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Disposable barrel plating nickel electrodes for use in flow injection analysis of trivalent chromium

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Abstract

We report a disposable barrel plating nickel electrode (Ni-BPE) coupled with a specifically designed electrochemical cell for use in flow injection analysis for the determination of trivalent chromium (Cr^{III}). The response of the activated Ni-BPE was found very sensitive under alkaline condition with a systematic increase in current signal upon successive addition of Cr^{III}. Under optimized conditions. the calibration curve showed a linear range up to 1 mM with a detection limit (S/N = 3) of 0.30 μ M. Continuous hydrodynamic flow of 0.1 M NaOH at regular Cr^{III} injections verify the reproducibility of the present system. The proposed method was successfully used to detect the amount of Cr^{III} in environmental water to show its potential use in real applications. © 2007 Elsevier B.V. All rights reserved.

Keywords: Chromium; Nickel electrode; Disposable; Flow injection analysis

1. Introduction

Trivalent chromium (CrIII) is an essential nutrient ion needed to maintain normal physiological functions. It is one of the essential trace elements in multivitamin with multimineral pharmaceutical formulations [1]. The detection of Cr^{III} that exists in many biological and industrial materials is of great interest [2]. Many methods, such as atomic adsorption spectrophotometer [3,4], plasma mass spectrometry [5], spectrofluorimetry [6], chemiluminescence [7-9], spectrophotometry [10] and electrochemistry in potentiometric measurement [11–17], have been employed for the determination of Cr^{III} . In general effective separation and preconcentration are both essential to obtain the best results, but the procedures are both complex and time consuming. Consequently, it is difficult to directly apply them *in situ* for monitoring Cr^{III} in aqueous environments. Direct oxidation of Cr^{III} is promising in this regard and

has been studied at platinum, stannum and diamond

Corresponding author. E-mail address: jmzen@dragon.nchu.edu.tw (J.-M. Zen). electrodes [18-21]. Notably, the oxidation of Cr^{III} was examined at polycrystalline gold and Au(111) single crystal electrodes [22,23] and the following mechanism was proposed for the overall electrode reaction:

$$CrO_{2}^{-} + OH^{-} \rightarrow e^{-} + H^{+} + CrO_{3}^{2-}$$
 (1)

$$CrO_3^{2-} \rightarrow e^- + H^+ + CrO_3^-$$
 (2)

$$CrO_{3}^{-} + OH^{-} \rightarrow e^{-} + H^{+} + CrO_{4}^{2-}$$
 (3)

In this paper the electrochemical oxidation of Cr^{III} is studied at an activated barrel plating nickel electrode (designated as Ni-BPE). It is anticipated the reaction mechanism of gold electrode might also be accessible at the activated Ni-BPE. Our previous study introduces an engineering process of barrel platting technology for mass production of disposable-type electrodes [24]. The primary function of barrel plating is to provide an economical means to electroplate manufactured parts that meets specific finishing requirements [25,26]. Since the fabrication cost of the Ni-BPE is cheap, it is thus disposable in nature. It was found that the activated Ni-BPE coupled with a specifically designed electrochemical cell allowed us to obtain

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a distinctive voltammetric profile towards the oxidation of Cr^{III} in flow injection analysis (FIA). To validate the applicability, the developed method was applied to the determination of Cr^{III} in real water samples.

2. Experimental

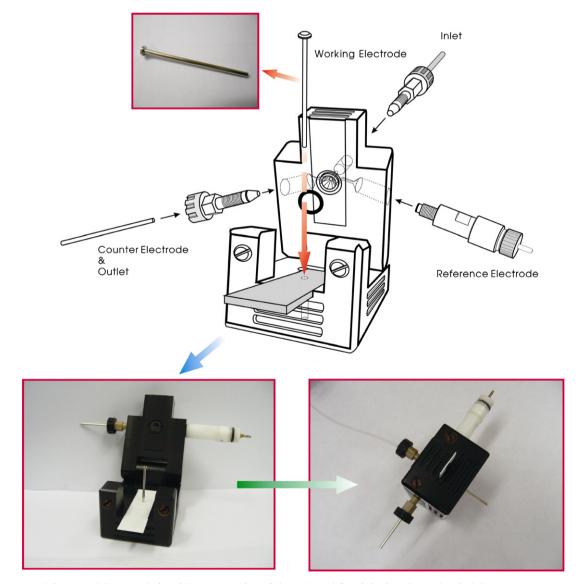
2.1. Reagents and chemicals

Chromic chloride (RDH, min. 96%) and sodium hydroxide (Showa, min. 96%) were used as received. All reagents were of analytical-reagent grade and prepared with high resistivity (18 M Ω /cm) de-ionised water. Natural water samples were collected in a polyethylene bottle from a lake at the campus of Chung Hsing University and kept under refrigeration below 4.8 °C and were filtered by 0.22 µm membrane (Millipore Inc.) before detection.

2.2. Apparatus and instrumentation

Cyclic voltammetric and chronoamperometric experiments were carried out using a CHI 900 electrochemical workstation (Austin, TX, USA). The three-electrode system consists of a Ni-BPE working electrode, an Ag/AgCl of reference electrode, and a platinum or stainless tube auxiliary electrode. The Ni-BPE (1.25 mm diameter, 31 mm length) with an average weight of $392.2 \pm 0.5 \text{ mg} (n = 10)$ was a special order from Zensor R&D (Taichung, Taiwan). The geometric surface area of the Ni-BPE was ~0.012 cm².

Scheme 1 shows typical pictures of the Ni-BPE working system used in this work. It consists of a Ni-BPE working electrode, a stainless tube counter electrode (outlet), an Ag/AgCl reference electrode. The flow injection analysis (FIA) system was equilibrated in 0.1 M NaOH carrier solution at +0.5 V until the current became constant. The



Scheme 1. Scheme and pictorial representation of the proposed flow injection electrochemical detector setup.

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