



Electrochemical detection of cupric ions with boron-doped diamond electrode for marine corrosion monitoring



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ABSTRACT

Corrosion induced structural failures continue to be a costly problem in many industrial situations, and the development of robust corrosion sensing systems for structural health integrity monitoring is still a demanding challenge. The applicability of corrosion monitoring of copper alloys using a boron-doped diamond electrode (BDD) has been performed based on determination of copper ions within localised corrosion microenvironments. The electrochemical behaviour of copper ions on the BDD electrode surface were first reported in details in 0.60 M NaCl aqueous solution, and the results revealed that the electrochemical processes of copper ions on the BDD electrode proceed as two successive single electron transfer steps producing two well-separated pairs of peaks in cyclic voltammograms in the chloride ion containing electrolyte solutions. Compared with perchlorate and sulphate ions, chloride ions were observed with a significant stabilization effect on copper ions via the formation of CuCl_2^- complex, thus having two well-separated pairs of peaks in the obtained cyclic voltammograms on the BDD electrode in the chloride ion electrolyte solution. The apparent rate constant for the redox couple of $\text{Cu}^{2+}/\text{Cu}^+$ in chloride ion electrolyte was determined as $0.94 \times 10^{-6} \text{ cm s}^{-1}$ by using quasi-steady polarisation technique, thus indicating a quasi-reversible electron transfer process of $\text{Cu}^{2+}/\text{Cu}^+$ redox couple. Moreover, differential pulse voltammetric results exhibited the BDD electrode is promising for corrosion monitoring of copper alloys with an excellent relationship between peak current and concentration of copper ions without significant interference from the commonly presented metal ions within the simulated marine corrosion environments.

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1. Introduction

Electrochemical detection technology has recently attracted significant attention among the development of fully-integrated sensing systems, due to its inherent miniaturization, low-power requirements, low limits of detection, compatibility with advanced micromachining systems, low instrumentation cost, and relative simplicity regarding to the procedure protocols [1–3]. Research into new and effective electrode materials has been chiefly driven in order to improve existing electrochemical sensing systems and to design new ones. Noble metals, such as platinum and gold, with

excellent chemical inertness, are often considered as the mainstays in the electroanalytical field. However, the detection of various analytes in aqueous media is often not feasible at high overpotentials, since these often result in either oxygen or hydrogen evolution on these metal electrodes in aqueous media [4]. In the past, due to the high overpotential towards hydrogen evolution, mercury electrodes were extensively exploited for trace metal analysis, however, its toxicity has promoted alternative research efforts to find replacements using less or non-harmful materials [5].

Boron-doped diamond (BDD) is increasingly of interest since its outstanding chemical and physical properties are unparalleled in comparison with other electrode materials [3–7]. The nil toxicity, the high overpotentials for oxygen and hydrogen evolutions [8], the high chemical and physical stability in addition to the low capacitive current in aqueous solutions [9], make BDD an attractive electrode material widely used in electroanalysis. One of the most extensively investigated BDD characteristics is the surface

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property and its influence on the electron transfer process. It has been widely shown that the electrochemical properties of the diamond electrode depend not only on the surface state, such as oxygen-, hydrogen- or fluorine- termination, but also on the way the surface modification is performed [10–17]. The advantages of BDD over conventional noble metals, carbon paste and glassy carbon electrodes in quantification of metal ions have been reported for the determination of trace metal ions for a broad range of examples: such as mercury in flue gas power plant sample [18], manganese in seawater [19] and marine sediment [20], arsenic in well water [21], and lead in river sediment [22].

Corrosion induced structural failure continues to be a costly problem in many industrial situations, especially for marine structures and platforms. The structural health integrity of marine structures can critically be affected by corrosion, in particular by localized corrosion, such as pitting and crevice corrosion. However, localized corrosion is extremely problematic to effectively detect due to limited access to affected areas, and the lack of robust corrosion sensing systems [23]. For example, non-destructive evaluation (NDE) methods, such as acoustic emission (AE), ultrasonic, and infrared thermography, have been improved significantly in recent years for inspection of pipelines and other large complex structures. However, these techniques are time consuming, and the limitations (e.g. service environment noise, temperature and access) associated with these methods cannot guarantee the inspection outcomes [24]. Electrochemical techniques have also been widely used to monitor corrosion rate of the structures or service environments corrosivity, but the reliability of these techniques is still limited for *in situ* corrosion monitoring, as summarized in Table 1. Chemical imaging methods have recently been proven more accurate in monitoring localized corrosion process by measuring local concentration of oxygen or ionic species (e.g. H^+ and/or metallic ions) at sites of interest using ion-selective microelectrodes (ISME) or pH sensors [25–29]. However, the nature of these corrosive environments, such as marine (both coastal and oceanic), and the area of application are such that robust sensors are required with the minimum of maintenance and capable of sustained operation over long timescales. Compared with current ISMEs, BDD electrode would be a better option for such applications due to its mechanical robust and stable surface properties, great resistance to surface fouling, and excellent electroanalysis performance.

Copper-based alloys are extensively used in marine structures, and are liable to localized corrosion in marine environments. For the commonly used copper alloys in marine environment (cupronickels, aluminium and nickel-aluminium bronzes), copper ions are main species initially produced by the corrosion process, while other metal ions, such as ferric, nickel and aluminium ions, are sometimes also produced as by-products [30–32]. Wharton et al. proposed that levels of metal ions produced within corrosion solution microenvironments could be used for determination of corrosion initiation locations and life-prediction of metal structures [30,32]. Corrosion sensing systems for copper-based marine

structural health monitoring are being developed based on electrochemical detection of metal ions produced by localized corrosion in our laboratory [33,34].

The electrochemical behaviour of copper ions on BDD electrodes is a subject of much attention due to its direct involvement in fundamental chemistry, in biological systems and in the industrial field. For example, Nakabayashi et al. [35] investigated the electrochemical response of the BDD and platinum electrodes to copper ions in 0.1 M sodium sulphate solution using cyclic voltammetry. They found that an intense reduction peak was observed on both BDD and platinum electrodes, but only a very small broad anodic peak was obtained with the BDD electrode compared to a strong sharp anodic stripping peak with the platinum electrode. This feature of a low anodic to cathodic charge ratio for the BDD electrodes in neutral sulphate solutions was attributed to the formation of the insulating oxide layer on the reduced copper clusters and the electrostatic repulsion between the BDD surface and the copper clusters, which force the reduced copper particles to peel off from the BDD surface and to diffuse away into the bulk solution [14,36]. Zak et al. [37] observed different cyclic voltammetric behaviour to copper ions on BDD electrodes in different electrolyte solutions of sulphuric, phosphoric and nitric acids using electrochemical atomic force microscopy. They reported that copper metal grains were formed and uniformly distributed over the diamond crystal facets during the cathodic process in the acidic solutions, then completely removed from the BDD surface with intensive anodic stripping peaks. They suggested that the thickness of the deposited metal layer on the BDD surface as well as the stripping signal in the anodic process may be influenced by the ability of the supporting electrolyte to form copper complexes. Tamilani et al. [38] also investigated the electrochemical reduction of copper ions on BDD films to explore the feasibility of electrochemical removal of copper from chemical-mechanical planarization generated wastewater. Based on their preliminary CV results, they proposed that in a 0.05 M potassium sulphate solution, copper ions were electrochemically deposited on the BDD surface in the form of copper clusters via either two successive one-electron transfer processes involving a combination of Cu^{2+}/Cu^+ and Cu^+/Cu^0 in pH 4 solution or three one-electron transfer processes with an additional Cu_2O/Cu^0 process in pH 6 solution. BDD electrodes have also been successfully employed for the determination of trace copper metal ions via anodic stripping voltammetry using nitric acid or acetate buffer solutions as the supporting electrolytes [5,39–41]. Nevertheless, these methods for determination of copper ions with BDD electrode critically depend on the use of specific supporting electrolyte and its concentration, and are not suitable for on-site detection of copper ions produced within the localized marine corrosion microenvironments.

This paper studies the feasibility of using BDD electrodes for corrosion monitoring of copper alloys. To our knowledge, the electrochemical behaviour of copper ions in chloride background electrolyte has not been fully understood on boron-doped

Table 1

Most commonly used electrochemical techniques for metallic structure corrosion monitoring [24].

Electrochemical techniques	Advantages	Limitations
Polarization resistance methods (PR)	Simple, rapid (typically within a few minutes), nearly non-destructive, good sensitivity to low corrosion rates	Only valid for general corrosion; Affected by solution resistance, scan rate and the presence of redox species
Electrochemical noise methods (EN)	Similar to PR methods; ability to indicate the type of corrosion	Data processing and interpretation complicated; Limited reliability.
Zero resistance ammetry (ZRA) and galvanic sensors	Better than PR or EN for fast localized corrosion processes in low resistance electrolyte	Accuracy influenced by time frame of corrosion, electrolyte nature and crevice geometry.
Coupled multielectrode array sensor systems (CMAS)	Ability to study localized corrosion and to quantify pitting and crevice corrosion.	High cost; Big data; Often underestimation of actual corrosion rate.

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