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Boron doped nanocrystalline diamond microelectrodes for the detection of Zn^{2+} and dissolved O_2

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ABSTRACT

Boron-doped nanocrystalline diamond (B-NCD) films were grown by the hot filament chemical vapor deposition (HFCVD) technique on top of sharp electropolished tungsten substrates, in order to create amperometric microelectrodes (MEs) for detection of Zn^{2+}(aq) and dissolved O_2. The boron source was a B_2O_3 + ethanol mixture dragged by Argon gas through a bubbler. Different B_2O_3 concentrations were used to study the doping effect on the electrochemical behavior. The B-NCD MEs exhibited a working potential window of about 3.5 V in 5 mM NaCl, with low background current and good chemical inertness. The best electrochemical kinetics was achieved for the ME with highest boron doping content. The linear relationship between zinc concentration and zinc reduction current was found in a wide concentration interval from 10^{-5} M to 10^{-2} M of $ZnCl_2$ in a 5 mM NaCl background. Measurements with a Fe–Zn galvanic couple immersed in 5 mM NaCl demonstrate potential applicability of the B-NCD ME for use in localized corrosion studies.

1. Introduction

Apart from its outstanding mechanical and thermal properties [1], CVD diamond has been object of intense study for the last two decades due to its promising electrical properties, when doped by other elements, particularly boron [2–4]. Therefore diamond was studied for electrochemical purposes [5] taking into account its superior chemical stability. Boron-doped CVD diamond was reported to exhibit a potential window of water stability wider than any other solid electrode material. A very low background current and extreme chemical inertness and resistance to fouling due to the non-polar H terminated surface can also be counted as important advantages [6–8]. The promising results have encouraged high interest on diamond to be applied for microelectrodes as well [9]. As a result of electrode miniaturization to a critical dimension of <25 μm [10], which enables working with enhanced mass transport and steady state currents, as well as measurements in high resistivity media, CVD diamond microelectrodes (MEs) became an increasing matter of research, mainly in the biological field.

A variety of microstructures ranging from microcrystalline to nanocrystalline diamond can be obtained by synthesis in metastable conditions, which is the case of CVD methods such as the hot filament assisted CVD (HFCVD). Nanocrystalline diamond is the most interesting for MEs because of its grain size allowing maximum miniaturization of the electrode [11]. Although there are many bio-related publications with diamond electrodes [12–17] and some works concerning the detection of trace metals and use of B-doped diamond electrodes in SECM [18–20], to our knowledge there are no published works applying B-doped diamond MEs to the corrosion field, where they can also play an important role.

Our main interest in this work was focused on optimization of the electrochemical properties of boron-doped nanocrystalline diamond (B-NCD) films to be used in amperometric MEs for corrosion studies. An example of such measurement is the distribution mapping of electrochemically active species generated or consumed in confined areas on corroding metal surface. Such experiments are of prime importance for understanding mechanisms and kinetics of corrosion and self-healing processes in the local defects of active coatings [21,22]. Particular interest is in the case of metal cations that are reduced at potential range where the reduction of water and dissolved oxygen can mask their amperometric detection. This is a limiting condition for most electrode materials currently in use but it may be an opportunity for B-NCD based MEs. One of the most corrosion relevant cases is determination of local concentration of zinc cations in the electrolytes near corroding surface of galvanized steel. Zinc has widespread applications of great importance such as galvanic coatings on steel, as anodes for common batteries or in brass metallurgy. It is also relevant in the metabolism of plants, animals and microorganisms [23–25].

The quantification of zinc is therefore a significant matter for many different areas, but the means available are limited mostly to spectroscopic and electrochemical stripping techniques [26–28].

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Recently, Strasunske et al. [29] obtained good results by using silver amalgam electrodes (3 mm in diameter) to analyze river water by differential pulse anodic stripping voltammetry. Tada et al. has reported the voltammetric detection of Zn^{2+} by using a small zinc disk electrode to probe the corrosion of Zn/steel couple, but within a narrow concentration range and with millimetric, not micrometric, resolution [30]. Attempts also have been made for localized potentiometric detection of Zn^{2+} with ion-selective microelectrodes but the electrodes still present low sensitivity, low selectivity, short lifetime and complex fabrication [31,32]. In terms of the use of B-NCD electrodes, the group of Swain has reported satisfactory results using B-NCD electrodes for the detection of Zn^{2+} and other heavy metals by anodic stripping voltammetry, although large metal deposits and electrode fouling were a problem [33,34]. However, the size of the electrode again does not allow the spatial mapping in the micrometric range.

In the present work, we report the fabrication of B-NCD microelectrodes and their use as probes for Zn^{2+} and oxygen detection by performing cyclic voltammetry (CV) and microamperometry measurements at fixed potential in zinc chloride solutions and in a model Zn–Fe galvanic corrosion system.

2. Experimental

2.1. Microelectrode fabrication

2.1.1. Substrate preparation

Electroposharpened tungsten wires (99.9%+, 125 μm, Goodfellow, England) were used as a body of electrode. The sharpening of the wires was performed via electropolishing in a custom-made dynamic flow system, using a 3 M NaOH solution. Each filament was connected as a working electrode (anode) in the electropolishing system and was sharpened by applying a potential difference of 10 V between the working and the counter electrode during 50 s while keeping the solution flowing. The tips were sharpened down to radii of <100 nm and ultrasonically cleaned with distilled water. Afterwards they were ultrasonically seeded during 10 min in a suspension of nanodiamond powder (~6 nm, 98+%, ABCR, Germany) in distilled water and ultrasonically cleaned during 15 min in ethanol to remove the rest of powder.

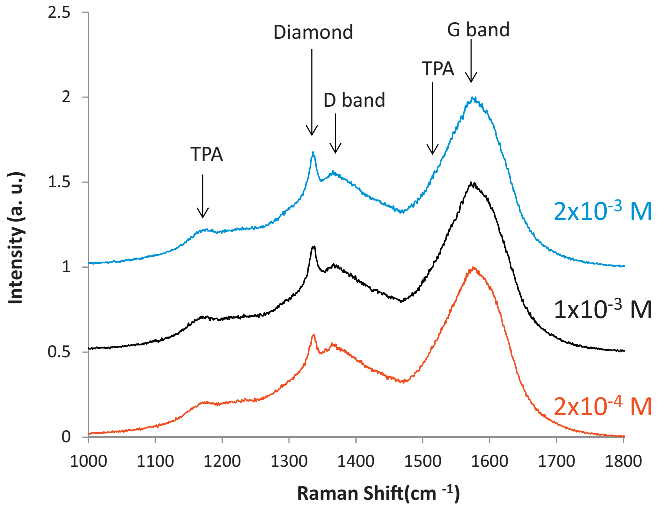

Fig. 1. Raman spectra (325 nm wavelength) of the B-NCD films grown with different B_2O_3 concentrations of 2×10^{-4}, 1×10^{-3} and 2×10^{-3} M. There are five main features: at 1140 and 1470 cm^{-1}, assigned to transpolyacetylene (TPA) in the grain boundaries; at 1333 cm^{-1}, indicating the presence of diamond crystals; at 1340 cm^{-1} and 1540 cm^{-1}, assigned to the D and G bands of graphite, respectively.

2.1.2. Diamond film growth

The diamond films were grown by HFCVD with four tungsten filaments at a temperature of 2300 °C that worked as gas activators and substrate heating sources. The sharpened tungsten tips were positioned horizontally on a substrate holder below the filaments at a distance of 7 mm. B-NCD films were grown during 30 min. The substrate temperature and the total gas pressure were kept constant at 770 °C and 180 mbar, respectively. The gas phase was composed by hydrogen and methane with a 0.07 CH_4/H_2 ratio with addition of the boron doping mixture. The boron source for doping the films was a solution of boron oxide (B_2O_3, 99.6%, ABCR) dissolved in ethanol inside a gas washing bottle. This boron-containing solution was dragged by argon gas into the CVD reaction chamber, with a constant $(Ar+B)/H_2$ ratio of 0.03. Solutions with three different B_2O_3 concentrations of 2×10^{-4}, 1×10^{-3} and 2×10^{-3} M were tested for the S1, S2 and S3 microelectrodes, respectively. The microstructure of the grown films was evaluated by scanning electron microscopy (Hitachi SU-4100). UV μ-Raman spectroscopy (HORIBA JOBIN YVON HR800UV), using the line 325 nm from a He–Cd laser (KIMMON IK series) for surface excitation, allowed the identification of the different carbon sp^2/sp^3 phases incorporated in the coatings and the presence of residual stresses.

2.1.3. Electroactive area delimitation

The B-NCD covered tungsten wires were partially insulated with acid resistant varnish (Lacomit, AGAR) with the aid of a micrometric manipulator under a microscope in order to limit the electroactive area just at the apex.

2.2. Electrochemical measurements

2.2.1. Electrode characterization

The electrochemical response of the B-NCD MEs was tested by cyclic voltammetry with a AUTOLAB PGSTAT302N potentiostat/galvanostat (Eco Chemie, The Netherlands). The electrochemical cell was kept inside a Faraday cage, open to air, and consisted on the B-NCD ME as working electrode, a platinum counter-electrode and a saturated calomel electrode (SCE) as reference. All potentials in this paper are referred to SCE except for the line and 2D-map scans in corrosion testing, where a Ag/AgCl electrode was used as reference. The electron transfer kinetics was evaluated in 10 mM $Fe(CN)_6{}^{3-/4-}$ in 5 mM NaCl (all reagents were *pro analysis* grade from Riedel-deHäen). The B-NCD MEs were compared with platinum and gold microelectrodes (10 μm discs embedded in cylindrical glass with a conical tip of 200 μm in diameter) for the detection of Zn^{2+} in $ZnCl_2$ solutions ranging from 10^{-6} M to 10^{-2} M in 5 mM NaCl (pH = 2). All potentiodynamic measurements were performed with a scan rate of 100 mV s^{-1}.

2.2.2. Application to corrosion testing

A model system consisting of a Fe–Zn galvanic couple immersed in 5 mM NaCl solution was used in order to evaluate applicability of the B-NCD MEs for mapping the distribution of Zn^{2+} and O_2 near active corroding metallic surfaces. Microamperometry measurements were performed with an IPA2 amplifier (Applicable Electronics Inc., USA) in the voltammetric/amperometric mode, using a 2 electrode arrangement, with a Ag/AgCl electrode as counter and reference electrode. Linear or 2D scans were done using B-NCD ME at a distance of 100 μm from the surface. Lines and maps were recorded at a potential of −0.9 V (vs. Ag/AgCl) for detection of dissolved O_2 and −1.6 or −1.3 V (vs. Ag/AgCl) for detection of Zn^{2+}.