Electrocatalytic Reduction of Nitrate in Water with a Palladium-Modified Copper Electrode

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ABSTRACT: A highly active electrocatalytic electrode for nitrate reduction was prepared by the electro-deposition of palladium onto a copper electrode. The capacity of nitrate reduction by a palladium-modified copper electrode has been studied using cyclic voltammetry (CV). The existence of a reduction peak at -0.605 V versus saturated calomel electrode in 0.1 -M sodium nitrate + 0.1 -M perchloric acid solution ($\text{pH} = 0.86$) can be found in the CV measurement. The influence of solution properties, such as pH, nitrate concentration, and other anions in solution, on nitrate reduction was determined in detail. Results showed that nitrate reduction was suppressed in alkaline solution, while it was beneficial to nitrate reduction in acid or neutral solution. At low nitrate concentrations (0.01 to 0.5 M), nitrate reduction current increased with increasing nitrate concentration, but was hindered by sulfate. At high nitrate concentrations (1 to 5 M), no significant difference on nitrate reduction was observed. Compared with other different electrodes prepared in our work (copper, titanium, and palladium-modified titanium electrodes), the palladium-modified copper electrode showed the highest electrocatalytic capacity and stability in the nitrate-reduction process. *Water Environ. Res.*, **78**, 724 (2006).

KEYWORDS: nitrate reduction, electrocatalysis, palladium-modified copper electrode, water treatment.

doi:10.2175/106143006X110665

Introduction

Increasing nitrate pollution in water has stimulated intensive research on the denitrification of drinking water, because nitrate causes serious health risks (Super et al., 1981). The toxicity of nitrate for human beings is a result of the body's reduction of nitrate to nitrite, responsible for Blue Baby Syndrome and a precursor to carcinogenic nitrosamines and other N-nitroso compounds (Pintar, 2003).

In this respect, there are many useful methods for the reduction of nitrate. Available physical-chemical processes for nitrate separation include ion-exchange, reverse osmosis, and electrodialysis (Kapoor and Viraraghavan, 1997). In these processes, nitrate ions are concentrated in secondary waste streams that must be treated and, thus, result in high process costs. Bionitrification (Flere et al., 1999; Rittmann and Huck, 1989) is currently the most promising technique to solve the nitrate problem. The main reasons for the slow transfer of technology to drinking water purification are possible bacterial contamination, the presence of residual organics, and the possible increase in chlorine demand in purified water (Kapoor and Viraraghavan, 1997). Chemical reduction of nitrate by using hydrogen over a solid catalyst, first described by Vorlop and Tacke (1989), offers an alternative and economically advantageous process to biological removal of nitrate from water. In this process, however, hydrogen is difficult to transport and conserve as a reducer and is very dangerous on a large scale. Therefore, further opti-

mization of current treatment techniques and the development of emerging processes for nitrate treatment in water are required.

Electrochemical methods are superior because of the use of clean reagents (i.e., electrons). Thus, electroreduction of nitrate is now receiving increased attention. Many results showed that the reduction of nitrate depended strongly on the nature of the electrode material, electrolyte pH (Peel et al., 2003), electrode potential, and the presence of molecular or ionic additives in the solution (Gootzen et al., 1997; Safonova et al., 1998).

The mechanism of nitrate electroreduction has been widely studied (Da Cunha et al., 2000). A number of studies provide a working hypothesis (Dima et al., 2003; El-Deab, 2004; Nishimura et al., 1991).

Firstly, the discharge of water molecules takes place on the cathode according to the following:

Where the subscript "(ads)" refers to adsorbed species. In the nitrate solution, the above reaction takes place concurrent with the electrochemical reduction of nitrate ions. Then, nitrate ions were reduced, as follows:

Where the subscript "(sol)" refers to the solution-phase ions.

Then, the chemisorbed nitrogen monoxide (NO) could be desorbed to the solution.

However, the chemisorption energy on transition-metal surfaces is sufficiently high (approximately 200 kJ/mol) so that little $NO_{(sol)}$ is observed (Ge and King, 1998; Loffreda et al., 1998).

The next series of reactions is the selectivity-controlling reaction step, where nitrogen monoxide (N_2O), nitrogen (N_2), ammonium (NH_4^+), and hydroxyl amine (NH_3OH^+) are the possible products, and N_2 is the desired product (Nishimura et al., 1991):

Recently, most of the research in this area has centered on determining the best material for the cathode and examining

modifications of its surface with a bound catalyst (Gootzen et al., 1997). In literature (Dima et al., 2003; De Groot and Koper, 2004), the authors found that a platinum or gold electrode was not a good electrocatalyst for the reduction of nitrate. Copper and silver, on the other hand, tended to exhibit a higher capacity of nitrate reduction; copper was very active. De Vooy et al. (2000) found that a copper-modified palladium electrode showed a higher capacity of nitrate reduction than a single metal. Also, Shimazu et al. (2002) found that the tin-modified platinum and palladium electrodes showed the highest electrocatalytic capacity of nitrate reduction. However, the use of expensive bulk platinum and palladium is a disadvantage from a practical viewpoint. Therefore, we want to prepare a new kind electrode with low palladium loading.

The aim of the present work is to prepare and use the palladium-modified copper electrode as a possible candidate cathode for more efficient electrochemical reduction of nitrate. The dependence of the capacity of nitrate reduction on the palladium coverage, the electrolyte pH, the concentration of nitrate, and other anions in solution is discussed using cyclic voltammetry (CV).

Experimental Conditions

Preparation of the Electrodes. The palladium-modified copper or titanium electrodes were prepared using the electro-deposition method. The copper or titanium flag electrode (all electrodes were at least 99.9% pure) was polished with emery paper (280 600-grit) first, then with a finer grade (1200-grit), to obtain a relatively mirror-like surface. After thorough rinsing, electrodes were cleaned by dipping in acetone solution and then in 70% phosphoric acid to ultrasonic treatments for 15 minutes, and finally rinsed with doubly distilled water. The electro-deposition of metallic palladium was carried out by dipping the cleaned copper or titanium electrode in dichlorodiamminepalladium $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ complex (plating solution), which was formed by 1-mM palladium chloride (PdCl_2) and 10-mM ammonium chloride solution. A deposition current of 4 mA/cm^2 was used. The thickness of the metallic palladium deposited on the electrode surface depends on the deposition time. The geometric area of the electrodes is 0.25 cm^2 .

All chemicals used in our work are analytical grade. The supplier of chemicals is Beijing Chemical Reagent Factory (China). The supplier of copper and titanium electrodes is General Research Institute for Nonferrous Metals (Beijing, China).

Instrumentation. Cyclic voltammetry was used to evaluate the electrocatalytic capacity of nitrate reduction by a palladium-modified copper electrode and determine the effect of the palladium coverage, electrolyte pH, nitrate concentration, and other anions in solution on the capacity of nitrate reduction.

All electrochemical experiments were performed using a Basic Electrochemistry System (PerkinElmer, Wellesley, Massachusetts) that was controlled by M270 electrochemical analysis software (Electrochemistry PowerSuit, PerkinElmer) at room temperature. A conventional three-electrode glass cell was used. A glass cloth divided the cell into two compartments; one contained the working electrode, and the other contained the counter electrode (platinum electrode). The reference electrode was connected to the working electrode compartment through a Luggin capillary filled with the test solution, and it was positioned near the working electrode surface. In all cases, the reference electrode was a saturated calomel electrode (SCE). All potentials given in this paper referred to the SCE. Copper, titanium, palladium-modified copper electrode, and palladium-modified titanium electrode were used as working

Figure 1—Cyclic voltammetric curves at 10 mV/s of the palladium-modified copper electrode in (a) 0.1-M HClO_4 solution and (b) 0.1-M HClO_4 + 0.1-M NaNO_3 , pH = 0.86 (scan from 0 V [versus open-circuit potential] to -1 V , then from -1 to 0 V [versus open-circuit potential]).

electrodes. The cell was purged with argon before all experiments for 10 minutes to displace ambient oxygen from the solution.

The CV experiments were carried out in 0.1-M perchloric acid (HClO_4) (or sodium perchlorate $[\text{NaClO}_4]$) solution with the addition of 0.1-M sodium nitrate (NaNO_3). Perchloric acid was selected because the anion was not adsorbed strongly and was believed not to influence the state of the electrode surface. The pH of the solution was fixed for pH-dependence studies using Tris (tromethamine) + HClO_4 buffer solution. All CV experiments were performed at a scan rate of 10 mV/s.

Results and Discussion

Electrocatalytic Capacity of Nitrate Reduction by the Palladium-Modified Copper Electrode. Figure 1 shows the CV curves observed from the palladium-modified copper electrode at 10 mV/s in (a) 0.1-M HClO_4 solution and (b) 0.1-M HClO_4 + 0.1-M NaNO_3 solution (pH = 0.86). Scan began from 0 V (versus open-circuit potential) to -1 V , then from -1 to 0 V (versus open-circuit potential). First, reduction current increased in both (a) blank solution and (b) NaNO_3 solution when the potential was lower than -0.4 V versus SCE, which may be a result of the reduction of hydrogen ion to adsorbed hydrogen atom. Then, the existence of a reduction peak at -0.605 V versus SCE in the case of the argon-saturated 0.1-M NaNO_3 solution can be found in the CV measurement (curve b), but is not observed in the blank solution (curve a). Consequently, it can be attributed to the electrochemical reduction of the nitrate anion. With decreasing potential, the reduction current increased significantly in the blank solution, but was not seen in the NaNO_3 solution. This fact suggested that hydrogen evolution occurred in the blank solution, but was suppressed in the NaNO_3 solution. We speculated that the reason for this was that the adsorbed hydrogen atom, which was necessary for the formation of hydrogen gas, was consumed by the reduction of nitrate in solution b, which was consistent with the mechanism proposed by El-Deab (2004) discussed in the introduction.

De Vooy et al. (2000) found that, for a copper-modified palladium electrode, the capacity of nitrate reduction varied from

Figure 2—Dependence of nitrate reduction current on deposition time of palladium in 0.1-M HClO₄ + 0.1-M NaNO₃ solution (pH = 0.86) at a potential scan rate of 10 mV/s.

copper coverage. To optimize the deposition time of palladium, the reduction current for the palladium-modified copper electrode in 0.1-M HClO₄ + 0.1-M NaNO₃ was plotted as a function of the deposition time of palladium on the copper electrode, as shown in Figure 2. First, the nitrate reduction current increased with deposition time and reached a maximum value of 61.52 mA/cm² over 20 minutes of deposition. Then, the nitrate reduction current was kept steady when the deposition time was higher than 20 minutes. Therefore, 20 minutes was enough for deposition in preparing the palladium-modified copper electrode in our work.

Recently, the mechanism of electrochemical reduction of nitrate has been widely studied. De Vooy et al. (2000) indicated that the adsorption of nitrate (NO₃⁻) onto the copper-modified palladium electrode (reaction 2), a fast and reversible process, was kinetically controlled. Therefore, nitrate reduction is strongly dependent on the adsorbed nitrate concentration and adsorbed hydrogen atom (H_(ads)) on the surface of the electrode. In addition, the coverage of NO₃⁻_(ads) can be influenced by the competing adsorption of anions from the supporting electrolyte. The surface coverage of H_(ads) is influenced by electrolyte pH. Therefore, the pH of the solution and the concentration of nitrate and anions in the solution all influence nitrate reduction.

Influence of Solution Properties on Nitrate Reduction. *pH of Electrolyte.* The dependence of the nitrate reduction process on pH was investigated using CV in tromethamine-perchlorate (Tris-ClO₄) solution, and the results are shown in Figure 3. When the pH value was 9.34, the nitrate reduction peak current almost cannot be identified, which means that nitrate reduction was suppressed in the alkaline solution. This fact showed that it was mainly the hydrogen atom, but not the electron, that reduced nitrate, because the nitrate reduction current should be identified in the alkaline solution if the electron reduced nitrate, which is contrary to the result. When the pH was 5.59 or 7.34, the nitrate reduction peak current occurred. This fact suggested that the pH values of 5.59 or 7.34 were beneficial to nitrate reduction in acid or neutral solution. In acid solution, hydrogen evolution was observed below approximately -0.8 V versus SCE, and an amount of hydrogen atoms adsorbed on

Figure 3—pH dependence of nitrate reductive current in 0.1-M NaNO₃ + 0.1-M NaClO₄ Tris-ClO₄ buffered solution; $v = 10$ mV/s (scan from 0 V [versus open-circuit potential] to -1 V, then from -1 to 0 V [versus open-circuit potential]).

the surface of the electrode above -0.8 V versus SCE; in neutral solution, the reaction shown in eq 1 may have occurred on the surface of the electrode. Thus, it was confirmed that enough adsorption of hydrogen in acid or neutral solution was provided, and the adsorbed hydrogen was necessary for nitrate reduction. Therefore, we speculated that the hydrogen atom was the main reason for nitrate reduction, which was consistent with the mechanism shown in the introduction. In addition, it was shown that the proposed electrocatalytic reduction process can be used for denitrification in a neutral pH condition if the solution has the capacity to buffer pH change.

Nitrate Concentration. The effect of the low nitrate concentration (in this paper, low nitrate concentration is defined as 0.01 to 0.5 M) was investigated for the palladium-modified copper electrode in a NaClO₄ solution (Figure 4a) and in a sodium sulfate (Na₂SO₄) solution (Figure 4b). The nitrate reduction peak current almost cannot be seen when the nitrate concentration was 0.01 M, whereas it was clearly identified when nitrate concentration was 0.1 or 0.5 M in both Na₂SO₄ and NaClO₄ solution. The result showed that the nitrate reduction peak current increased with the nitrate concentration under two solution conditions; this was consistent with work of Dima et al. (2003), who found that current density was related to the nitrate concentration by a positive reaction order lower than one. This positive reaction rate was most likely caused by the fact that nitrate adsorbates increased with nitrate concentration.

Figures 5a and b show the concentration dependence for high nitrate concentrations (in this paper, high nitrate concentration is defined as 1 to 5 M) in (a) NaClO₄ solution and (b) Na₂SO₄ solution. It was shown that no significant difference in the nitrate reduction peak current was observed in both Na₂SO₄ and NaClO₄ solutions when the nitrate concentration was 1, 3, and 5 M. This might be a result of enough nitrate adsorbates being present on the surface of the electrode. In addition, there was an increase in the reduction current for potentials below -0.7 V, which may be because of the fact that hydrogen evolution in place of nitrate reduction dominates in the reduction current.

Figure 4—Cyclic voltammetry of nitrate reduction in (a) 0.1-M NaClO_4 solution and (b) 0.1-M Na_2SO_4 solution at low nitrate concentration (0.01 to 0.5 M); pH = 7.34, $v = 10 \text{ mV/s}$ (scan from 0 V [versus open-circuit potential] to -0.9 V , then from -0.9 to 0 V [versus open-circuit potential]).

Other Anions in the Solution. There are many kinds of anions in surface water and groundwater, such as sulfate (SO_4^{2-}), chlorine (Cl^-), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), and their effect on the electroreduction of NO_3^{2-} has not been well known. This paper will discuss the influence of SO_4^{2-} on electroreduction of nitrate, for example.

At a fixed nitrate concentration (0.1 M), electrolytes containing NaClO_4 showed a higher nitrate reduction current than that containing Na_2SO_4 (Figure 6), which was a result of the difference in adsorption strength between ClO_4^- and SO_4^{2-} (Dima et al., 2003). Furthermore, with increasing concentrations of SO_4^{2-} , the nitrate reduction current decreased. This result indicated that the presence of SO_4^{2-} in solution could hinder nitrate reduction, which could be explained by the effect of the competitive adsorption between NO_3^- and SO_4^{2-} . This result was well-documented in the literature (Dima et al., 2003; Horanyi and Rizmayer, 1982).

Comparison with Other Electrodes. To compare the electrocatalytic capacity of nitrate reduction by the palladium-modified copper electrode with other electrodes (copper, titanium, and

Figure 5—Cyclic voltammetry of nitrate reduction in (a) 0.1-M NaClO_4 solution and (b) 0.1-M Na_2SO_4 solution at high nitrate concentration (1 to 5 M); pH = 7.34, $v = 10 \text{ mV/s}$ (scan from 0 V [versus open-circuit potential] to -0.9 V , then from -0.9 to 0 V [versus open-circuit potential]).

palladium-modified titanium electrode) in 0.1-M $\text{NaClO}_4 + 0.1\text{-M}$ NaNO_3 solution at neutral pH, the CV was measured. Figure 7 shows that the titanium electrode performed very little nitrate reduction. The nitrate reduction current by the copper electrode was approximately the same as that by the palladium-modified titanium electrode and was higher than the titanium electrode, which showed that copper was favorable for the reduction of nitrate. This inference was also obtained by the result that the capacity of nitrate reduction by the palladium-modified copper electrode was higher than that by the palladium-modified titanium electrode; the capacity of nitrate reduction by the palladium-modified titanium electrode was higher than that by the titanium electrode. Also, the nitrate reduction current by the palladium-modified copper electrode was 16.6% higher than that of the copper electrode. These results indicate that palladium was beneficial for the reduction of nitrate. Thus, both copper and palladium were beneficial for the reduction of nitrate, which was consistent with the result that the palladium-modified copper electrode showed the highest nitrate reduction current in our work; that is, the nitrate reduction reaction was favored using the

Figure 6—Cyclic voltammetry of nitrate reduction in 0.1-M NaClO_4 solution and in different concentrations of Na_2SO_4 solution at a fixed nitrate concentration (0.1 M); pH = 7.34, $v = 10$ mV/s (scan from 0 V [versus open-circuit potential] to -0.9 V, then from -0.9 to 0 V [versus open-circuit potential]).

palladium-modified copper electrode compared with other electrodes prepared in our work.

To evaluate the stability of the electrodes, the constant potential experiment was conducted in 0.1-M NaNO_3 + 0.1-M NaClO_4 stirred solution. Figure 8 shows a typical time course of the nitrate reduction current at a potential of -0.65 V for the palladium-modified copper electrode and -0.8 V for the palladium-modified titanium electrode. As can be seen, when using the palladium-modified copper electrode, the nitrate reduction current remained stable, at approximately -3.1 mA/cm² over 8 hours. For the palladium-modified

Figure 7—Comparison of the reductive current of copper, palladium-and-copper, titanium, and palladium-and-titanium electrodes in 0.1-M NaClO_4 + 0.1-M NaNO_3 solution; pH = 7.34, $v = 10$ mV/s (scan from 0 V [versus open-circuit potential] to -1 V, then from -1 to 0 V [versus open-circuit potential]).

Figure 8—Time course during the reduction of nitrate on the palladium-and-copper or palladium-and-titanium electrode in 0.1-M NaClO_4 + 0.1-M NaNO_3 solution; pH = 7.34.

titanium electrode, the nitrate reduction current initially was kept at approximately -2.6 mA/cm², and then a gradual decrease was observed after 2 hours. The nitrate reduction current showed a 69.1% decrease compared with the maximum value at the initial stage after 8 hours. Therefore, the result indicated that the palladium-modified copper electrode prepared in our work was more stable than the palladium-modified titanium electrode. This feature was very important for its use as a practical electroreduction mechanism.

Conclusion

The palladium-modified copper electrode showed higher electrocatalytic capacity and stability in the nitrate reduction process than other electrodes (copper, titanium, and palladium-modified titanium electrode) prepared in our work. The capacity of nitrate reduction was dependent on the palladium coverage.

The nitrate reduction was suppressed in the alkaline solution, while it was beneficial to nitrate reduction in an acid or neutral solution. At low nitrate concentrations (0.01 to 0.5 M), the nitrate reduction current increased with the nitrate concentration, showing that the nitrate reduction current depended on the amount of NO_3^- (ads) on the surface. In addition, the adsorption of NO_3^- from solution can be seriously hindered by sulfate. At high nitrate concentrations (1 to 5 M), no significant difference in the nitrate reduction current was observed.

The results of this study indicate that electrocatalytic reduction is a potential application for removing nitrate in groundwater, and the palladium-modified copper electrode shows high electrocatalytic capacity of nitrate reduction. However, to be implemented on a large scale, further research exploring the selectivity and the mechanisms of the reaction is required.

Acknowledgments

Credits. The authors appreciate the generous financial support of this work by the National Science Fund for Distinguished Young Scholars (Beijing, China) (No. 50225824) and the National Natural Science Foundation of China (Beijing, China) (No. 20337020).

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Submitted for publication October 8, 2004; revised manuscript submitted July 18, 2005; accepted for publication July 25, 2005.

The deadline to submit Discussions of this paper is October 15, 2006.

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