

The interplay between hydrogen evolution reaction and nitrate reduction on boron-doped diamond in aqueous solution: the effect of alkali cations



A. Manzo-Robledo^{a,c}, C. Lévy-Clément^b, N. Alonso-Vante^{a,*}

^a IC2MP- UMR-CNRS 7285, University of Poitiers, 4 rue Michel Brunet, F-86022 Poitiers Cedex, France

^b Institut de Chimie et Matériaux de Paris-Est (ICMPE), CNRS-UMR 7182, 2-8 rue Henri Dunant, 94320 Thiais Cedex, France

^c Escuela Superior de Ingeniería Química e Industrias Extractivas (ESIQIE), Instituto Politécnico Nacional (IPN), 07738 México D.F., Mexico

ARTICLE INFO

Article history:

Received 23 August 2013

Received in revised form

27 November 2013

Accepted 28 November 2013

Available online 11 December 2013

Keywords:

Boron-doped diamond

HER

nitrate reduction

DEMS

cation effect.

ABSTRACT

The nitrate ion reduction was studied on boron-doped diamond (BDD) electrodes by real-time on-line differential electrochemical mass spectrometry (DEMS) coupled with chronoamperometry in K^+ , Na^+ cation-containing electrolyte solutions. It was found, via steady state voltammetry, that the hydrogen evolution reaction (HER) was affected by the presence of K^+ or Na^+ . A moderate HER occurs in K^+ -containing electrolyte solution favoring the reaction between NO_3^- and H_2 species, whereas in Na^+ -containing electrolyte solutions, the HER kinetics was more important leading to a suppression of molecular nitrogen generation. The use of isotope-labeled nitrogen and DEMS confirmed the influence of alkali cations toward the nitrate ion reduction.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The large use of nitrogen-based compounds in agriculture [1,2] and biological applications [3] has increased considerably the amount of nitrate ions in ground and surface waters. Depending on its concentration, nitrate ions may promote detrimental effects on human health and environment [4]. As a result, the interest for the detection of these ions using various analytical techniques, namely, cyclic voltammetry [5] ring-disk electrodes [6–8] or voltammetry in combination with HPLC [9] has been reported. Diamond electrodes have been studied with the aim of developing highly efficient electrochemical processes for water disinfection for domestic water treatment purposes [10] or industrial water-cooling systems. Synthetic boron-doped diamond (BDD), with its high anodic stability and wide potential window for water discharge has undoubtedly proved to be an excellent material for the complete combustion of organics in wastewater treatment and water disinfection [10,11].

The doping with boron plays an important role in the BDD electrode electrochemical efficiency. Ndao et al. [12] investigated the influence of boron concentration in diamond films and observed that only metallic conductive (highly boron-doped) diamond films

are efficient for nitrate reduction. Lévy-Clément et al. [12,13] also evaluated the behavior of several metallic conductive diamond electrodes grown at different laboratories and studied the influence of the growth techniques and boron doping on the nitrate reduction-mechanism in concentrated solutions [5].

In order to introduce a well defined and interesting alternative to eliminate nitrate ions, BDD electrodes are used in this paper to study the nitrate reduction in K^+ and Na^+ -containing electrolyte solutions via coupling some pertinent electrochemical techniques with DEMS to illustrate the complexity of such multi-electron charge transfer reaction. Such combination puts in light the influence of the effect of alkali cations (K^+ and Na^+) during the electro-reduction process.

2. Experimental

2.1. Electrode preparation

Polycrystalline highly boron-doped diamond films (BDD) were grown by HFCVD (Hot Filament Chemical Vapour Deposition) by CSEM, Neuchâtel (Switzerland) on (100)-oriented p^+ -type silicon substrates. The preparation was described in ref. [12]. BDD films had an equivalent of 6000 ppm B (5×10^{20} atoms cm^{-3}) with a resistivity of $\rho = 0.6 \Omega cm$, a grain size of $0.4 \mu m$ and thickness of $1 \mu m$. Prior to any electrochemical measurements, the diamond

* Corresponding author.

E-mail address: nicolas.alonso.vante@univ-poitiers.fr (N. Alonso-Vante).

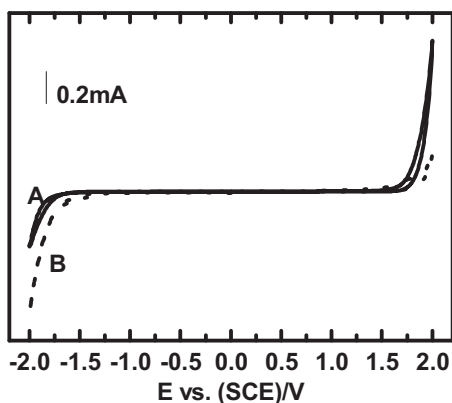


Fig. 1. Current-potential voltammograms on BDD electrode in (A) KCl 1.0 M and (B) NaCl 1.0 M solutions. Scan rate was 100 mV/s.

electrodes (typically having a 0.012 or 0.018 cm² surface) were cleaned first in acetone for 10 min in an ultrasonic bath, rinsed with Milli-Q water and then in aqua regia for 15 min at 70 °C, and rinsed twice with Milli-Q water in an ultrasonic bath for 20 min. Ohmic contact to a carbon rod was made with an In-Ga amalgam and Ag epoxy (Loctite 388). Isolation of the back contact was done with an epoxy (Loctite 3430).

2.2. Electrochemical measurements and DEMS experiments

The electrochemical measurements were performed with a potentiostat-galvanostat (Autolab 30-2) in a three-electrode standard electrochemical cell where a carbon plate and Saturated Calomel (SCE) were used as counter and reference electrodes, respectively. For DEMS experiments, a home-made electrochemical cell made of Teka-Peek was used. A gold wire served as a counter-electrode; the scheme of the DEMS setup and further experimental details can be found in reference [14]. Current-potential characteristics recorded in both systems were similar. The electrochemical techniques employed were cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry. Briefly, the electrochemical cell was connected to the chamber containing the quadrupole mass spectrometer (MS) with a Channeltron detector (Prisma QMS200, Balzers) through a pneumatic valve, which allows the isolation of the ion source from the electrochemical cell forming a small pre-chamber. A rotary vane pump evacuates the latter, whereas the vacuum in the chamber containing the MS is obtained from a turbo molecular pump (the working pressure was ca. 8×10^{-6} mbar). The amount of species reaching the MS, throughout a porous membrane (Scimat, 60 μ m thick, 0.2 μ m pore diameter, and 50% porosity) can be controlled with the dosing valve located between the electrochemical cell and the pre-chamber. Mass spectrometric profiles (ionic current (I_i) versus potential (E)) and faradic current (I_F) versus potential (E) for selected mass to charge ratios (m/z) were recorded simultaneously. Solutions of KCl (99.5%) + KNO₃ (98%) and/or NaCl (99%) + NaNO₃ (99%) from Acros Organics, and Na¹⁵NO₃ (98%) or K¹⁵NO₃ (98%) from Aldrich were used as supporting electrolyte at different concentrations, without further purification and prepared with Millipore-Q water. All solutions were purged with argon gas prior to any experiment.

3. Results and discussion

3.1. Current-potential behavior

The cyclic voltammograms (CV) in 1 M KCl and 1 M NaCl on BDD electrode is depicted in Fig. 1. The material shows the typical

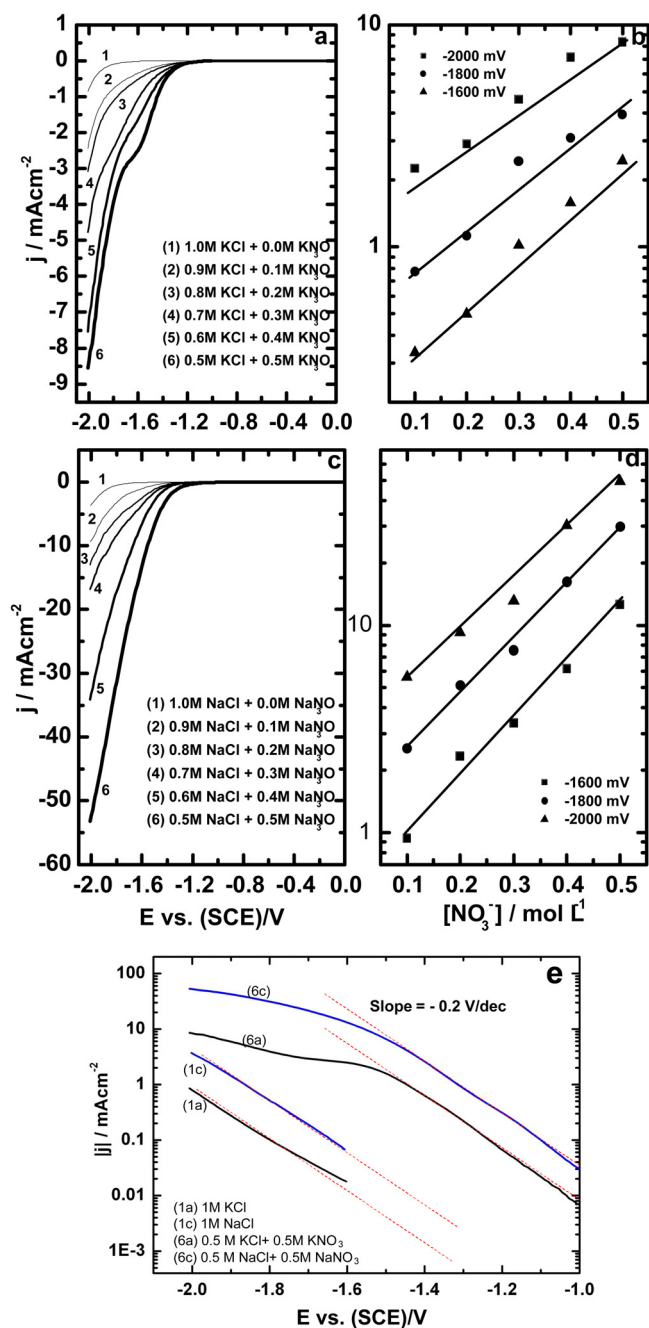


Fig. 2. (a, c) Current density-potential characteristics at a scan rate of 1.0 mV/s, and (b, d) current density-nitrate ion concentration, for K⁺- and Na⁺-containing electrolytes. (e) Tafel plot of curves 1 and 6 of Fig. 2a, and 2c. In Fig. 2b and 2d the current density is in the Log scale.

current-potential profiles where the oxidation and reduction process of water occurs at a high overpotential in agreement with the literature data [12,13]. A closer look at the anodic and cathodic faradic current reveals that their magnitudes are different. The hydrogen evolution reaction (HER) is more important in NaCl-containing electrolyte, whereas the oxygen evolution reaction (OER) is higher in KCl-containing electrolyte. This interfacial phenomenon is apparently dependent on the nature of the cation since it plays a role in the generation of nitrates species, see below.

3.2. HER Kinetics

The kinetics of the hydrogen evolution reaction was investigated as a function of nitrate ions concentration [NO₃⁻] using a

Download English Version:

<https://daneshyari.com/en/article/186744>

Download Persian Version:

<https://daneshyari.com/article/186744>

[Daneshyari.com](https://daneshyari.com)