromate by conductive ppy polymers has been extensively studied in many previous articles [4–10]. Other heavy metals such as copper, silver, cadmium, and gold cyanide can be effectively removed from outlet wastewater using ppy-modified electrodes [11–15]. While the effectiveness of these conductive polymers for heavy metals removal have been proved in these reports, no detailed study has so far characterized this new material and clarified its advantage for electrochemical treatment. In this study, we provided comparative investigations for Cu(II) reduction using ppy-modified electrode and stainless steel (SS) electrode. SS is one of the most commonly used electrode materials in practical application, and it was, therefore, chosen for this comparative study. The removal percentage

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and current efficiency were focused on under potentiostatic and potentiodynamic conditions. In this study, ppy showed favorable advantages in terms of high Cu(II) removal percentage and extremely high current efficiency, which made this new material an appealing alternative for Cu(II)-containing wastewater treatment. We found that the side reaction of hydrogen evolution was drastically alleviated on ppy, leading to significantly high current efficiency of this process. This result may be greatly and positively favorable in the case of heavy metal reduction and other fields in electrochemistry, since many electrochemical procedures heavily depend on hydrogen evolution kinetics.

2 Experimental

Ppy synthesis was carried out in a single compartment cell containing 0.10 M pyrrole and 0.14 M *p*-toluene sulphonic sodium (pTSNa) at a potential of 0.8 V under nitrogen atmosphere, using stainless steel (φ10 mm) and platinum (15 mm × 15 mm) plates as working and counter electrodes. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was polished with water-proof sand paper and rinsed, respectively, in acid solution and distilled water prior to each experiment. Except for pyrrole which was distilled before use, all reagents were of analytical grade and used without pre-treatment.

Electroreduction of Cu(II) under potentiostatic condition was carried out at a constant potential of −0.8 V in 20 mL acidified $CuSO_4$ solution (with concentration of 1.0×10^{-3} M, pH of 1.0) for 24 min. Electroreduction of Cu(II) under potentiodynamic condition was carried out at a scan rate of 100 mV/s in 20 mL acidified $CuSO_4$ solution (with concentration of 1.0×10^{-3} M, pH of 1.0) for 24 min. Concentrations of copper in all samples were determined by Perkin flame atomic adsorption spectrophotometer Model AA-646 (Japan). All the electrochemical measurements were performed on a Potentialstat/Galvanostat Model 263A of Princeton Applied Research (America). All potentials in the text versus SCE reference electrode were measured. The electric conductivities of samples were measured by a 4-terminal method using SX1934 (SZ-82) conducting meter (China).

3 Results and discussion

3.1 Reduction of Cu(II) under potentiostatic condition

3.1.1 Effect of potentials

Current and consumed charge for ppy-modified electrode and SS electrode were shown in Figs. 1 and 2, respectively. It can be observed that the current curves for ppy-modified

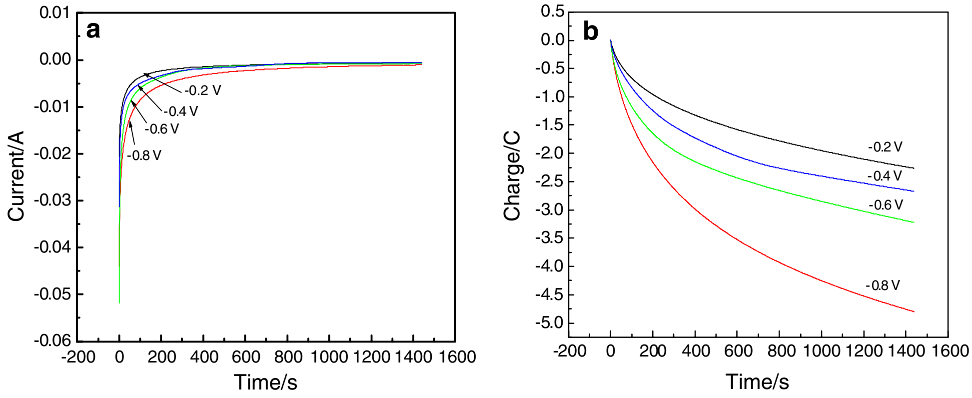

Fig. 1 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on ppy-modified electrode at different potentials in acidified Cu(II) solution

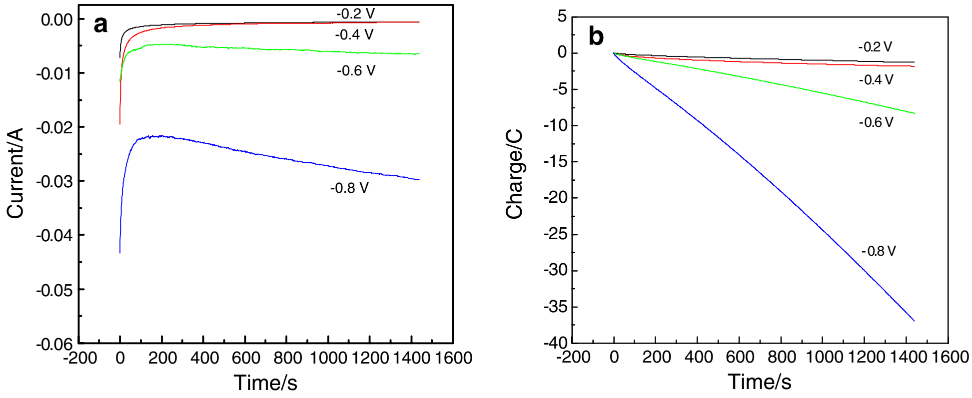

Fig. 2 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on SS electrode at different potentials in acidified Cu(II) solution

electrode at different potentials were similar, but those obtained on SS differed considerably from each other, especially for the potentials of −0.8 and −0.6 V. This clearly indicated the influence of hydrogen evolution on SS electrode at more negative potentials. The reduction charge calculated at −0.8 V was only −4.8 °C for ppy-modified electrode, but it was −37 °C for SS electrode. This result indicated that the undesired side reaction of hydrogen evolution had been greatly reduced on the ppy-modified cathodic electrode.

Table 1 showed the effect of potentials on Cu(II) recovery at ppy-modified electrode and SS electrode. In all cases, ppy-modified electrode achieved higher removal percentage and much higher current efficiency than SS electrode, further confirming the results in Figs. 1 and 2. When the applied potential decreased from −0.2 to −0.8 V, Cu(II) removal percentage increased, but current efficiency decreased which may be due to the increase of hydrogen evolution at more negative potentials.

3.1.2 *Effect of stirring speed*

In order to investigate the effect of stirring speed in aqueous solution on Cu(II) reduction, polarizations at −0.8 V for ppy-modified electrode and SS electrode were carried out. Current and charge measurement were displayed in Figs. 3 and 4, respectively. The negative current increased in magnitude with the rotation speed for both electrodes, indicating the presence of diffusion-limited behavior. Strong hydrogen evolution led to significant change on current curves of SS electrode compared with ppy-modified electrode. The consumed charge obtained on SS electrode was extremely higher than the ppy-modified electrode, indicating the considerably strong side reaction of hydrogen evolution on SS electrode.

Table 2 showed the effect of stirring speed on Cu(II) reduction under the applied potential of −0.8 V. When the process was carried out at faster stirring speed, higher Cu(II) removal percentage and current efficiency were obtained due to the contribution of fast diffusion of copper ions from the bulk solution to the ppy^0/solution interface. Comparatively, the removal efficiency of ppy-modified electrode was greater than the SS electrode and markedly, current efficiency of the former was 10 times greater than the latter, further confirming the different behaviors of ppy-modified electrode and SS electrode.

3.1.3 *Effect of temperature*

Current and charge measurements for ppy-modified electrode and SS electrode at different temperatures were displayed in Figs. 5 and 6, respectively. The magnitude of reduction current (plotted as negative) was increased with temperature. The current and the consumed charge for ppy-modified electrode were only related to the reduction of the polymer since no obvious hydrogen evolution was

Table 1 Effect of potential on Cu(II) removal percentage and current efficiency at ppy-modified electrode and SS electrode

Potential/V	ppy		SS	
	Removal percentage/%	Current efficiency/%	Removal percentage/%	Current efficiency/%
−0.8	79	64	65	6.8
−0.6	66	80	53	25
−0.4	57	83	31	64
−0.2	50	85	22	68

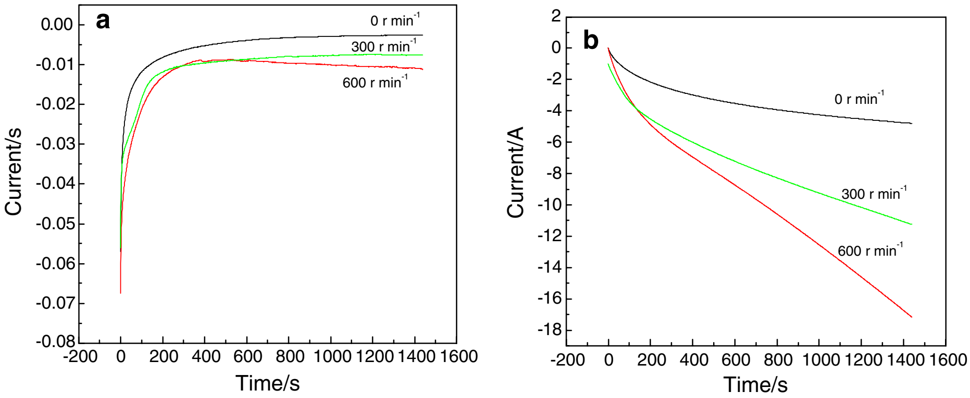

Fig. 3 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on ppy-modified electrode at −0.8 V with different stirring speed in acidified Cu(II) solution

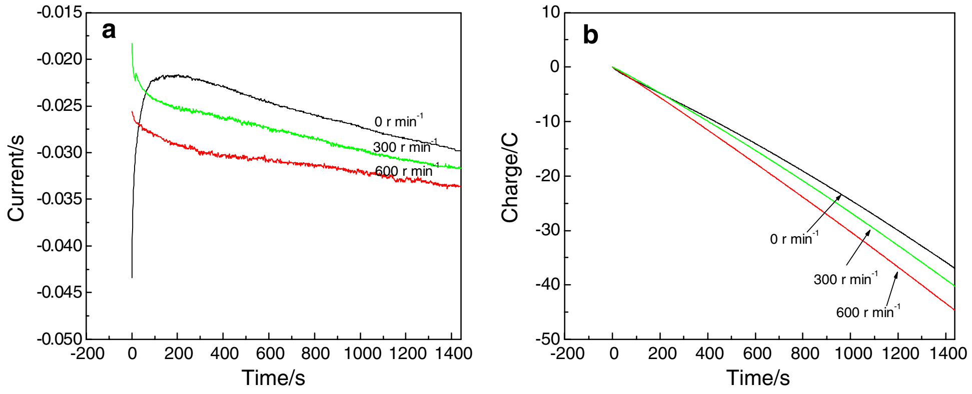

Fig. 4 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on SS electrode at −0.8 V with different stirring speed in acidified Cu(II) solution

Table 2 Effect of stirring speed on Cu(II) removal percentage and current efficiency at ppy-modified electrode and SS electrode

Rotation speed/r min^{-1}	ppy		SS	
	Removal percentage/%	Current efficiency/%	Removal percentage/%	Current efficiency/%
0	79	64	65	6.8
300	98	83	82	7.9
600	100	92	96	8.4

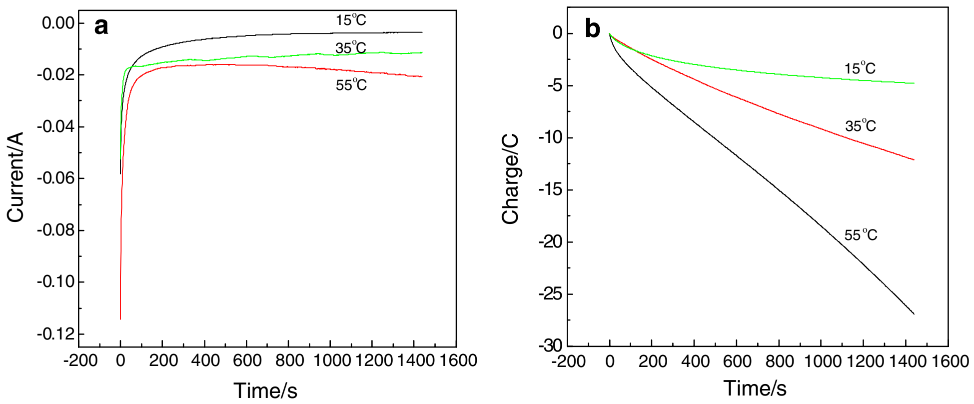

Fig. 5 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on ppy-modified electrode at −0.8 V with different temperatures in acidified Cu(II) solution

observed. Comparatively, strong hydrogen evolution had made great contribution to the large reduction current and consumed charge for SS electrode.

Table 3 showed the effect of temperature on Cu(II) reduction process at ppy-modified electrode and SS electrode. As can be seen, the Cu(II) removal percentage and current efficiency increased with the increase of temperature for both electrodes. Higher temperature normally increased the ion transfer from the bulk solution to the electrode surface, consequently improving the Cu(II) removal percentage and current efficiency. Also, the removal efficiency of ppy-modified electrode was greater than the SS electrode and the current efficiency of the former was 10 times greater than the latter, suggesting favorable to use ppy-modified electrode at high temperature.

3.2 Reduction of Cu(II) under potentiodynamic condition

Reduction of Cu(II) under potentiodynamic condition was carried out to clarify the mechanism of the process. Figure 7 showed the typical series of voltammograms obtained at ppy-modified electrode and SS electrode. The anodic and cathodic peaks at 0.38 and −0.41 V in the first scan obtained on SS electrode were assigned to copper dissolution and metallic deposition. The corresponding anodic and cathodic peaks of ppy-modified electrode turned to broad wave due to the large background current value of the polymers. Obviously, the cathodic deposition and metallic dissolution at SS electrode and ppy-modified electrode took place alternatively at every cycle of the scan in the potential scope of −0.8 to 0.8 V. In comparison with

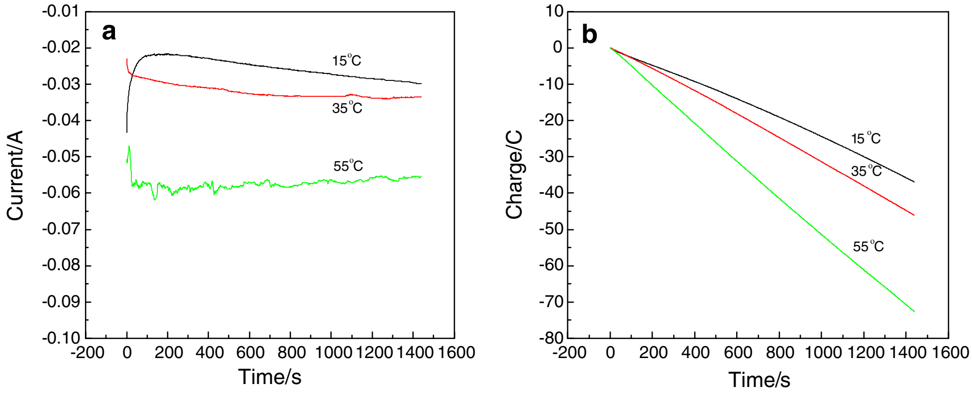

Fig. 6 Current vs. time (**a**) and consumed charge vs. time (**b**) curves obtained on SS electrode at −0.8 V with different temperatures in acidified Cu(II) solution

Table 3 Effect of temperature on Cu(II) removal percentage and current efficiency at ppy-modified electrode and SS electrode

Temperature/°C	ppy		SS	
	Removal percentage/%	Current efficiency/%	Removal efficiency/%	Current efficiency/%
15	79	64	65	6.8
35	95	75	78	7.5
55	100	81	85	8.1

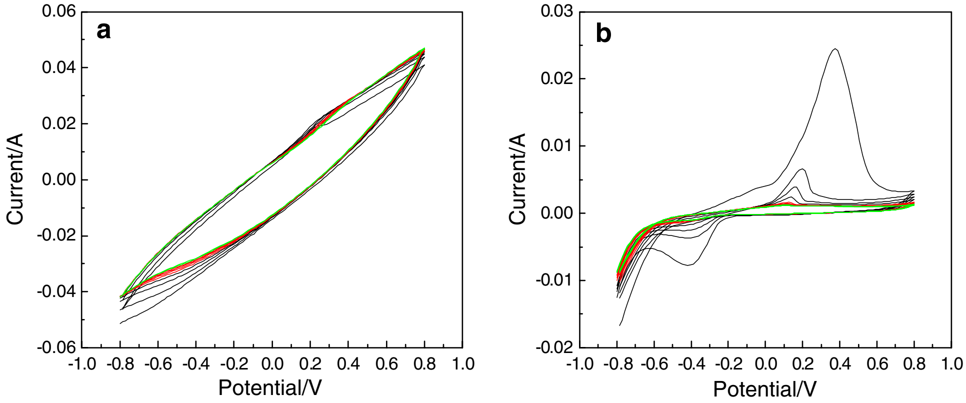

Fig. 7 Cyclic voltammograms scanned from −0.8 to 0.8 V on ppy-modified electrode (**a**) and SS electrode (**b**) in acidified Cu(II) solution

these voltammograms shown in Fig. 7, it can be seen that no significant losses in electroactivity within the 40 cycles on ppy-modified electrode. But the oxidative and reduction peaks related to copper dissolution and deposition processes decreased dramatically on SS electrode. This assumed that at long period of time, the concentration of copper ions was gradually depleted within the zone of the electrode for diffusion-controlled process. This result can be well described the effect of concentration polarization for Cu(II) reduction on the naked SS electrode. Also, it should be noted that the current values obtained on ppy-modified electrode were much higher than the SS electrode, indicating that ppy-modified electrode had displayed electrocatalytic effect on Cu(II) reduction.

The cyclic voltammograms obtained at SS electrode and ppy-modified electrode ranged from −0.8 to 0 V were shown in Fig. 8. These voltammetric curves showed significant difference, indicating that ppy-modified film greatly affected the electrochemical behavior. It can be seen that the cyclic voltammograms were featured by cathodic hydrogen evolution at potentials negative to −0.5 V on SS electrode. However, no obvious hydrogen was observed to release from the surface of the polymer, indicating that the side reaction of hydrogen evolution can be extremely reduced by applying this new material of ppy. The voltammetric data of ppy-modified electrode showed that the current values were close to zero in the later cycles, meaning that ppy was at insulating state at negative potentials. However, this reduced ppy, ppy^0 exhibited better reduction ability as shown in Table 4, in which the Cu(II) removal efficiency under potentiodynamic condition had been calculated and recorded. Both ppy-modified electrode and SS electrode performed high removal efficiencies in the range of −0.8 to 0 V than the range of −0.8

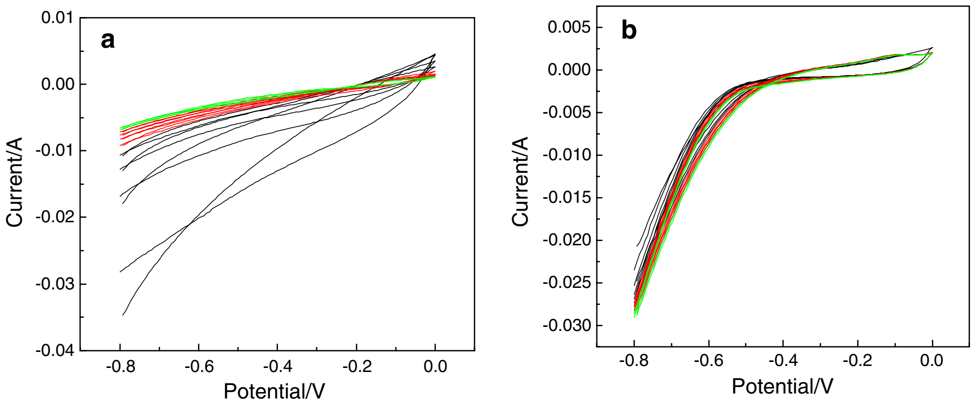

Fig. 8 Cyclic voltammograms scanned from −0.8 to 0 V on ppy-modified electrode (**a**) and SS electrode (**b**) in acidified Cu(II) solution

Table 4 Comparison of Cu(II) reduction with ppy-modified electrode and SS electrode by potentiodynamic process

Electrode	Removal efficiency/%	
	−0.8–0.8 V	−0.8–0 V
ppy	28	86
SS	13	71

to 0.8 V. The possible reason may be that potentiodynamic cycling from −0.8 to 0 V avoided the copper dissolution process and thus increased the reduction process. It also should be noted that Cu(II) removal efficiency of ppy-modified electrode was much higher than the SS electrode due to the role of ppy film as an electrocatalyst.

As we know, direct reduction took places on SS electrode, but mediated reduction occurred at the support electrode/ppy film boundary. The oxidized ppy (ppy+) was reduced by the electron transfer from the support matrix. Then these neutral ppy^0 sites subsequently transferred the charge to the Cu(II) ions. Ppy itself turned to its oxidative state after the whole process. In this way, ppy had played a role as an electrocatalyst, thus increasing the Cu(II) reduction rate.

Effects of stirring speed and temperature on Cu(II) reduction were similar with that in the process of potentiostatic reduction (PSR). The data describing the two variables were omitted here.

3.3 Comparison on Cu(II) reduction through potentiostatic and potentiodynamic processes on ppy-modified electrode and SS electrode

Cu(II) removal percentage and current efficiency obtained from ppy-modified electrode and SS electrode through PSR and potentiodynamic reduction (PDR) processes were listed in Table 5. In all cases, ppy-modified electrode showed favorable advantages with high Cu(II) removal percentage and significantly high current efficiency due to its electrocatalytic role and inhibition effect on hydrogen evolution as stated above. Take a group of data for example. In PSR process, the Cu(II) removal percentage and current efficiency under rotation speed of 300 r min^{-1} were 98 and 83% for ppy-modified electrode, but only 82 and 7.9% for SS electrode, respectively. This indicated that large quantity of charge was applied for hydrogen evolution at SS electrode, but only a small part of charge was consumed for the side-reaction on the conductive polymer. The result exhibited the most significant advantage for applying ppy as the electrode material relative to the conventional SS electrode. In comparison with the data of PSR and PCR, it demonstrated that the reduction of Cu(II) under potentiodynamic condition was also effective, although it showed slight lower Cu(II) removal efficiencies and current efficiencies than that under potentiostatic condition as expected.

Table 5 Comparison on Cu(II) reduction with ppy-modified electrode and SS electrode through potentiostatic reduction (PSR) and potentiodynamic reduction (PDR)

	ppy		SS	
	Removal percentage/%	Current efficiency/%	Removal percentage/%	Current efficiency/%
Rotation speed: 0 r min^{-1}				
PSR	79	64	65	6.8
PDR	67	52	52	3.3
Rotation speed: 300 r min^{-1}				
PSR	98	83	82	7.9
PDR	83	73	76	7.1
Rotation speed: 600 r min^{-1}				
PSR	100	92	96	8.4
PDR	96	82	86	13

Potentiostatic reduction condition: −0.8 V

Potentiodynamic reduction condition: −0.8–0 V, Scan rate: 100 mV s^{-1}

In order to investigate the stability of ppy films, room-temperature conductivity measured in air was listed in Table 6. No significant difference between the conductivities of oxidized ppy-modified electrode and reoxidized ppy-modified electrode after PSR or PDR process suggested that ppy-modified electrode still maintained good

Table 6 Conductivities of ppy films treated under different experimental conditions

ppy film	Conductivity/Scm^{-1}
Oxidized ppy film[a]	11.3
Reduced ppy film[b]	0.23
Reoxidized ppy film after PSR process[c]	10.9
Reoxidized ppy film after PDR process[d]	10.5

[a] Oxidized ppy prepared at 0.8 V in a solution containing 0.1 M pyrrole and 0.14 M pTSNa

[b] Oxidized ppy treated by reducing at −0.8 V in 0.1 M Na_2SO_4 solution for 36 min

[c] ppy reoxidized at 0.8 V in 0.1 M Na_2SO_4 solution for 36 min after PSR process at −0.8 V (deposited copper is removed by washing it in 1 M H_2SO_4 solution)

[d] ppy reoxidized at 0.8 V in 0.1 M Na_2SO_4 solution for 36 min after PDR process from −0.8 to 0 V (deposited copper is removed by washing it in 1 M H_2SO_4 solution)

stability due to the application of negative potentials to avoid the overoxidation under very positive potentials. The conductivity of reduced ppy-modified electrode was much lower, revealing that the film reduced for a long time at a high cathodic potential was in the semiconductor range. Thus, water hydrolysis can be inhibited with the simultaneous achievement of high current efficiency during the reduction process.

4 Conclusions

The electroreduction of Cu(II) can be accomplished by both ppy-modified electrode and SS electrode under potentiostatic and potentiodynamic conditions. Effect of potentials, stirring speed, and temperature on Cu(II) reduction were evaluated. The electroreduction efficiency increased with the potential shift to the negative direction, and the improvement of stirring speed and temperature. Compared to SS electrode, ppy-modified electrode had shown favorable advantages with high Cu(II) removal percentage and significantly high current efficiency due to its electrocatalytic role and inhibition effect on hydrogen evolution. Conductivity measurements illustrated that ppy film kept good stability after PSR or PDR process. These results suggested that ppy is a promising material for heavy metals treatment and other fields in electrochemistry.

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