Catalytic activity for nitrate electroreduction of nano-structured polypyrrole films electrochemically synthesized onto a copper electrode

Thi Phuong Thoa Nguyen¹, Viet Thinh Nguyen¹,² and Viet Hai Le¹

¹ University of Science, Vietnam National University-Ho Chi Minh City, 227 Nguyen Van Cu, District 5, Ho Chi Minh City, Vietnam
² Tien Ging University, 119 Ap Bac, My Tho, Tien Giang, Vietnam
E-mail: ntpthoa@hcmus.edu.vn

Received 24 February 2010
Accepted for publication 4 April 2010
Published 13 May 2010
Online at stacks.iop.org/ANSN/1/015003

Abstract
Polypyrrole film was synthesized electrochemically onto a copper electrode in oxalate, oxalic acid and salicylic acid solutions. The electrochemical oxidation of pyrrole to form polypyrrole film and the electroreduction of nitrate and nitrite ions at synthesized Ppy modified copper electrodes (Ppy/Cu) in potassium chloride aqueous solutions were studied by cyclic voltammetry. Polypyrrole nano-porous film formation and the activity of the modified Ppy/Cu electrode for nitrate reduction were found to be dependent on the synthesis medium and conditions: pH; content and concentrations of the electrolytes; pyrrole concentration; electrode potential; electrolysis duration; drying time and temperature for finishing the Ppy/Cu electrode and immersion time in water for storing the Ppy/Cu electrode before use. High catalytic activity for nitrate reduction was found for composite electrodes with nano-porous structured Ppy films. The Ppy/Cu electrodes prepared in oxalate buffer and salicylic acid solutions perform more stable catalytic activity for nitrate reduction; their service life is about ten times longer than for an electrode prepared in oxalic acid solution.

Keywords: copper electrode, cyclic voltammetry, electropolymerization, nitrate reduction, polypyrrole

Classification numbers: 5.00, 5.07

1. Introduction

Water pollution by nitrate ions has become a serious and growing environmental problem. Elevated levels of nitrate in shallow groundwater associated with agricultural activities have been widely documented. The World Health Organization reported that nitrate concentrations in surface water had increased in many countries due to the increasing use of artificial fertilizers [1]. The concern regarding nitrate contamination arises from its health risk to humans and its impact on aqueous ecological systems [2].

Several technologies for the reduction of nitrate contamination have been developed including ion exchange, electrodialysis, reverse osmosis, biological denitrification, chemical reduction and electrochemical reduction. Among them, the electrochemical reduction of nitrate into nitrogen has been intensively studied during the last decade [3–5]. Most research on the electroreduction of nitrate and nitrite ions has been carried out on various noble metal and noble metal-modified electrodes in acidic [6, 7], alkaline [8–10] and neutral solutions [11–14]. The catalytic activity of copper (Cu) in the reduction of nitrate and nitrite ions has been shown in some papers [7, 8]. However in our preparative investigation it was found that the main product of nitrate electroreduction on copper electrode in a neutral medium was nitrite, which is more toxic than nitrate itself. So the...
selectiveness of nitrate reduction without forming nitrite compounds was the purpose of our research.

The application of conducting polymer as a support for electrocatalytic microplates has been the subject of numerous investigations. As one of the inherent conductive polymers, polypyrrole (Ppy) has been extensively studied as a modification layer of various sensors [15–19]. In our previous papers [20–23] Ppy has shown catalytic activity for nitrate reduction and good selectiveness, i.e. avoiding nitrite formation.

The aim of this work was to study the effect of synthesis conditions of the Ppy film on its electrocatalytic performance toward nitrate reduction. Ppy/Cu modified electrodes were prepared by electrochemical chronoamperometric oxidation pyrrole and were used as the working electrodes in the study of electroreduction of nitrate ions in neutral solutions using CV techniques. We were interested in the morphology of Ppy film on the copper substrate and its relationship with the electrolysis conditions and electrode catalytic activity for nitrate reduction. We were also concerned with the dry, storage and handling procedures of the Ppy/Cu electrodes.

2. Experiment

2.1. Apparatus

Electrochemical measurements were carried out in a three-electrode electrochemical cell using an Autolab PGSTAT302N and a homemade potentiostat/galvanostat PGS-HH9 (Vietnam). The morphology of the synthesized material was investigated by scanning electron microscopy (SEM, JSM 6480LV, Jeol Co., Japan). All solutions were prepared with twice distilled water. All experiments were performed at ambient temperature.

A three-electrode, one-compartment cell was used with pretreated copper or Ppy/Cu working electrode, platinum wire counter electrode and saturated silver chloride (Ag/AgCl) reference electrode. All potentials in the paper were reported with respect to the saturated Ag/AgCl electrode.

2.2. Preparation of the Ppy/Cu electrode

Copper rods mounted in epoxy with various exposed areas of 0.01 to 7.0 cm² were used as anodes for electrodeposition of polypyrrole film. Before electropolymerization the copper working surface was polished with 1200 grit emery paper, rinsed with distilled water and degreased with ethanol, then soaked in 0.5 M HCl for about 30 min and rinsed with distilled water. Polymerization of pyrrole was performed in oxalic acid, oxalate buffer and salicylic acid solutions with various concentrations containing different concentration pyrrole (0.05–0.15 M). From the results of our previous paper [14] we chose an anode potential range of 1.6 to 2.0 V (Ag/AgCl) and electrolysis duration from 60 to 240 s for the present study.

Freshly prepared Ppy/Cu electrodes were usually conditioned in water for 24 h and then dried in a dryer at temperatures of 30–55 °C for 1 to 12 h. The Ppy/Cu electrodes were stored in distilled water.

2.3. Nitrate electroreduction study

The CV experiments were conducted using 0.15 M potassium chloride (KCl) solution as a supporting electrolyte. Sodium nitrate (NaNO₃) solution was prepared just prior to use. The cyclic voltammetry experiments were run with a potential scan rate of 0.01 V s⁻¹. The electrochemical measurements were carried out in deaerated solutions in pure nitrogen atmosphere.

3. Results and discussion

3.1. Formation of polypyrrole film on copper substrate and its morphology

Cyclic voltammograms (CVs) of the pyrrole electrooxidation on a copper electrode in the studied electrolytes are plotted in figure 1. As we can see, pyrrole oxidation started at an anodic potential of about 0.70 V (Ag/AgCl) but with low current density until the anodic potential reached 1.2–1.3 V. The anodic peak current (iₚ) in oxalate buffer (figure 1(b)) was smaller than one in oxalic acid (figure 1(a)), i.e. the oxidation of Py in oxalate buffer solution to form Ppy occurred with a lower rate. Figure 1(c) showed very large anodic polarization of the pyrrole oxidation in salicylic acid on the copper electrode.

It can be seen from figure 1 and table 1, at a constant anode potential (for example, 1.6 V), the oxidation current

![Figure 1. CVs on the copper electrode in solutions of (a) 0.2 M oxalic acid (1) and 0.2 M oxalicacid + 0.1 M Py (2), (b) 0.2 M oxalic acid + 0.2 M ammoniumoxalate (1) and 0.2 M oxalicacid + 0.2 M ammoniumoxalate + 0.1 M Py (2) and (c) 0.01 M salicylicacid + 0.1 M Py.]
Figure 2. SEM image of Ppy film synthesized in solutions of (a) oxalic acid, (b) oxalate buffer and (c) salicylic acid.

Figure 3. Surface SEM images of 9-month-stored-in-water Ppy/Cu electrodes, synthesized in oxalate buffer (a) and salicylic acid (b) solutions.

Figure 4. CVs in 0.15MKCl + 0.01MNaNO₃ on Ppy/Cu formed in salicylic acid (1) and in oxalate buffer (2) solutions.

decreased in the following order: oxalic acid > oxalate buffer > salicylic acid solutions. Table 1 shows a very low rate of pyrrole oxidation in salicylic acid solution in comparison with oxalate solutions (about 100 times lower at 1.6 V anodic potential). However, under high anodic polarization, pyrrole oxidation current in salicylic acid sharply augmented while it decreased in oxalate solutions (the third column in table 1).

From analyzing CV curves, pyrrole polymerization was carried out under potentiostatic conditions. The Ppy film on copper surface in oxalic acid and oxalate buffer solutions was synthesized at an anodic potential of 1.6 V for 60 s electrolysis duration, while for salicylic acid solution it was 2.0 V and 240 s, respectively.

Morphologies of the synthesized Ppy films were studied by SEM and are shown in figure 2. The Ppy film formed in oxalate buffer solution (figure 2(b)) was better structured (tiny grains of almost the same size) than that formed in the oxalic solution (figure 2(a)). The Ppy film formed in salicylic acid solution (figure 2(c)) was the best structured. This may be caused by the anodic polymerization of the pyrrole oxidation process in salicylic acid solution.

SEM images of the surface of the Ppy/Cu electrode formed in oxalate buffer or salicylic acid solution in figure 3 showed the nanoporous structure of Ppy films. The grain size (from 50 to 150 nm) of Ppy film synthesized in salicylic acid solution is smaller than that (100 to 200 nm) in the oxalate buffer solution. Obviously this may be one of the reasons explaining the long-term stability of Ppy/Cu electrodes synthesized in oxalate buffer or salicylic acid solutions.

3.2. Influence of the preparation conditions of the Ppy/Cu electrode synthesized in oxalic acid solution on its catalytic activity for nitrate reduction

3.2.1. Electrolyte nature. The Ppy film synthesized in oxalic solution on a copper electrode was damaged after 1-month storage in water. However, the Ppy films synthesized in oxalate buffer or salicylic acid solutions still performed good catalytic activity for nitrate reduction even after 9-months soaking in water. After 9-months storage in distilled water, the Ppy/Cu electrode formed in salicylic acid solution showed larger nitrate reduction current density than that produced in oxalate buffer solution (figure 4).

The stability of the Ppy film regarding catalytic activity for nitrate electroreduction may be related to the properties
Table 2. Parameters of the cyclic voltammograms in the 0.15 M KCl + 0.01 M NaNO₃ solution on Ppy/Cu synthesized in the solution 0.1 M pyrrole + x M oxalic acid.

| Concentration of oxalic acid, x (M) | −Eₚ (V) | −iₚ (mA cm⁻²) |
|------------------------------------|---------|----------------|
| 0.02 | 1.07 | 5.2 |
| 0.05 | 1.08 | 4.2 |
| 0.20 | 1.10 | 4.7 |

Table 3. Parameters of cyclic voltammograms in the 0.15 M KCl + 0.01 M NaNO₃ solution on Ppy/Cu synthesized in the solution 0.2 M oxalic acid + y M pyrrole.

| Concentration of pyrrole, y (M) | −Eₚ (V) | −iₚ (mA cm⁻²) |
|---------------------------------|---------|----------------|
| 0.5 | 1.10 | 6.3 |
| 0.10 | 1.08 | 3.8 |
| 0.15 | 1.05 | 3.4 |

of passive layers formed on the copper surface during the oxidation process. As we know, formation of conductive polymer coatings can only occur on oxidizable metals when the electrochemical conditions can lead to passivation of the metal surface without preventing electropolymerization. It has been shown that dibasic acids can passivate a metal surface while providing adequate adhesion of conducting polymers [20]. It may be that the conjunction ability of salicylic acid (C₆H₄(OH)(COOH)) is stronger than that of oxalic acid (HCOO-COOH) thanks to the aromatic hydrocarbon cyclic structure.

The electrolyte nature also affects the long-term stability of Ppy/Cu electrodes, i.e. the electrolyte was an important factor for high and stable catalytic activity of the synthesized electrodes.

3.2.2. Oxalic acid and pyrrole concentration. Very little influence of oxalic acid concentration on the nitrate reduction catalytic activity of the synthesized Ppy/Cu electrodes can be seen from table 2: the nitrate cathodic reduction peak current density (iₚ) only increased from 4 to 5 mA cm⁻², and peak potentials (Eₚ) stayed almost unchanged (−1.05 to −1.10 V) when the oxalic acid concentration changed from 0.02 to 0.2 M. So, 0.2 M oxalic acid concentration was chosen for the following experiments to maintain the stable conductivity of the electrosynthesis solution.

The influence of pyrrole concentration on the nitrate reduction catalytic activity of the Ppy/Cu electrode is shown in table 3. The modified electrode formed with 0.05 M pyrrole concentration showed the highest cathodic current density; however the Ppy film did not cover the whole surface of the copper electrode. So the pyrrole concentration for experiments hereafter was chosen as 0.1 M.

3.2.3. Anode potential and electrolysis duration. The electrolysis duration also affects the nitrate reduction catalytic activity of the synthesized electrodes. Table 4 showed that at an anode potential of 1.6 V, Ppy/Cu electrodes formed with electrolysis duration of 60 s performed better nitrate reduction catalytic activity than the ones with electrolysis duration of 80 s or 100 s: the cathodic peak current was higher by 1.5 to 3.0 times.

Table 4. Influence of the polymerization duration (t) and anodic potential (Eₚ) on the nitrate reduction catalytic activity of the Ppy/Cu electrode.

| t (s) | −Eₚ (V) | −iₚ (mA cm⁻²) |
|-------|---------|----------------|
| 60 | 1.13 | 3.2 |
| 80 | 1.09 | 2.0 |
| 100 | 1.04 | 1.0 |

Table 5. Influence of the drying temperature and duration on nitrate reduction parameters using the Ppy/Cu, X electrode.

| Drying duration (h) | −Eₚ (V) | −iₚ (mA cm⁻²) |
|---------------------|---------|----------------|
| 3-h drying | 0.15 | 6.3 |
| 40–45°C | 0.14 | 4.0 |

Figure 5. Typical SEM micrograph of the Ppy/Cu, X electrode dried at 40–45°C for 5 h.

The influence of electrolysis potential on the characteristics of Ppy film is also described in table 4. With the same 60-s electrolysis duration, the modified electrode synthesized at 1.6 V has the highest cathodic peak current density. Hereafter this electrode is denoted as Ppy/Cu, X.

3.2.4. Drying temperature and duration. The effect of drying temperature for the synthesized Ppy/Cu electrodes on nitrate reduction catalytic activity is presented in table 5. In three studied temperature ranges (30–35°C; 40–45°C and 50–55°C), the Ppy/Cu, X electrode dried with temperature range 40–45°C performed the highest nitrate reduction current density.

Drying duration also influenced the nitrate reduction catalytic activity of the Ppy/Cu electrode. From table 5 we can see that 5-h drying at 40–45°C gives the maximum peak current density. So 5 h drying duration was chosen for the subsequent experiments.

The SEM image of the surface of the Ppy/Cu, X electrode dried at 40–45°C in 5 h shown in figure 5 indicates that the Ppy film was better structured and consisted of smaller grains, so the surface area was highly enlarged compared with the freshly prepared Ppy film in figure 2(a). Clearly this is one
Figure 6. CVs in 0.15 M KCl + 0.01 M NaNO$_3$ on the Ppy/Cu$_X$ electrode stored in distilled water for 1 h (1-red line); 3 days (2-brown); 6 days (3-blue); 9 days (4-black) and 13 days (5-green).

Table 6. Influence of the oxalate/oxalic acid ratio on the nitrate reduction parameters.

| Oxalate/Oxalic acid ratio | pH  | $-E_p$ (V) | $-i_p$ (mA cm$^{-2}$) |
|--------------------------|-----|------------|------------------------|
| 0/1                      | 3.65| 1.08       | 4.0                    |
| 1/10                     | 3.70| 1.09       | 4.9                    |
| 1/5                      | 3.79| 1.13       | 6.3                    |
| 1/2                      | 3.96| 1.12       | 7.5                    |

of the reasons for the better catalytic performance of this electrode in nitrate reduction.

3.2.5. Water treatment. After preparation Ppy/Cu$_X$ was stored in distilled water. Within the first two weeks, as the immersion time increases, the cathodic current density increases and the reduction peak for nitrate ions shifts toward more negative potentials (figure 6). After immersion in distilled water for about two weeks, the modified electrodes showed stable catalytic performance for nitrate reduction.

3.3. Characteristics of the Ppy/Cu electrode synthesized in oxalate buffer solution

With increasing oxalate concentration in the oxalate buffer solution, the cathodic peak current increased and the peak potential of the nitrate reduction shifted toward more negative values, shown in table 6.

During the electropolymerization in oxalic acid 0.2 M + Py 0.1 M solution the pH decreased slightly from an initial value of 3.65 to 3.55 after 10-min electrolysis duration at 1.6 V. This might be explained due to the formation of hydrogen ions during electrochemical oxidation of pyrrole [19]. In oxalate buffer solution (0.2 M oxalic acid + 0.1 M ammonium oxalate + Py 0.1 M) the pH value before electrolyzing was 3.96, and after 10 min electrolysis duration at 1.6 V the pH value was 3.93. Clearly, the oxalate buffer neutralized hydrogen ions formed during Ppy synthesis and balanced the pH value of the solution.

4. Conclusions

Modified Ppy/Cu electrodes for nitrate electroreduction were prepared by electrochemical oxidation of pyrrole to form polypyrrole film on the copper surface in oxalic acid, oxalate buffer and salicylic solutions. The Ppy/Cu modified electrode has an obvious electrocatalytic effect on the electroreduction of nitrate ions.

It was found that the optimal conditions for electrode preparation in oxalic acid solution were as follows: anodic potential of 1.6 V; electrolysis duration of 60 s; pyrrole concentration of 0.1 M, oxalic acid concentration of 0.2 M. For the best catalytic performance, freshly synthesized Ppy/Cu electrodes have to be dried at 40–45°C for 5 h and stored in distilled water for about 2 weeks before use.

The characteristics of the Ppy/Cu electrodes prepared in oxalate buffer or salicylic acid solutions were much better than those prepared in oxalic acid solution; specifically, their long-term stability was found, over 9 months, to be about ten times longer than that for the latter.

Among the three electrolytes, the Ppy film synthesized in salicylic acid solution performed the best electrocatalytic effect and was nanoporous structured. A relationship was found between high anodic polarization (2.0 V) for Ppy-film formation in salicylic acid and Ppy-film morphology with catalytic activity for nitrate electroreduction.

The Ppy/Cu modified electrode could be used in environmental remedies for nitrate removal from water by electrochemical methods.

Acknowledgments

The financial support for this work from the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03.120.09 is appreciated. The authors would also like to acknowledge the University of Science Ho Chi Minh City and the Tiengiang University for technical support.
References

[1] Health Hazards from Nitrate in Drinking Water, Report on a WHO meeting, Copenhagen 5–9 March 1984
[2] Cantor K 1997 Cancer Causes Control Pap. 8 292
[3] Dima G, de Voors A and Koper M 2003 J. Electroanal. Chem. 554 15
[4] Reyter D, Bélinger D and Roué L 2010 Water Res. 44 1918–26
[5] Jiefei Y and Kupferle M 2009 Water Air Soil Pollut.: Focus 9 245
[6] de Groot M and Koper M 2004 J. Electroanal. Chem. 562 81
[7] Tada K, Kawaguchi T and Shimazu K 2004 J. Electroanal. Chem. 572 93
[8] Armijo F, Isaacs M, Ramirez G, Trollund E, Canales J and Aguirre M 2004 J. Electroanal. Chem. 566 315
[9] de Voors A, van Santen R and van Veen J 2000 J. Mol. Catal. A 154 203
[10] Casella I and Gatta M 2004 J. Electroanal. Chem. 568 183
[11] El-Deab M 2004 Electrochim. Acta 49 1639
[12] Paidar M, Bouzek K and Bergmann H 2002 Chem. Eng. J. 85 99
[13] De D, Kalu E, Tarjan P and Englhardt J 2004 Chem. Eng. Technol. 27 56
[14] Zhang et al 2005 Synth. Met. 155 95
[15] Da Silva S, Cosnier S, Almeida M and and M 2004 J. Electrochem. Commun. 6 404
[16] Koizumi M, Tanaka M, Nishiki Y, Sekimoto M, Furuta T, Inoue H and Iwakura C 2006 Res. Chem. Intermed. 32 585
[17] Tian Y, Wang J, Wang Z and Wang S 2005 Sensors Actuators B 104 23
[18] Ashrafi A, Golozar M and Mallakpour S 2008 J. Appl. Electrochem. 38 225
[19] Trung T and Van Tri N 2006 Electrosynthesis and studies on polypyrrole composites Functional Materials (Series EUROMAT 99) ed K Gnassie, E Thuckhoff, G Wagner, J Hausselt and H Hinselka (Published online: 27 April 2006) pp 309–15
[20] Thinh N V, Thoa N T P and Hung L Q 2007 J. Chem. (Vietnam) 45 213
[21] Thinh N V, Hai L V, Nguyen B N, Thoa N T P and Hung L Q 2008 J. Sci. Technol. (Vietnam) 46 85
[22] Thinh N V, Hai L V, Nguyen B N, Kim Thoa D T and Thoa N T P 2008 J. Sci. Technol. Dev. 11 68
[23] Thinh N V, Thoa N T P and Hung L Q 2009 J. Chem. (Vietnam) 47 204