



Nickel-ion detection on a boron-doped diamond electrode in acidic media

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ABSTRACT

This work demonstrates the potential to assess Ni(II) concentration in neutral and acidic chloride environments on a boron-doped diamond electrode, without the introduction into the solution of an external chelating agent or markedly raising the pH. The nickel-ion quantification was achieved in solutions with pH values ranging from 8 to 4 using the electrochemical response associated with the Ni(II)/Ni(III) transition on a bare boron-doped diamond electrode. The associated electrochemical reaction was determined to be sensitive to the pH with a dependence relying on a proton stoichiometric number of 0.5 per mole of electrons. The detection protocol consisted of a reagentless electrodeposition of Ni in neutral or acidic solutions followed by oxidation to Ni(III) using differential pulse anodic voltammetry. This allowed the nickel-ion quantification with a limit of detection of 26.1 μM and a linearity over the concentration interval from 10 to 500 μM in a solution pH of 6.2. The regeneration of the pristine electrode surface was also achieved in the sample solution with an electropolishing treatment by holding the applied potential at +1.3 V vs. Ag/AgCl for 30–240 s, thus allowing a fast and efficient surface recovery.

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1. Introduction

Nickel-ion quantification has been carried out using a wide number of different analytical techniques, such as ion chromatography [1], absorption spectrometry [2], capillary electrophoresis [3] and electrochemical techniques [4–8]. Of these, electrochemical techniques offer sensitive, inexpensive and rapid ways of trace metal determination and the possibility of being used in miniaturised and portable ion detecting devices. The most common protocol for the electrochemical detection of nickel ions is based on adsorptive stripping voltammetry (AdSV), which relies on the formation of a Ni(II)-complex using a suitable chelating agent, which is initially adsorbed on the electrode surface and then stripped by scanning the electrode potential. The use of a chelating agent in these AdSV methods is indispensable since the redox system Ni(II)/Ni displays an irreversible electrochemical behaviour [7], therefore not employable for the actual metal ion detection. In addition to AdSV, nickel-ion detection has also been achieved using a cathodic stripping voltammetry (CSV), studying the redox couple Ni(III)/Ni(II) hydroxide to avoid the introduction of the essential chelating agent into the sample solution. In particular, the nickel-ion determination has been carried out on a bare glassy carbon electrode [5] and on a bare boron-doped diamond electrode (BDD) [6] initially depositing metallic nickel on the electrode surface in a strongly alkaline solution (pre-concentration

step), then oxidising it to Ni(III) hydroxide (transformation step) and finally reducing the electro-formed Ni(III) hydroxide to Ni(II) hydroxide by a sensitive voltammetry technique. However, due to the instability of the nickel hydroxides in acidic and neutral pH solutions [9], the procedure strictly required an alkaline environment, a 0.1 M NaOH/0.1 M NH_4NO_3 solution [5,6], for the transformation Ni(III)/Ni(II). The cleaning of the electrode surface immediately after the formation of the nickel hydroxide layer in alkaline environment has been reported to be a problem whenever the recovery of the initial electrode surface condition was required. Mechanical polishing [5], ultrasonic cleaning [5] and electrochemical cleaning in acidic solution (0.1 M H_2SO_4) [6] have been used to re-generate the electrode surface.

For the purpose of *in situ* corrosion monitoring, in particular crevice corrosion, the introduction of a chelating agent in the monitoring environments, as well as the change of the solution pH, are not feasible in most cases since this will significantly modify the operating system environments, possibly adversely affecting performance [10]. Indeed, it has been reported that when crevice corrosion process initiates the pH of the environment rapidly decreases to values typically ranging between 3 and 4 [11]. Therefore, the severe conditions generally employed for nickel-ion detection protocols, *i.e.*, alkaline environment [5,6] and presence of chelating agents [4,8], often do not adapt well within crevice corrosion solutions.

The aim of the present study is to develop an electrochemical methodology for nickel-ion detection that is suitable for systems which possess an acidic solution environment and where chelating agents cannot be introduced into the solution. The electrochemical

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detection of nickel ions has been performed on BDD electrode in a 0.6 M NaCl solution at different pH values, ranging from 8.0 to 3.0, in the concentration range of the metal ions likely to be present within the Cu–Ni based alloy crevice corrosion environment. The analytical protocol consisted of deposition of metallic nickel onto the bare BDD surface followed by the detection process, the latter performed by sweeping from cathodic to anodic potentials using differential pulse voltammetry. In addition, preliminary investigations were also carried out using electrochemical impedance spectroscopy and cyclic voltammetry to better understand the underlying electrochemical process of the metal-ion detection.

2. Experimental

2.1. Electrodes and electrochemical cell

Electrochemical measurements were carried out in a single compartment three-electrode cell with a platinum wire and a silver/silver chloride (Ag/AgCl) as counter and reference electrodes, respectively, using a Gamry REF600 potentiostat and Framework 5.61 software. The working electrode was a BDD electrode supplied by Diamond Detectors Ltd (UK) with an oxygen terminated surface (surface roughness less than 5 nm) and a nominal active surface area of 0.198 cm². The electrode was highly doped with a doping level of 10²⁰ boron atom cm⁻³. Prior to electrochemical testing, the BDD electrode was cleaned in 0.5 M sulphuric acid solution by cycling between -0.6 V and +1.4 V vs. Ag/AgCl until a reproducible electrode response was achieved. The electrode was then rinsed with deionised water and finally cleaned by cycling between -1.5 V and +1.3 V vs. Ag/AgCl in a 0.6 M NaCl solution to give a stable and reproducible response.

2.2. Chemicals

All the solutions were prepared with deionised water (≥ 18.2 M Ω cm, Millipore) using analytical grade chemicals. Either phosphate pH-buffered or 0.6 M NaCl (at different pHs) were used as support electrolytes for the electrochemical testing. The former solution was prepared using NaH₂PO₄ and Na₂HPO₄ (concentrations ranging from 0.2 M to 2.0 M) within the pH interval from 8 to 6; the buffer pH solutions were eventually adjusted to the desired pHs using either HCl or NaOH of 1.0 M solutions. Stock solutions, containing 0.1 and 0.01 M of Ni²⁺, Fe³⁺, Cu²⁺, Al³⁺, Ca²⁺, Mg²⁺, PO₄³⁻, SO₄²⁻ and NO₃⁻ were made daily and used to prepare standard solutions by diluting with a 0.6 M NaCl solution.

2.3. Electrochemical behaviour tests of nickel ions in the solution with different pH values

Preliminary tests, *i.e.*, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were carried out on the same BDD Ni-modified electrode at room temperature and without oxygen degassing of the solutions. The BDD Ni-modified electrode was obtained by: (i) electrodepositing metallic nickel on the electrode surface at -1.5 V vs. Ag/AgCl for 300 s in a 0.6 M NaCl + 3 mM Ni²⁺ stirred solution and (ii) oxidising the deposited metal at +0.7 V vs. Ag/AgCl for 200 s in alkaline solutions (NaOH), *i.e.*, pH 14.0, 13.5, 13.0, 12.5 and 12.0, where the ionic strength of all the tested solutions was maintained at 1.6 mol L⁻¹ by adding appropriate aliquots of 1.0 M NaClO₄. In between the electrodeposition process (i) and the oxidation procedure (ii), the electrolyte of 0.6 M NaCl + 3 mM Ni²⁺ was siphoned away and replaced with the NaOH alkaline solution at different pHs.

CV tests were performed in the chosen potential range at a scan rate of 10, 25, 50, 100 and 200 mV s⁻¹ and a step potential of 1 mV, whereas EIS measurements were performed by applying a potential

perturbation of ± 5 mV over a frequency range from 1 MHz to 1 mHz, with 10 frequency points per decade at OCP (+0.32 V vs. Ag/AgCl).

2.4. Analytical protocol for electrochemical detection of nickel ions

The protocol for Ni²⁺ detection was performed using either a phosphate-buffer solution or 0.6 M NaCl at different pH values (from pH 10.0 to pH 3.0), and differential pulse anodic voltammetry (DPAV). Prior to the DPAVs, a deposition process was carried out in a stirring Ni²⁺ containing solution by imposing a potential of -1.5 V vs. Ag/AgCl for 30 s. DPAV were performed at a scan rate of 10 mV s⁻¹ in the anodic sweep range of -1.1 V to +1.3 V vs. Ag/AgCl. A potential pulse size of 25 mV, a step potential of 2 mV, a pulse time of 0.1 s and an interval time of 0.2 s were chosen for the differential pulse technique. Throughout the above described protocol the electrode was not removed from the sample solution.

The electrode-regeneration treatments were carried out in the same electrolyte solution without adding any complexing agents or acids, by applying +1.3 V vs. Ag/AgCl for a duration which depended on the amount of nickel deposited on the electrode surface. Prior to performing each set of voltammetry experiments, a control test was carried out in the support electrolyte.

The validation of the electrochemical detection protocol was achieved using capillary electrophoresis analysis. The system employed was a Prince Technologies PrinCE-560 capillary electrophoresis instrument with a TraceDec contactless conductivity detector with a 100-cm-long fused silica capillary (93 cm effective length and a 50 μ m internal diameter). The CE analyses were made using a solution containing 10 mM of 2,6-pyridinedicarboxylic acid (PDCA), as a chelating-agent solution, at pH 4.

3. Results and discussion

3.1. Influence of the pH on Ni(II)/Ni(III) behaviour in chloride media

Prior to establishing the procedure for the nickel determination, studies on the Ni(II)/Ni(III) hydroxide behaviour were carried out in 0.6 M NaCl solutions (constant ionic strength of 1.6 M) at different pH values (14.0, 13.5, 13.0, 12.5 and 12.0) using CV and EIS, as described in Section 2.3, and DPAV in 0.6 M NaCl and phosphate-buffer solution in pH solutions ranging from 10.0 to 3.0.

Fig. 1 shows an overlay of cyclic voltammograms for the Ni(II)/Ni(III) hydroxide couple recorded in 0.6 M NaCl solution at different pH values. A deposition of nickel on the electrode was visually observed after the cathodic treatment distinguished by the presence of a thin grey metallic nickel layer on the black BDD surface. It is apparent that as the pH of the solution is increased both peaks of the redox couple shifted towards more cathodic potentials. The dependence of the peak potentials of the Ni(II)/Ni(III) hydroxide couple on the pH is clearly depicted in the inset of Fig. 1, which shows the excellent linear relationship between the anodic peak potential and the pH of the solutions investigated, with R², least square residual, of 0.995.

A slope of -65 mV per pH unit was estimated from the plot of the anodic peak potentials against the solution pH, which is approaching the thermodynamic value of -59 mV per pH unit for one-proton one-electron exchange reaction. The observed behaviour corroborated the involvement of one-proton one-electron process in the electrochemical response of Ni(II)/Ni(III) hydroxides couple. A greater peak potential shift of -88 mV per pH unit was reported for the Ni(II)/Ni(III) couple by Toghiani et al. [12] and attributed to possible potassium intercalation products, such as K₂O, within the hydroxide layer originated from the 1.0 M

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