

Mechanism of electrochemical reduction of nitrate at boron-doped diamond electrodes.

C. Lévy-Clément¹, A. Manzo-Robledo², A. Katty¹, A. Deneuille³, A. Fujishima⁴, N. Alonso-Vante²

1. LCMTR, CNRS, 2/8 rue Henri Dunant, 94320 Thiais, France

2. Laboratory of Electrocatalysis, Université de Poitiers, 40 Ave du Recteur Pineau, F-86022 Poitiers, France

3. LEPES, CNRS, BP 166, 38042 Grenoble, France

4. University of Tokyo, Tokyo, Japan

Due to the large overpotential towards hydrogen reduction, boron-doped diamond (BDD) films are very efficient electrodes for the reduction of nitrate ions [1] which cannot be efficiently done at metallic electrodes. The electrochemical reduction of nitrate is a multielectronic charge transfer and various nitrogenous species can be formed. Development of a clean electrochemical process for the remediation of nitrate ions from waste water and transformation into nitrogen gas is an important challenge for environmental science. The aim of this paper is to study the mechanism of nitrate reduction at diamond electrodes, in order to find the parameters which might play a role in the selectivity of the generated nitrogenous species.

Boron-doped diamond electrodes with metallic conductivity ($[B] > 10^{21} \text{ cm}^{-3}$) made by MPCVD (microwave plasma enhanced chemical vapor decomposition) were used. Electrolysis performed in 1 M KNO_3 solution and analytical studies showed that the potential applied to the diamond electrode plays a major role on the efficiency of the nitrate reduction and nature and amount of species formed. The quantitative analysis of various dissolved species (NO_2^- , N_2H_4 , NH_4^+) formed upon the reduction of nitrate ions was done by spectrophotometric analysis. The amount of gas formed was deduced from the total nitrogen concentration in solution measured before and after electrolysis. The NO_3^- ions are mainly reduced to gaseous products when the electrode is polarized between -1.5 and -1.7 V/SCE. At potentials more negative than -1.7 V/SCE, gaseous species and (NO_2^-) nitrite ions are formed in equal parts [1].

The composition of the gas was determined by DEMS (in-situ electrochemical mass spectroscopy), coupling the voltammetric and mass spectroscopy techniques. A conventional three-electrode arrangement with a platinum wire as counter electrode and SCE as a reference electrode was used at room temperature in 1M NaNO_3 . The electrochemical cell was connected to the chamber containing the quadrupole mass spectrometer (MS) with a Channeltron detector (Prisma QMS 200, Balzers) through a pneumatic valve, which allows the isolation of the ion source from the electrochemical cell forming a small pre-chamber. The latter is evacuated by a rotary vane pump, whereas the vacuum in the chamber containing the MS is produced by a turbomolecular pump. The amount of species reaching the MS can be controlled with the dosing valve located between the electrochemical cell and the pre-chamber. The interface between the cell and the vacuum consists of a porous Teflon membrane (Scimat, 60 μm thick, 0.2 μm pore diameter, 50 % porosity).

The current-potential characteristic of the BDD electrode is shown in Fig. 1 together with the simultaneously recorded mass signals (m/z) of nitrogen species (N_2 , H_2 , NO_2 , NO , NH_3 , and N_2O) at a scanning rate of 5mV/s. From the figure it is seen that all faradic processes begin at the current onset potential. N_2 is the desired product. However, under our working conditions (NaNO_3 medium, pH) other nitrogen species in particular NH_3 are also formed, thus reducing the selectivity. These latter species may

be favored via a strongly adsorbed intermediate species (NO), as discussed recently [2].

Acknowledgments. This work was partially funded by a NEDO International Joint Research Grant 01MB9. AMR acknowledges financial support from Conacyt (Mexico)-Sfere (France).

References

- [1] C. Lévy-Clément, N.A. Ndao, A. Katty, M. Bernard, A. Deneuille, C. Comninellis, A. Fujishima, *Diamond Relat. Mater.* In print
- [2] A.C.A. Vooys, R.A. van Santen, J.A.R. van Veen, *J. Mol. Cat. A: Chem* 154 (2000) 203).

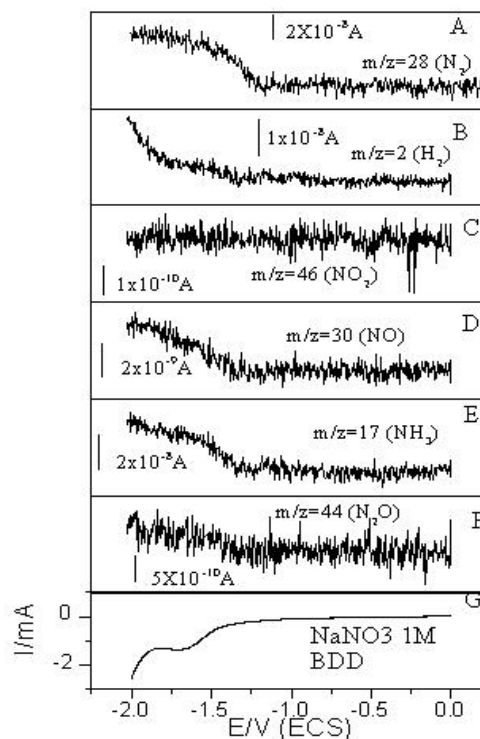


Fig. 1 Current- and mass (nitrate species)-potential characteristics at RT of a diamond electrode in 1M NaNO_3 solution (pH 7). Scan rate 5mV/s. Electrolyte flow is 8.4 $\mu\text{L/s}$, in order to keep, within the limits of the experimental error, a constant pH at the electrode/electrolyte interface.