ELECTROCATALYTIC REDUCTION OF NITRITE IN WATER AT CUO/CU ELECTRODE

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Abstract

Nitrite plays an important role in environment and life process. As an alarming pollutant to the environment and human health, various techniques have been developed to determine nitrite. Electrochemical methods, especially the chemically modified electrodes (CMEs) have utilized extensively, due to several advantages in comparison with other methods, such as quick response, high sensitivity, low detection limit and simple use.Nanostructured CuO was directly grown on copper foam by cyclic voltammetry method, The electrocatalytic reduction of nitrite at **CuO/Cu** has been investigated using 0.5 M H_2SO_4 solution.The proposed method was successfully applied in the detection of nitrite in real water samples and obtained satisfactory results.

Keywords: Cupper substrate, Cupper oxide, nitrite reduction, Electrocatalyst.

1. Introduction

In recent years, drinking water is increasingly contaminated with nitrite (NO_2^-), resulting from the overuse of fertilizer in agriculture and the discharge of industrial wastewater [1]. Because nitrite overexposure in the human body can cause cancer, lung disease and blue-baby syndrome [1–3], theWorld Health Organization and European Community have determined 0.1 and 0.02 mg/L as the permissible nitrite levels, respectively [2,4]. Because of increasing concerns on the nitrite pollution, various physicochemical (e.g., ion exchange and reverse osmosis) and biological treatments have been used for the nitrite reduction [5,6]; however, each process revealed disadvantage such as need of the secondary treatment process in the former and slow reaction rate in the latter [6].

To solve these problems, Vorlop and Tacke first reported a catalytic reduction method [7] which is performed under mild conditions (T = 25 ◦C and P = 1 atm) using a single noble metal supported catalyst and hydrogen gas as the reducing agent, and the reaction is as follows [8]:

$NO^{2-} + 3H_2 \rightarrow N_2 + 2H_2O + 2OH^-$

Hörold et al. tested diverse noble metal impregnated catalysts, which were Pd, Pt, Ru, Ir and Rh on Al_2O_3 support, and found that only the Pd supported catalyst was effective

for the nitrite reduction [2,8]. Along with active metals, many studies aimed to investigate suitable supports such as Al_2O_3 [9,10], carbon fiber [11] and conducting polymers [12], because different surface state of the utilized supports could enhance the nitrite reduction.
In this work, we reported the first successful preparation of morphology-controlled CuO nanostructures supported on Cu foam substrate electrochemically synthesized, towards NO_2^- electroreduction. Electrochemical experiments revealed that the as-prepared samples exhibited excellent catalytic activity towards NO_2^- electroreduction in acid medium.

2. Experimental
2.1. Preparation and characterization of CuO grown on Cu foil
The preparation of CuO grown on Cu foil was carried out as follows. Typically, a Cu foil (99.99% in purity) was degreased with acetone, etched with 2 moldm^{-3} HCl for 10 min and rinsed with distilled water extensively. The treated Cu foil was modified electrochemically by Cyclic voltammetry a three electrode cell with Cu foam working electrode, platinum foil counter electrode and saturated calomel reference electrode in 5 M KOH solution (>99.0%). After reaction for Cu electrooxidation in 5 M KOH solution at room temperature (Fig.1), the sample was removed from the solution, washed with distilled water thoroughly and dried in air at room temperature. The shiny Cu foil surface turned to complete black after the reaction. The obtained electrode (denoted as CuO/Cu).

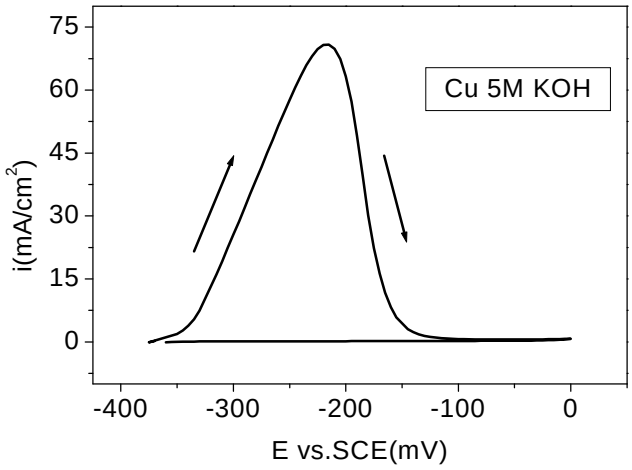

Fig.1- Cyclic voltammograms of the Cu electrode in 5 moldm^{-3} KOH at 500 mVmin^{-1} in the potential range of -0.375 to 0 V.
3. Results and discussion
3. Electrocatalytic performance of the CuO/Cu electrode for NO_2^- reduction
Fig.1 shows the cyclic voltammograms (CVs) of the Cu electrode in 5 moldm^{-3} KOH solutions at a scan rate of 500 mVmin^{-1} in the potential range of -0.375 to 0 V. The obtained electrode (denoted as CuO/Cu) which is the range at which NO_2^- electroreduction occurs. Electroreduction of nitrite was performed in 200 ml one-compartment electrolytic cell using a potentiostat/galvanostat (PGS-HH9). A three-electrode was used with a CuO/Cu working electrode with a 2 Cm^2 exposed area, platinum wire counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode.Cyclic voltammetry (CV) experiments were conducted using

0.5 M (H_2SO_4), solution as a supporting electrolyte. Sodium nitrite ($NaNO_2$) solutions were prepared just prior to use.

References

[1] W. Gao, J. Chen, X. Guan, R. Jin, F. Zhang, N. Guan, Catal. Today 93–95 (2004) 333–339.
[2] S. Hörold, K.-D. Vorlop, T. Tacke, M. Sell, Catal. Today 17 (1993) 21–30.
[3] N. Barrabés, J. Sá, Appl. Catal. B 104 (2011) 1–5.
[4] WHO, Guidelines for drinking-water quality, in: fourth ed., World Health Organization, 2011.
[5] N. Barrabés, J. Just, A. Dafinov, F. Medina, J. Fierro, J. Sueiras, P. Salagre, Y. Cesteros, Appl. Catal. B 62 (2006) 77–85.
[6] V. Höller, K. Rådevik, I. Yuranov, L. Kiwi-Minsker, A. Renken, Appl. Catal. B 32 (2001) 143–150.
[7] K.D. Vorlop, T. Tacke, Chem. Ing. Tech. 61 (1989) 836–837.
[8] S. Hörold, T. Tacke, K.D. Vorlop, Environ.Technol. 14 (1993) 931–939.
[9] A. Pintar, J. Batista, J. Levec, Water Sci. Technol. 37 (1998) 177–185.
[10] A. Pintar, G. Berciˇ c, J. Levec, AIChE J. 44 (1998) 2280–2292.
[11] J.K. Chinthaginjala, J.H. Bitter, L. Lefferts, Appl. Catal. A 383 (2010) 24–32.
[12] I. Dodouche, F. Epron, Appl. Catal. B 76 (2007) 291–299.