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Electrocatalytic Study at Silver/Polypyrrole Nanowires Composite Modified Electrodes

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Silver modified composite electrodes were prepared by electrochemical method on the polypyrrole (PPy) nanowires modified electrodes. The surface behaviour of it was investigated by scanning electronic microscopy and energy-dispersive X-ray analysis (EDX). The electrocatalytic activity of it was characterized by electroreduction of nitrate and their reduction products. The effect of solution pH, electrolytic potentials and electrolytic current density on nitrate electrolysis and the product were also examined. The experimental results indicate that Ag/PPy nanowires composite modified electrodes have higher catalytic activity toward nitrate reduction, the nitrite and ammonia in the resulted solution products are always at low concentration. This result shows that the electrodes have promising application in environmental remediation.

Key Words: Polypyrrole, Nanowires, Silver modified electrodes, Electrocatalytic study.

INTRODUCTION

Electricity is the main operating cost of the electrochemical method. Consequently, research and development efforts have been directed towards minimizing ohmic resistance, lowering over-potential through improving cell and electrode designs and using electrode material with higher electrocatalytic activity. Although the mesoporous character of the electrode could significantly apply the corresponding current, decreasing the over-potential by increasing the effective surface area of the electrode, it is seldom reported except the use of porous nickel. Because of their high stability, high conductivity, facile and changeable synthesis process, conductive polymers have been attracting much interest in electrochemistry and analytical chemistry. As a most studied inherent conductive polymer, polypyrrole (PPy) has been extensively studied as a modification layer of various sensors[1-3]. Dispersion of the catalysts throughout a polymer matrix might enhance catalytic activity relative to that of pure metals. This is attributed to the three-dimensional reaction zone of

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the modified electrode[4-6]. These advantages make the modified electrode have much higher effective surface area than ordinary electrode. The researches on polypyrrole nanowiress modified electrode will provide helpful information for electrocatalytic reation of a certain substance, which makes it important for theory study and practical application. The aim of the present work is to study the electrocatylic effect of Ag/PPy nanowires modified composite electrodes toward natrate ions.

EXPERIMENTAL

All chemicals are analytical grade and used without any purification. Pyrrole is purified before use by vacuum distillation and stored at low temperature in dark. Sodium nitrite and sodium nitrate are prepared before use.

Polymerization of pyrrole and the electrochemical experiments are carried out in an environment of pure nitrogen using model Reference 600 Electrochemical System (U.S.A. AMETEK). Scanning electronic microscopy (SEM) is taken at XL30 (PHILIPS, USA). The concentration of nitrate and nitrite are taken by use of model ICS-90 Ion chromatograph (U.S.A. Dionex).

Preparation of PPy nanowire and Ag/PPy composite modified electrodes: A three-electrode, one-compartment cell was used with a diameter of 10 mm pretreated graphite rod working electrode, platinum wire counter electrode and saturated calomel reference electrode (SCE). Before polymerization conducted, electrolyte solutions were desecrated thoroughly with pure nitrogen. Unless stated otherwise, all pyrrole polymerization were conducted at ambient temperature and potentiostatically 0.85 V *vs.* SCE. in aqueous solution containing 0.15 mol/L pyrrole, 0.10 mol/L $LiClO_4$ and 0.10 mol/L carbonate. Freshly prepared PPy nanowires electrodes were usually conditioned in 0.10 mol/L $HClO_4$ solution for 24 h to remove the carbonate ions.

The Ag/PPy nanowires composited modified electrodes were prepared by potentiostatically deposition Ag under potential of 0.85 V *vs.* SCE for 300 s in a mixture of 0.5 mol L^{-1} $AgNO_3$. A three-electrode, one-compartment cell was used with PPy nanowires modified graphite rod working electrode, platinum wire counter electrode and saturated calomel reference electrode (SCE).

All electrolytic reduction experiments of nitrate were carried out with two-appartment cell and the working electrode placed in one cell and the reference electrode and the auxiliary electrode were placed in the other cell. Before the electrolysis started, the solutions were bubbled with high purify nitrogen at least 20 min to remove the dissolved oxygen.

Measurement: The concentration of nitrate and nitrite in the resulted solution was determined by ion chromatograph method. The ammonia concentration in the same solution was determined at 420 nm by spectrophotometric method using Nesster's reagent as chromogenic developer. The SEM picture of the Ag/PPy nanowire composited modified electrode surface was presented in Fig. 1.

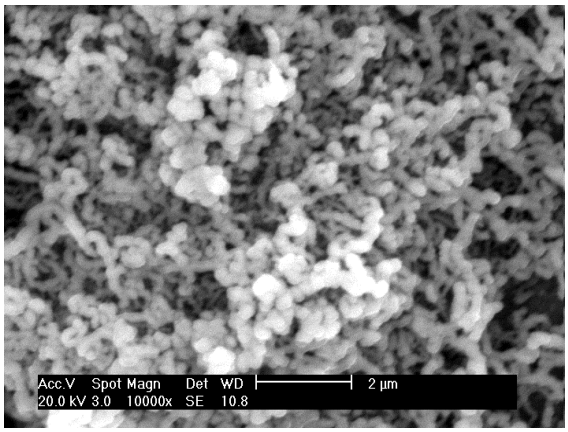

Fig. 1. SEM picture of the Ag/PPy nanowire composite modified electrode surface

RESULTS AND DISCUSSION

Effect of solution pH on the electrolysis of nitrate and the product: The effect of solution pH on nitrate electrolysis and the product were examined. Fig. 2 shows the effect of solution pH on nitrate electrolysis at constant current density 2 mA/cm^2. From Fig. 2, it is clear that the amount of nitrate be electrolyzed is getting more as pH increase, but when pH is more than 7, the amount of nitrate be electrolyzed is getting less. Figs. 3 and 4 show the effect of solution pH on nitrite and ammonia formed in the resulted solution, respectively. The tendency of nitrite and ammonia formed is the same as the Fig. 2. Fig. 5 is the amount of nitrite and ammonia formed by one nitrate at different pH in the result solution. The amount of nitrite and ammonia formed by one nitrate is the least when pH is 6.89. So the suitable electrolysis acidity should be medium pH.

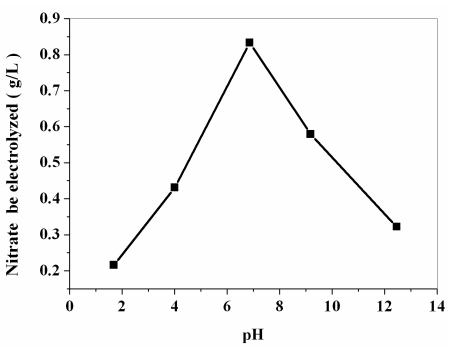

Fig. 2. Nitrate electrolyzed at different pH at Ag/PPy nanowire composite modified electrode. (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, electrolytic current: 2 mA/cm^2, electrolytic time: 0.5 h)

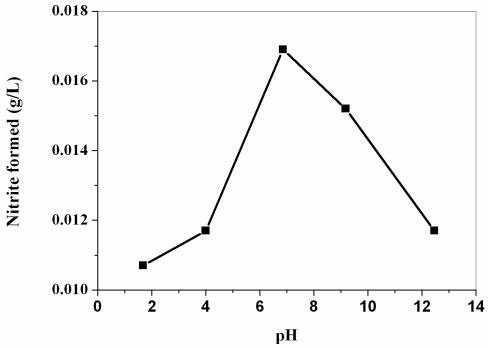

Fig. 3. Nitrite formed at different pH. (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, electrolytic current: 2 mA/cm^2, electrolytic time: 0.5 h)

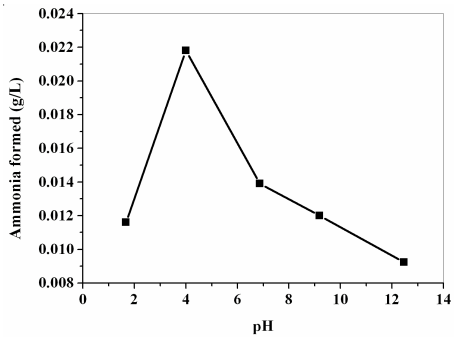

Fig. 4. NH_3 formed at different pH (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, electrolytic current: 2 mA/cm^2, electrolytic time: 0.5 h)

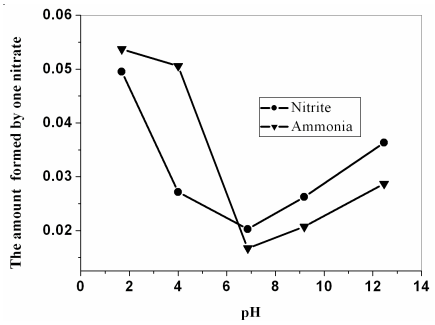

Fig. 5. Amount of nitrite and NH_3 formed by one nitrate at different pH (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, electrolytic current: 2 mA/cm^2, electrolytic time: 0.5 h)

Effect of electrolytic potentials on the electrolysis of nitrate and the product: Fig. 6 shows that NO_3^- be electrolyzed per C at different electrolytic potentials at Ag/PPy nanowire composite modified electrode. The amount of NO_3^- be electrolyzed per C decreases when the electrolytic potential changed more negative. Fig. 7 shows the relationship between the concentration of nitrite and ammonia formed and electrolytic potentials. It shows that the concentration of nitrite and ammonia formed increases with the increase of electrolytic potentials when electrolytic potential is more than 1.2. The tendency of amount formed is on the contrary when electrolytic potential is less than 1.2. Fig. 8 indicates the amount of nitrite and ammonia formed at different electrolytic potentials by one nitrate, The relationship is similar to the Fig. 7. Considering nitrite is toxic and the nitrite formed is the least per nitrate electrolyzed at the electrolytic potential of 1.2 V, the suitable electrolytic potential should be conducted at lower potential.

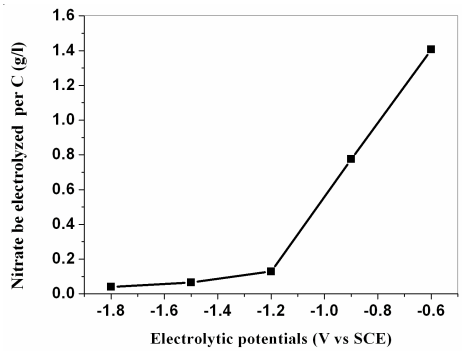

Fig. 6. NO_3^- be electrolyzed per C at different electrolytic potentials at Ag/PPy nanowire composite modified electrode (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, electrolytic time: 0.5 h)

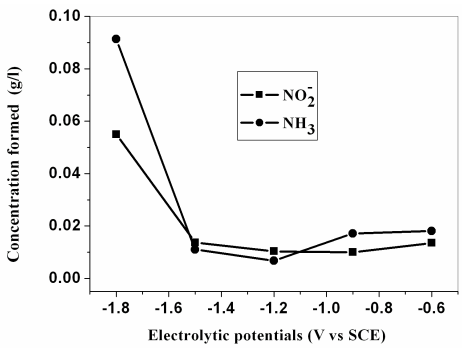

Fig. 7. Nitrite and ammonia formed at different electrolytic potentials (Experimental conditions: 100 mL, 0.10 mol L^{-1} $NaNO_3$, electrolytic time: 0.5 h)

Effect of current density on the electrolysis of nitrate and the product: Fig. 9 shows that nitrate electrolyzed at different current density with 2.0 C charge. When the current density is less than 4.5 mA/cm^2, the amount of the nitrate electrolyzed decreases with the increase of current density. When the current density is more than 4.5 mA/cm^2, the trend is contrary. The formation of ammonia formed at different current density is shown in Fig. 10. The amount of ammonia formed is contrary to the nitrate removal amount at different current density. Fig. 11 shows that ammonia formed per nitrate at different current density. The trend of Fig. 11 is the same as shown in Fig. 10. The nitrite formed is low at all current density. Beause the nitrite and ammonia is not the product of our expectation, the electrolysis of nitrate should be conducted at low current density.

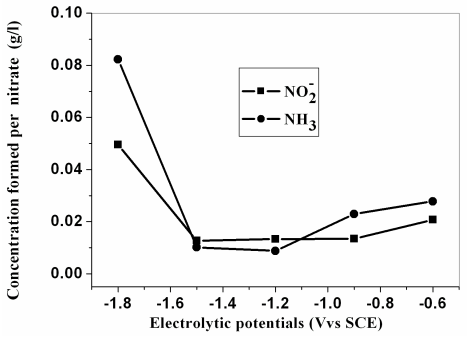

Fig. 8. Nitrite and ammonia formed at different electrolytic potentials by one nitrate (Experimental conditions: 100 mL, 0.10 mol L^{-1} $NaNO_3$, electrolytic time: 0.50 h)

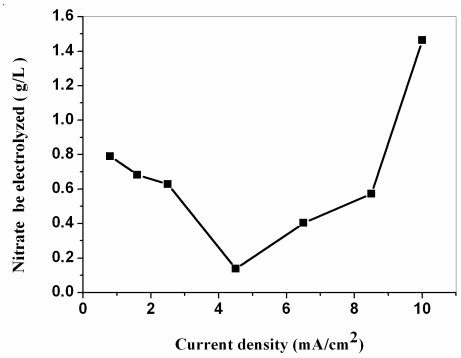

Fig. 9. Nitrate electrolyzed at different current density at Ag/PPy nanowire composited modified electrode (Experimental conditions: 0.10 mol·L^{-1} $NaNO_3$, consumed charge: 2.0 C)

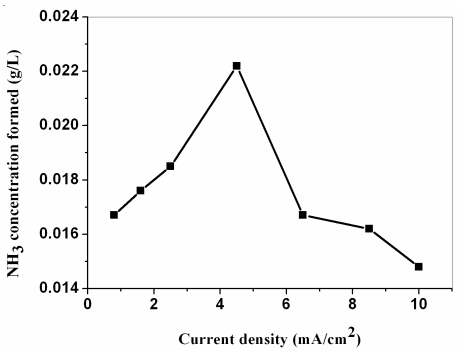

Fig. 10. NH_3 formed at different current density at Ag/PPy nanowire composite modified electrode (Experimental conditions: 0.10 mol L^{-1} $NaNO_3$, consumed charge: 2.0 C)

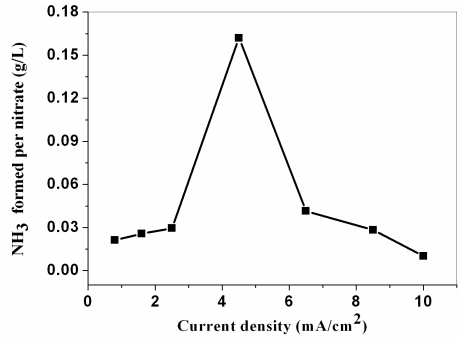

Fig. 11. NH_3 formed per nitrate at different current density at Ag/PPy nanowire composite modified electrode (Experimental conditions: 0.10 mol·L^{-1} $NaNO_3$, consumed charge: 2.0 C)

In conclusion, considering the environmental protection and energy consumption, the electrolysis of nitrate should be conducted at lower potential, medium pH and low current density at the Ag/PPy nanowires composited modified electrodes. The Ag/PPy nanowires composited modified electrodes prepared have good electrocatalytic reduction activity to nitrate and may be used in the environmental protection.

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