



# The electrochemical reduction of nitrate over micro-architected metal electrodes with stainless steel scaffold



Jenn Fang Su<sup>a</sup>, Inci Ruzybayev<sup>b</sup>, Ismat Shah<sup>b,c</sup>, C.P. Huang<sup>a,\*</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA

<sup>b</sup> Department of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA

<sup>c</sup> Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA

## ARTICLE INFO

### Article history:

Received 7 April 2015

Received in revised form 6 June 2015

Accepted 16 June 2015

Available online 20 June 2015

### Keywords:

Nitrate reduction

Bimetallic

Cu/SS

Pd–Cu/SS

Nitrogen

## ABSTRACT

Cu and Pd–Cu (Pd = 40 wt%) electrodes supported on stainless steel (Cu/SS and Pd–Cu/SS) were prepared using electrodeposition methods and characterized by X-ray diffraction, scanning electron microscope, and X-ray photoelectron spectroscopy. The electrocatalytic reduction of nitrate on Cu/SS and Pd–Cu/SS electrodes was studied in sodium perchlorate electrolyte. By tuning the applied potential, nitrate was found to be selectively reduced to different products, indicating a strong dependence of nitrate reduction reaction on the applied potential. Moreover, the effect of electrode material on nitrate reduction was studied also. Results showed that the nitrate reduction over the two electrodes was different due in part to distinct surface morphology. Results demonstrated a novel avenue to improve the selectivity of nitrate reduction products through controlling the applied potential and selection of electrode material. Results also showed strategy warrant further studies on nitrate conversion to harmless nitrogen gas.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Nitrate is a known harmful chemical species commonly present in natural water systems such as ground water, lakes, and rivers [1]. High nitrate level in drinking water can cause methemoglobinemia in infants and gastrointestinal cancer in adults [2,3]. The World Health Organization (WHO) has proposed a maximum nitrate concentration of 50 ppm in drinking water [4]. Therefore, the removal of nitrate from water has drawn considerable attention from the water supply industry. In order to develop sustainable water purification technology, it is reasonable to convert nitrate to gaseous N<sub>2</sub> directly without other byproducts especially ammonia, which requires further separation [5]. Biological denitrification is able to selectively transform nitrate into harmless N<sub>2</sub> [6]. However, the success of the process, mostly dependent on bacterial activities, has relatively low reaction rate, produces undesired byproducts, and requires precision process control algorithm such as nitrate concentration and pH [7,8]. Catalytic hydrogenation of nitrate to nitrogen with H<sub>2</sub> as electron donor over solid catalysts is another option. Yoshinaga et al. has showed that a catalyst, Pd–Cu supported on active carbon, could yield 75% of N<sub>2</sub> during nitrate reduction by hydrogenation [8]. However, catalytic reduc-

tion by hydrogen is not suitable for large scale application. Also, this method requires continuous feeding of H<sub>2</sub> [9–12]. Therefore, electrochemical reduction method becomes an alternative for overcoming the limitations of biological denitrification and catalytic hydrogenation. Electrochemical reduction on solid electrodes offers a promising approach to remove nitrate from water because of its high treatment efficiency, lack of sludge production, and relatively low investment costs [13–19]. Li et al. have showed that nitrate can be successfully reduced and converted to N<sub>2</sub> by electrochemical reduction over a Cu–Zn cathode and a Ti/IrO<sub>2</sub>–Pt anode [20]. Also, de Vooy et al. have demonstrated that the conversion from nitrate to N<sub>2</sub> can be controlled by Cu loading on the Pd–Cu electrode [21]. Although electrochemical reduction of nitrate to N<sub>2</sub> has been widely studied, the mechanism still remains relatively unknown due to high reactivity and instability of nitrate reduction products. Moreover, in most cases, nitrate has been converted to unwanted byproducts such as nitrite and ammonia, which are toxic to many aquatic lives. To improve the selectivity of nitrate reduction toward N<sub>2</sub>, a wide variety of cathodic metals and alloys, such as Pb [22,23], Ni [22,24,25], Fe [22], Cu [21,26–28], Pt [24,29–31], Zn [23], Ru [31], Pd [21,31,32], C [19,22], and Ir [29,31], Pt–Ir [29], Pd–Cu [8,12,21] have been studied. Among these materials, Cu was the most studied due to its high selectivity and efficiency [26] for the conversion of nitrate into nitrite, which has been reported to be the rate-determining step in the nitrate reduction mechanism [31]. However, nitrate reduction on Cu electrode mainly leads to

\* Corresponding author. Fax: +1 302 831 3640.  
E-mail address: [huang@udel.edu](mailto:huang@udel.edu) (C.P. Huang).

the formation of nitrite and ammonia [26,33]. Vorlop and Tacke [12] were the first to report that a second metal, Pd, in addition to Cu could improve the N<sub>2</sub> selectivity during the electrochemical reduction of nitrate. Cu exhibits a catalytic effect that restricts the adsorption of hydrogen on the cathode surface thereby enhancing the adsorption of nitrate [34]. After the adsorption of nitrate, Cu has a negative influence both on the activity and selectivity of nitrite reduction towards N<sub>2</sub>. Both de Vooy et al. [21] and Ghodbane et al. [14] have reported that nitrogen generation increases with increasing amount of Pd on the electrode surface; that is, Pd gives high reactivity on nitrite reduction.

Many have reported electrochemical nitrate reduction using various metal electrodes, but only a few have discussed the effect of applied potential on the nitrate reduction products. Ryter et al. [33] reported that the nitrate electroreduction process was strongly dependent on the applied potential. For example, nitrate was reduced to nitrite at  $-0.9\text{ V}$  (vs. Hg/HgO) but was reduced to hydroxylamine at  $-1.1\text{ V}$  (vs. Hg/HgO) using Cu electrode. Their results demonstrated that an optimum applied potential was important to effective nitrate conversion in order to avoid the formation of unwanted byproducts and additional post-treatment of the finished water.

The objective of this study was to determine the effect of applied potential and electrode material on nitrate reduction and its byproducts. The cyclic voltammetric curve was convoluted to establish the potential corresponding to the individual half redox reaction. Additionally, the electrode materials were characterized via X-ray diffraction (XRD) and scanning electron microscope (SEM) as to assess the effect of electrode material on nitrate reduction.

## 2. Experimental

### 2.1. Materials

Sodium nitrate, sodium nitrite, sodium carbonate were obtained from Fisher Scientific, Pittsburgh, PA, USA and were of certified grade according to American Chemical Society (ACS). Sodium perchlorate (purity >98%) and sodium bicarbonate (purity >99.7%) were purchased from ACROS, Fair Lawn, NJ, USA. Sodium hydroxide (purity >97.0%) and methanesulfonic acid were purchased from Sigma-Aldrich, St Luis, MO USA. Deionized water was treated with Mega-Pure System (Model MP-290). Platinum wire (Fisher Scientific, 1284987, od: 0.5 mm) was purchased from Fisher Scientific, Pittsburgh, PA, USA. Stainless steel mesh (corrosion-resistant 304 stainless steel woven wire cloth, 100 × 100 mesh, or 0.0045" wire diameter) was obtained from McMaster-Carr Co., Elmhurst, IL, USA. For catalytic material preparation, cupric sulfate (purity >99%), and palladium chloride (purity >98%) were purchased from Sigma-Aldrich, St Luis, MO, USA.

### 2.2. Electrode preparation

The raw stainless steel mesh was cut into small pieces (ca. 5 cm × 10 cm) and washed in detergent solution. After cleaning, the mesh was rinsed with deionized water and dried in a dryer for 1 h. The metal ion solutions were prepared by dissolving an appropriate amount of cupric sulfate and palladium chloride in deionized water at concentration range of 0.01 and 0.1 M, respectively. All electrodeposition experiments were carried out at room temperature by using a two-electrode system, which was connected to a potentiostat (Model WP705B, Vector-VID) [35]. The washed stainless steel mesh was used as working electrode and graphite was selected as the counter electrode. Both electrodes were immersed in the metal ion solution in a 250-mL beaker. Cu metal deposition process was performed at constant current of 0.3 A for 5 min, and

then current was increased to 0.6 A for additional 3 min at each side. Pd metal deposition process was operated at constant current of 0.3 A for 1.5 min and then the current was increased to 0.6 A for 1.5 min at each side. After deposition, the metal coated stainless steel mesh was washed with deionized water and dried under ambient environment. The electrodeposited Pd-Cu composition was calculated from the Faraday's laws. The Pd-Cu electrode so fabricated had a Pd weight fraction of 0.4. Note that in order to avoid overloading the instrument during cyclic voltammetric runs, the electrodes were cut into small pieces as to minimize the current output.

### 2.3. Voltammetry experiments

All experiments were carried out in a three-electrode system at room temperature. The three electrodes were connected to a potentiostat (model AFRDE 4, Pine Instrument Inc., USA), which controlled the applied voltage and recorded corresponding current. The stainless steel supported Cu (Cu/SS) or Pd-Cu (Pd-Cu/SS) electrode was the working electrode. A platinum wire and a saturated calomel electrode (SCE) were the counter electrode and the reference electrode, respectively. The reaction vessel was a 500-mL glass beaker. NaClO<sub>4</sub> solution at a concentration of 0.05 M was the electrolyte. The pH value during electrolysis experiment was controlled by the NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> buffer. Voltammetry experiments were operated at a sweep rate of 10 mV/s between  $-1.0\text{ V}$  and  $0.6\text{ V}$  (vs. SCE) to evaluate the activity of the electrode in nitrate reduction. In all cases, the voltammetric experiment was scanned 5 times in the above potential range to achieve a stable voltammogram.

### 2.4. Analytical methods

Nitrate and nitrite were measured by a Dionex ion chromatograph (IC) system equipped with a GP50 pump, ED 40 conductance detector, Dionex IonPac AC20 column (4 mm × 250 mm.), and Dionex AS 40 automatic sampler. The effluent mobile phase was a mixture of deionized water and 50 mM NaOH and the injection volume was 25 μL, which yielded a flow rate of 1 mL/min. At different time intervals, 3 mL of sample were withdrawn from the electrochemical cell for chemical analysis. A Dionex ion chromatograph (IC) system equipped with a GP40 pump, CD 20 conductance detector, Dionex IonPac CS16 column (0.5 mm × 250 mm.), and Dionex AS 3500 automatic sampler was used to measure the ammonium concentration. The effluent mobile phase was a mixture of deionized water and 0.1 M methanesulfonic acid and the injection volume was 25 μL, which delivered a flow rate of 1 mL/min. The concentration of nitrogen gaseous species was quantified by mass-balance.

### 2.5. Surface characterization

The crystallinity of Cu and Pd-Cu catalysts were identified by X-ray diffraction (XRD, Rigaku D-Max B) with Cu K $\alpha$  radiation. Each sample was operated at 30 kV beam voltage and 30 mA current, and scanned between 30° and 90° at a scan rate of 0.6 (deg/min). The elements and crystal structures were characterized by matching the XRD pattern of each sample against library data (JCPDS, PDF no. 85-1326). Surface morphology and structure of the deposits were investigated by a scanning electron microscopy (SEM, JSM 7400F) at an accelerating voltage of 3 kV. The composition of each sample was determined by X-ray photoelectron spectroscopy (XPS, Omicron EA125). Non-monochromatic Al X-rays (1486.5 eV) were employed. CasaXPS software was used to convolute the peaks. C 1s peak related to the C-C bond located at 284.6 eV was used as a reference peak for calibration.

Download English Version:

<https://daneshyari.com/en/article/45235>

Download Persian Version:

<https://daneshyari.com/article/45235>

[Daneshyari.com](https://daneshyari.com)