Electroreduction of hexavalent chromium using a polypyrrole-modified electrode under potentiostatic and potentiodynamic conditions

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A R T I C L E   I N F O

Article history:
Received 30 November 2011
Received in revised form 19 April 2012
Accepted 23 April 2012
Available online 28 April 2012

Keywords:
Polyppyrole
Electroreduction
Stainless steel
Cr(VI)
Potentiostatic condition
Potentiodynamic condition

A B S T R A C T

Polyppyrole (ppy)-modified electrode was used for electroreduction of Cr(VI) and showed favorable advantage with extremely higher removal percentage and current efficiency over stainless steel (SS) electrode. In potentiostatic (PS) process and in stagnant solution, ppy electrode achieved a Cr(VI) removal efficiency of 16% and a current efficiency of 23% compared to 0 for SS electrode at a potential of −0.8 V. In potentiodynamic (PD) process and in stagnant solutions, ppy electrode exhibited a Cr(VI) removal efficiency of 56% at a potential range from −0.8 to 0.8 V whereas SS electrode presented none at the same condition. Solution stirring promoted mass transportation and dramatically improved Cr(VI) removal efficiency, achieving 92% (ppy electrode) and 18% (SS electrode) in PS process and 100% (ppy electrode) and 36% (SS electrode) in PD process at 100 rpm. ppy electrode exhibited an efficient Cr(VI) reduction at a wide potential range from −0.8 to 0.8 V than the potential ranges of −0.8 to 0 V and 0−0.8 V. While ppy stability under PD condition of −0.8 to 0.8 V was not as satisfactory as PS condition at −0.8 V, but better than PS condition at 0.8 V. These results demonstrate that ppy-modified electrode in PD process may be a promising alternative for Cr(VI) electroreduction.

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1. Introduction

Cr(VI) is used in a variety of applications including electroplating and electrodeposits, metal finishing, dye production, and lumber and wood product processes [1]. Toxic effects of Cr(VI) moieties is the focus for environmental pollution abatement. Reduction of Cr(VI) to Cr(III) which is less toxic, less bioavailable and more able to be absorbed to soil particles is an effective treatment strategy. Among all the methodologies of Cr(VI) reduction, electrochemical methods (with electrogenerated Fe(II)) provide interesting alternatives due to less sludge production and low operating costs [1,2]. Direct electroreduction of Cr(VI) is commonly regarded to be a cleaner method but suffers from slow kinetics and large energy consumption [3,4]. The development of new processes to improve the reduction kinetics is needed to achieve an economical operation.

The rate of Cr(VI) reduction in acid solution is influenced by the nature of the electrode material, whereby the process is electrocatalytic in character with active surface metal atoms such as gold and platinum, playing a significant role in hexavalent chromium reduction [5]. Conductive polymer is a new kind of electrode material exhibiting catalytic properties for improving Cr(VI) reduction [6–9]. Polypyrrole (ppy) has attracted much attention due to its high electronic conductivity and favorable chemical stability. Metals including Cr(VI), Cu(II), Ag(I) and Cd(II) can be effectively reduced using ppy under open circuit conditions [10–19]. However, the use of ppy under open circuit conditions led to ppy degradation after several cycles, making the process high cost and inapplicable in industrial scale. Potentiostatic (PS) process is effective for heavy metals removal [20–22] whereas potentiodynamic (PD) process for heavy metals reduction is not found, although is the latter has been extensively used for electro synthesis of ppy and other materials [23–27].

The rate of Cr(VI) reduction depends considerably on pH, which determines the dominant species with different reaction activity[28]. In our test acidified Cr(VI) solution (with a concentration of 1.0 mmol L−1 Cr(VI) and 0.1 mol L−1 H2SO4), the HCrO4− ions are considered the dominant species and to be the electrochemically active species according to the Pourbaix diagram [28].

In this study, electroreduction of Cr(VI) was examined based on a comparison of ppy electrode and stainless steel (SS) electrode under both PS and PD conditions. Following these investigations, studies were further focused on Cr(VI) reduction under PD process.
where the influences of potential and scan rate were investigated. Next, the effect of solution stirring both for PS and PD processes was also examined. Last, the ppy stability under PS and PD conditions for Cr(VI) reduction were assessed.

2. Materials and methods

2.1. Ppy synthesis and Cr(VI) electroreduction conditions

Ppy synthesis was carried out in a single compartment cell containing 0.10 mol L\(^{-1}\) pyrrole and 0.14 mol L\(^{-1}\) sodium p-toluenesulphonate at a potential of 0.8 V under nitrogen atmosphere, using SS (Ø15 mm) plates as working and counter electrodes. The film thickness is about 13 µm controlled by the consumed charge of 3 C during ppy synthesis. A saturated calomel electrode (SCE) was used as a reference electrode. The SS working electrode was firstly polished with water-proof sand paper and then rinsed in acid solution followed by distilled water prior to each experiment. All reagents were of analytical grade. Pyrrole was also analytical grade and it was distilled before use.

Ppy films deposited on the surface of SS were prepared for electroreduction after rinsed thoroughly by distilled water. In order to have a suitable ratio of electrode surface area and solution volume, 20 mL acidified Cr(VI) solution (with a concentration of 1.0 mmol L\(^{-1}\) Cr(VI) and 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\)) was used here for electroreduction of Cr(VI) under PS condition at a constant potential of \(-0.8 V\), 0 V and 0.8 V respectively for 36 min. Electroreduction of Cr(VI) under PD was carried out at potential range of \(-0.8 \text{ to } 0.8 V\), \(-0.8 \text{ to } 0 V\) and 0 to 0.8 V, respectively and at a scan rate of 20 mV s\(^{-1}\) in the same 20 mL acidified Cr(VI) solution for 36 min.

Temperature was controlled at 20 ± 0.1 °C by immersing the whole cell in a water bath for ppy electroreduction, cyclic voltammetry (CV) measurement and Cr(VI) electroreduction.

2.2. Analysis and calculations

Cr(VI) concentrations were measured with a 721 spectrophotometer (Shanghai, China) using the standard method of the diphenylcarbazide. Cr(VI) removal efficiency was calculated based on the following equation:

\[
R = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where \(C_0\) is the initial concentration of Cr(VI) and \(C_t\) is the concentration of Cr(VI) after a certain time of electroreduction using ppy or SS electrodes.

Current efficiency was calculated as:

\[
\eta = \frac{Q_t}{Q_p} \times 100\% = 96,500 \times \frac{ncVR}{Q_p} \times 100\%
\]

where 96,500 is Faraday constant (C mol\(^{-1}\)); \(\eta\) is the current efficiency (%); \(R\) is removal efficiency calculated according to Eq. (1) (%); \(Q_t\) is the theoretical charge needed to reduce Cr(VI) (C); \(Q_p\) is the practically consumed charge for Cr(VI) reduction (C) obtained by multiplication of constant current and collapsed time for PS process; \(c\) is the molar bulk concentration of Cr(VI) (mol L\(^{-1}\)); \(V\) is the electrolyte volume (L); \(n\) is the number of electrons, here is 6 according to Eq. (3).

The real area of ppy film was measured by chronocoulometry technique with the potential pulse of \(\Delta E = 10\) mV in 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution (figure not shown here), and calculated by the formula of \(A = C_0t/C_0\), where \(A\) is the real area of ppy film; \(C_0\) is the capacity of ppy film recorded on chronocoulometry diagram; \(C_0\) is the standard capacity based on the smooth surface of pure mercury, it is 20 µA cm\(^{-2}\). The real surface area was 18.3 cm\(^2\) for ppy film while the apparent surface area was 1.8 cm\(^2\) for the naked SS electrode (Ø15 mm).

CV analysis on ppy and SS electrodes in an acidified Cr(VI) solution (with a concentration of 1.0 mmol L\(^{-1}\) Cr(VI) and 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\)) was carried out at a scan rate of 20 mV s\(^{-1}\). All the electrochemical measurements were performed on a Potentiostat/Galvanostat Model 263A of Princeton Applied Research (USA). All potentials in the text were measured versus SCE reference electrode.

3. Results and discussion

3.1. Comparison between ppy electrode and SS electrode for Cr(VI) reduction under PS condition

The chronoamperograms polarized at potentials of \(-0.8 V\), 0 V and 0.8 V in an acidified Cr(VI) solution showed clearly different characters between ppy and SS electrodes, especially for the curves at \(-0.8 V\) (Fig. 1). At this highly negative potential, hydrogen was drastically evolved on the SS electrode. However, it was not observed on the ppy electrode. Under this condition, the consumed charge was recorded to be only \(-8\) C on the ppy electrode in comparison with the \(-41\) C on the SS electrode (figure not shown here). The low charge consumption on the ppy electrode was attributed to the inhibition effect for hydrogen formation, which saved more electrons for Cr(VI) reduction and consequently improved the current efficiency.
At a potential of −0.8 V and in stagnant solution, a Cr(VI) removal efficiency of 16% and a current efficiency of 23% were achieved for ppy in comparison with no Cr(VI) reduction for SS. These results indicate the favorable advantage of ppy-modified electrode with extremely higher removal percentage and current efficiency for Cr(VI) reduction over the SS electrode.

For ppy electrode, Cr(VI) removal efficiencies were 16% at a potential of −0.8 V, 9.6% at 0 V and 2.1% at 0.8 V (Table 1), indicating that a negative potential was favorable for Cr(VI) reduction. This result demonstrated potentials lower than 0 V may create electrons from the supportive electrode and led to the reduction of the inner and outer layers of the oxidized ppy (ppy+), which exhibited abilities for Cr(VI) reduction. The oxidized ppy film polarized at 0 and 0.8 V also removed a small amount of Cr(VI) probably due to the adsorption process.

Cr(VI) reduction on the ppy and SS electrodes showed different mechanisms (Fig. 2). For the SS electrode, direct electroreduction occurred on SS/solution boundary. For the ppy electrode, however, the oxidized ppy (ppy+) was firstly transferred to the reduced state by trapping the electrons from the substrate electrode. These neutral ppy0 sites then subsequently transferred the charges to Cr(VI) ions. In this way, ppy played an important role as an electrocatalytic media in improving Cr(VI) removal percentage and current efficiency.

Thus, Cr(VI) reduction at the ppy-modified electrode can be described as:

\[
\text{Cr}_2\text{O}_7^{2−} + 14\text{H}^+ + 6\text{ppy}_0 \rightarrow 2\text{Cr}^{3+} + 6\text{ppy}^+ + 7\text{H}_2\text{O}
\]

where ppy0 and ppy+ denote the reduced and oxidized states of the polymer film.

### 3.2. Comparison between ppy electrode and SS electrode for Cr(VI) reduction under PD condition

CV showed significant differences between ppy and SS electrodes (Fig. 3). For the ppy electrode, the distinct anodic peaks around 1.2 V at cycle 2 and 1.4 V at cycle 4 were mainly due to the overoxidation of ppy film. The current responses decreased dramatically from cycle 2 to cycle 4 and the absence of corresponding reduction peaks at cycle 4 indicated that the overoxidation process was irreversible. Therefore, the potential range, especially the positive potential limit should be discreetly selected to avoid ppy overoxidation for Cr(VI) electroreduction under PD condition.

The minor cathodic peaks at 0.2 V were preliminarily attributed to Cr(VI) reduction, while the absence of corresponding oxidation peaks in the potentials studied indicated a chemically irreversible reaction. For the SS electrode, CV curves were featured by the oxygen evolution at potentials more positive than 1.2 V. Cathodic peak attributed to Cr(VI) reduction on the SS electrode could not be observed, implying that Cr(VI) reduction was more difficult to be accomplished on the naked SS electrode than the ppy electrode. The differences between ppy and SS electrodes as shown in CVs revealed two features that are diagnostic of the role played by the ppy film as an electrocatalyst with the increase current responses due to the enlarged surface area (the real area of 18.3 cm² for ppy film versus the apparent surface area of 1.8 cm² for naked SS electrode) and the presence of the cathodic Cr(VI) reduction peak, as compared to the naked SS electrode.

Cr(VI) reduction was carried out by PD process on both ppy and SS electrodes at a potential range of −0.8 to 0.8 V and a scan rate of 20 mV s⁻¹ in an acidified Cr(VI) solution (Fig. 4). On the ppy electrode, CVs were featured by a broad oxidation peak A and a sharp reduction peak B associated with the oxidation and reduction processes of ppy film [29–32]. On the SS electrode, CVs were characterized by cathodic hydrogen evolution at potentials negative to −0.5 V, demonstrating that hydrogen evolution was a strong side reaction on the naked SS. However, hydrogen was extremely decreased by the application of the conductive ppy film. The drastic alleviation of hydrogen evolution on the ppy electrode was in favor

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**Table 1**

Comparison of PS condition and PD condition for Cr(VI) electroreduction on ppy and SS electrodes in an aqueous solution.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Cr(VI) removal efficiency</th>
<th>Current density / A cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr2O7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>−0.8 V</td>
<td>16</td>
<td>0.015</td>
</tr>
<tr>
<td>0 V</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>0.8 V</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>−0.8 V</td>
<td>16</td>
<td>0.015</td>
</tr>
<tr>
<td>0 V</td>
<td>0</td>
<td>0.010</td>
</tr>
<tr>
<td>0.8 V</td>
<td>0</td>
<td>0.010</td>
</tr>
</tbody>
</table>

**Fig. 2.** Schematics of electro-reduction of Cr(VI) on the SS and ppy electrodes.

**Fig. 3.** Cyclic voltammograms at the potential range from 0 to 1.6 V on the ppy and SS electrodes in an acidified Cr(VI) solution with a concentration of 1.0 mmol L⁻¹ Cr(VI) and 0.1 mol L⁻¹ H₂SO₄.

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**Fig. 4.** Cyclic voltammograms at the potential range from 0 to 1.6 V on the ppy and SS electrodes in an acidified Cr(VI) solution with a concentration of 1.0 mmol L⁻¹ Cr(VI) and 0.1 mol L⁻¹ H₂SO₄.
of Cr(VI) reduction with an achievement of low energy consumption.

It should be noted that the current responses obtained on the ppy-modified electrode were much higher than those on the SS electrode, indicating that the ppy-modified electrode displayed an electrocatalytic effect on Cr(VI) reduction [9], and consequently increased Cr(VI) reduction rate and removal percentage compared to the SS electrode.

In stagnant solution, Cr(VI) removal efficiencies were 56% at a potential range of −0.8 to 0.8 V, 42% at −0.8 to 0 V and 12% at 0 to 0.8 V for the ppy electrode. However, Cr(VI) removal efficiencies were 0 for the SS electrode in all of the cases (Table 1). Obviously, the ppy electrode showed great advantages with extremely higher removal efficiencies over the SS electrode due to the important role of ppy in the PD process. For the applied potential scopes, Cr(VI) removal efficiencies obtained at −0.8 to 0.8 V were the highest, −0.8 to 0 V were the next, and 0 to 0.8 V were the lowest. The reasons may be presumably attributed to the fact of Cr(VI) anion which were different from other heavy metal cations, such as Cu(II), Cd(II) and Ag(I). Cr(VI) anions in solution could preferably move to the electrode with opposite charges by the force of electrode field. Thus, positive potentials can promote the transportation rate of Cr(VI) ions and were favorable for anions capture on the electrode surface. The captured Cr(VI) ions could be then reduced at negative potentials. In this way, PD scans alternatively at each cycle and at a range of −0.8 to 0.8 V was more effective for Cr(VI) capture and reduction than the potential ranges of both −0.8 to 0 V and 0 to 0.8 V.

The effect of scan rate on Cr(VI) reduction was carried out for ppy electrode in stagnant solution under PD condition at a potential range of −0.8 to 0.8 V (Fig. 5). Cr(VI) removal efficiency increased with scan rate, from 56% at a scan rate of 20 mV s⁻¹ to 67% at 160 mV s⁻¹, which was presumably due to the mass acceleration as a result of the diffusion gradient increase in Cr(VI) ions with increasing scan rate for diffusion-limited Cr(VI) reduction process.

3.3. Influence of solution stirring on Cr(VI) reduction

The influence of solution stirring on Cr(VI) reduction was carried out at rotation speeds of 0 and 100 rpm. Data in Table 1 show that Cr(VI) removal efficiencies for both PS and PD processes was dramatically improved with the increase of stirring speed. Take the ppy electrode for instance. In the case of PS condition, Cr(VI) removal of 16% was obtained at 0 rpm whereas it evidently increased to 92% at 100 rpm. Under PD condition, Cr(VI) removal of 56% at a potential range of −0.8 to 0.8 V was achieved at 0 rpm compared to the 100% at 100 rpm.

According to Eq. (3), reaction rate was the result of both electron transfer and ionic transport between solution and a limited number of sites in the ppy film. For electron transfer process, most of the ppy⁺/ppy⁰ redox sites within the film could not exchange rapidly with the underlying support. Only the innermost layers of the oxidized ppy (ppy⁺) were reduced by the electrons transferred from the supportive electrode. These neutral ppy⁰ sites subsequently transferred the charges to neighboring ppy⁺ sites via site to site electron hopping. However, solution stirring had no effect on electron transfer process and only promoted ionic transfer as a result of high Cr(VI) removal efficiency with the increased stirring speed, implying that Cr(VI) reduction was diffusion-limited process.

3.4. Comparison between PD and PS conditions for Cr(VI) reduction

In all the cases (Table 1), PD process showed higher Cr(VI) removal efficiency over PS process for both ppy and SS electrodes, indicating the former was more effective for Cr(VI) reduction, especially at relatively low rotation speeds. This result was disagreement with previous points, in which a constant negative potential was favorable for metals reduction [20–22]. This may be presumably attributed to the following processes Cr(VI) anions experienced: (1) Cr(VI) anions was preferably moved to the electrode with opposite charges by the force of electrode field; (2) positive potentials can promote the mass transportation rate of
Cr(VI) ions and was favorable for anions capture on the electrode surface; (3) the captured Cr(VI) ions was reduced at negative potentials. In this way, PD scans was an effective procedure for Cr(VI) capture and reduction alternatively at each cycle. In contrast, for PS process, the electrode was exerted on a negative potential. Cr(VI) anions could be repulsed to close to the electrode surface, as both the electrode and Cr(VI) ions took the same charges. Therefore, for the ppy electrode and in stagnant solution, relatively lower removal efficiency of 16% at a potential of −0.8 V was achieved at PS process compared to 56% at −0.8 to 0.8 V at PD process. In addition, for solution with stirring at 100 rpm, ppy achieved Cr(VI) removal of 92% under PS condition in comparison with 100% under PD condition. For the SS electrode, PD process was also more effective than PS process. Since convection has played dominant role for Cr(VI) feeding rather than natural diffusion in solution without stirring, as a result, the difference in terms of Cr(VI) removal percentage between PS and PD processes in stirring solution was not conspicuous as that in stagnant solution, although PD process is also more effective than PS process in stirring solution.

Considering the reasons mentioned above in terms of Cr(VI) reduction, PD process was apprehensible to be a more effective and better alternative than PS process. However, in terms of Cu(II) removal, PD process was not effective compared to PS process because the cathodic Cu(II) deposition and metallic dissolution of deposited copper on electrode could take place alternatively at every cycle during PD scans and consequently led to much less Cu(II) removal [33].

Electroactivity of ppy film was tested at potentials of −0.8 V and 0.8 V (PS process), and −0.8 to 0.8 V (PD process) (Fig. 6). In comparison with the voltammograms before and after eight successive contact cycles, a clear decrease in current response was observed. This current loss was connected with the degradation of the polymer. Electrochemical degradation represented an irreversible change that occurred upon anodic polarization leading to an irreversible decrease in its redox activity and/or electronic conductivity. One characteristic of the overoxidized ppy was the presence of C=O functional groups in the polymer backbone at sufficiently positive potential. Another important characteristic of the overoxidation was that the polymer was reserved in the doped state with the anions expelled from the polymer. These structure changes of the ppy film disrupted the conjugated structure of ppy and led to the loss of electroactivity capacity [34]. The more positive the potential was, the more serious the degradation would be, due to the irreversible overoxidation [35]. Therefore, among the electroreduction conditions of −0.8 V (PS process), 0.8 V (PS process) and −0.8 to 0.8 V (PD process), film degradation was the most serious under 0.8 V, and it was the slightest at −0.8 V, while the film degradation under −0.8 to 0.8 V was in-between. The electroactivity loss of ppy film could be described by the area loss of the CV curve, which was 18% at a potential of −0.8 V and 81% at 0.8 V, and 49% at −0.8 to 0.8 V, which indicated that ppy stability at −0.8 to 0.8 V was better than that at 0.8 V, but worse than that at −0.8 V.

4. Conclusions

Cr(VI) electroreduction using ppy-modified and SS electrodes under PS and PD conditions was compared. The extremely higher Cr(VI) removal percentage was achieved on the ppy electrode due to the electrocatalytic role of ppy toward Cr(VI) reduction. The inhibition effect of hydrogen formation on the ppy electrode saved more electrons for Cr(VI) reduction and consequently improved current efficiency. In stagnant solution, Cr(VI) removal efficiencies at a potential of −0.8 V were 16% for ppy and 0 for SS in PS condition whereas these values increased to 92% (ppy) and 18% (SS) at a stirring speed of 100 rpm. Under PD condition, Cr(VI) removal efficiencies at a potential range of −0.8 to 0.8 V were 56% (ppy) and 0 (SS) in stagnant solution in comparison with 100% (ppy) and 36% (SS) at a stirring speed of 100 rpm. While PD process overmatched PS process for Cr(VI) reduction on both the ppy and the SS electrodes, the effectiveness of PD process at a potential range of −0.8 to 0.8 V was better than those at −0.8 to 0 V and 0 to 0.8 V. Although the ppy stability under PD condition at a potential range of −0.8 to 0.8 V was not as satisfactory as that in PS process at −0.8 V, ppy-modified electrode in PD process may be a promising alternative for Cr(VI) electroreduction.

Fig. 6. Cyclic voltammograms of the ppy electrode before and after eight successive contact under PS and PD conditions in an acidified Cr(VI) solution with a concentration of 1.0 mmol L−1 Cr(VI) and 0.1 mol L−1 H2SO4.
Acknowledgements

The authors would like to acknowledge the financial support from the Natural Science Foundation of China (Nos. 51078050, 51178077 and 21077017) and Key Laboratory Program of Industrial Ecology and Environmental Engineering, Ministry of Education (MOE).

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