

## Nitrate reduction mechanism at boron-doped diamond electrodes using voltammetry, spectrophotometry and DEMS. Influence of the cation

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One of the most efficient and promising applications of boron-doped diamond (BDD) electrodes is their use for the electroreduction of compounds that are difficult to reduce. This is the case of nitrates, which in the environment represent a health risk. Previously we have shown that reduction of nitrate occurs very efficiently at heavily boron doped diamond electrode ( $[B] < 10^{21} \text{ cm}^{-3}$ ), thanks to the large electrochemical window [1]. The electrochemical reduction of nitrate is a multielectronic charge transfer process and the reactional mechanism is very complex. A large variety of nitrated compounds can be formed such as  $\text{NO}_2^-$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{NH}_2\text{OH}$ ,  $\text{N}_2\text{H}_4$  and  $\text{NH}_4^+$  ( $\text{NH}_3$ ) which are dissolved in the solution or are volatile compounds. The reduction potential and the nature of the products of nitrate reduction strongly depend on experimental conditions such as pH, applied potential, and coexisting ions. Also the quality of the current-potential curves is highly dependent on the electrode surface state. The selective formation of electrochemically generated nitrated species, especially not harmless product such as nitrogen gas, is a challenge for material and environmental science.

In the present work we have studied the influence of the chemical nature of the cation, ( $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{H}^+$ ) on the reactional mechanism at BDD electrodes, using cyclic voltammetry and analyzing the dissolved and volatile species using spectrophotometry and mass spectroscopy coupled with electrochemistry (DEMS).

B-doped diamond electrodes with  $[B] > 10^{21} \text{ cm}^{-3}$  synthesized by microwave plasma assisted chemical vapor deposition (MPCVD) or hot filament (HFCVD) were indifferently used. Prior to electrochemical measurements, the diamond electrodes were cleaned in aqua regia at 70 °C for 15 min and rinsed twice in 18 M $\Omega$  cm ultrapure boiling water in ultra sonic bath for 15 min. The solutions were deoxygenated with a vigorous purge of Argon during 10-15 min prior to the experiments and stirred and bubbled too during the voltammetry and electrolysis experiments. Electrolytic solutions were prepared with chemical pure products in ultrapure water. Electrolysis in nitrate solutions (1M  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{HNO}_3$ ) was performed under potentiostatic condition in a two-compartment electrochemical cell (all potentials are quoted versus SCE). An especially designed electrochemical cell was used for the DEMS experiments. Mass spectrometry cyclic voltammograms were recorded simultaneously with cyclic voltammograms. In this way gaseous and volatile species formed or consumed during electrochemical process were determined on line.

The various Tafel slopes ( $2.3 \text{ RT}/\alpha n_e F$ ) for the electrochemical reduction of nitrates in  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{HNO}_3$  were analyzed as well as those for water reduction in KCl and HCl, for comparison. A linear Tafel slope around 200 mV/dec is observed between -1.5 and -2 V and -1.35 and -2 V in KCl and HCl, respectively

where hydrogen evolution takes place. The slope corresponds to the hydrogen adsorption-evolution reaction. In the presence of nitrate, two linear regions with negative slopes are observed on the  $\log i$  vs.  $E$  curves. The Tafel slope in region I is around 140 mV/dec (between -1.5 and -1.7 V in neutral solutions and between -1 to -1.25 V in acidic solution) and in region II the slope increases ca. 440 to 667 mV/dec. The values of the charge transfer coefficients,  $\alpha$ , corresponding to the two slopes (taking  $n = 1$ ) are low about 0.25 and 0.1, suggesting that nitrate reduction on the diamond is a surface sensitive process. Therefore, the modification of the Tafel slopes might be an indication of a change in the reactional mechanism of nitrate (as indicated below by the formation of nitrites in  $\text{KNO}_3$  and  $\text{NaNO}_3$  and ammonium in  $\text{HNO}_3$  when the electrolysis is performed at potentials more negative than -1.7 V). The change in the reactional mechanism may be also due to the competition between adsorption of hydrogen during the reduction of water and adsorption of nitrated species on the diamond surface.

The reduction of nitrate after electrolysis at BDD electrodes in 1M  $\text{KNO}_3$  and  $\text{NaNO}_3$  solutions during 16 hours is equal to 10 % and nitrated gaseous species are formed in majority when the potential applied to the BDD electrodes varies between -1.5 and -1.7 V. At more negative potentials, in addition to the gaseous products, nitrites are formed in equal parts while 50 % of the nitrates are reduced and water starts to be reduced with formation of  $\text{H}_2$ . Nitrate reduction is more efficient when the surface of the diamond is oxidized after boiling in aqua regia. XPS analysis showed that the surface of the diamond, after boiling in aqua regia and after nitrate electrolysis, is covered by an oxide [2], which may favor the adsorption and subsequent reduction of the nitrate ions.

In  $\text{HNO}_3$  solutions, up to 60 % of the nitrates are reduced and nitrated gaseous species are formed in majority when the applied potential varies between -1.5 and -1.7 V. At more negative potential, the nitrate reduction increases slightly but in addition to gaseous products, ammonium ions are formed.

In all cases, the nitrate reduction process is not inhibited at BDD electrodes when water decomposition occurs concomitantly, which is not the case at the platinum electrode [2].

$\text{N}_2\text{O}$  formation was observed by DEMS at polarization more negative than -1.7 V. The Tafel slope of the ion current due to  $\text{N}_2\text{O}$  production is 10 times larger in  $\text{KNO}_3$  than in  $\text{NaNO}_3$ , showing that  $\text{N}_2\text{O}$  formation is favored in presence of the  $\text{Na}^+$  cation. The production of  $\text{N}_2$  expected to be favored by the formation of  $\text{N}_2\text{O}$  should be larger in presence of  $\text{Na}^+$ . It was observed that in fact  $\text{N}_2$  formation strongly depends on the history of the electrode.

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### References

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