

Nitrate reduction on hydrogenated nitrogen carbon films.
Cations effect.

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Reducing the amount of nitrates in the environment is a major issue because of the health risks. Therefore, many methods have been proposed to reach this goal : among them, ion-exchange or biofiltration [1], the direct reduction with H₂ using a catalyst (palladium/copper electrodes) [2], have been envisaged with specific merits or drawbacks. More recently, the Boron-doped diamond (BDD) films and more generally the diamond-like-carbon (DLC) materials have emerged as promising new electrode materials in Electrochemistry in view of their wide available potential window in aqueous solvents [3].

It has been shown in particular that nitrates can be reduced with a significant yield on BDD [4] and that the reduction rate depends on the Boron doping level [5].

We recently elaborated nitrogen-incorporated hydrogenated amorphous carbon films [6] with similar performances with respect to both potential window in water and electrochemical reactivity towards outer sphere redox reactions. It was therefore reasonable to expect the same improvements with respect to nitrate reductions as those already shown with BDD, considering in addition that the presence of nitrogen as dopant in the film could play a specific role in this mechanism.

The deposition conditions have been detailed in [6]. Films, 60 nm thick, were grown on n-type highly doped (100) Si. It was then shown that electrochemical reactivity and electronic resistivity vary in opposite directions for N atomic ratios between *ca* 5 and 30%. For these measurements, a mid doping level of 15% was chosen.

The curves in Figure 1 have been plotted at different rotation speeds (the electrode was mounted as a RDE) for a 0.5 M KNO₃ solution. The nitrate reduction starts at -1.2 V/SCE but it can be noticed that these currents are extremely low regarding the nitrate concentration, though a Levich-like behavior can be observed. A first assumption was drawn about the possible influence of co-adsorption of Hydrogen and cation (here K⁺) in the cathodic range.

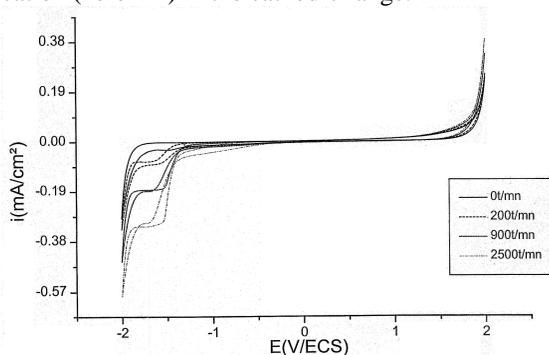


Figure 1 : Current-potential curves on nitrogen hydrogenated amorphous carbon film grown on Silicon (N%=15) mounted as a RDE. KNO₃ (0.5 M) solution. Different rotation speeds are indicated in the insert.

To specifically emphasize the cation effect, a nitrate with a larger size cation was chosen, Nbu₄NO₃. Much higher currents were then obtained so that it was possible to decrease the nitrate concentration. The current potential curves displayed in Figure 2 correspond to a 10⁻³ M nitrate solution where the mass transfer dependence is still observed

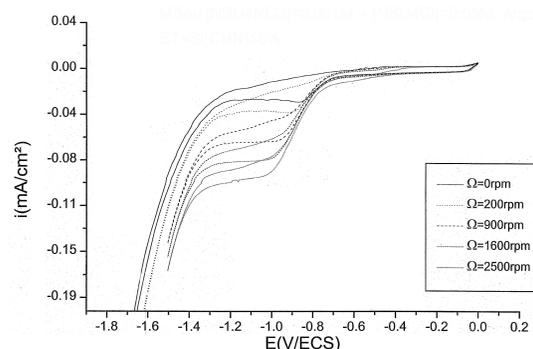


Figure 2 : Figure 1 : Current-potential curves on nitrogen hydrogenated amorphous carbon film grown on Silicon (N%=15) mounted as a RDE. Nbu₄NO₃ (0.001 M), Nbu₄Cl (0.1 M) solution. Different rotation speeds are indicated in the insert.

Sodium nitrate was also further investigated with results very close to those found for potassium nitrate.

These different behaviors confirm the above assumption of a competitive adsorption between hydrogen and the cation and should be taken into account in selecting a mechanism [7].

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