

Amorphous carbon nitrides $a\text{-CN}_x$ as substitutes to BDD: Electron transfer and surface reactivity

P. Tamiasso-Martinhon, H. Cachet, C. Debiemme-Chouvy, C. Deslouis*

Université Pierre et Marie Curie-Paris 6, Laboratoire Interfaces et Systèmes Electrochimiques;
CNRS, UPR15-LISE, 4 Place Jussieu, Paris, F-75252 cédex, France

*Corresponding author. E.mail : claude.deslouis@upmc.fr

•
Thin films of amorphous carbon nitrides $a\text{-CN}_x$ presents strong similarities with boron doped diamond (BDD), with respect to their wide potential window in aqueous media and good electrochemical reactivity towards outer sphere redox reactions. This work was aimed at characterizing more specifically the surface reactivity by use of a redox probe and in particular at showing that their electrochemical reactivity is sensitive to the surface state as their BDD analogues. $a\text{-CN}_x$ materials have been elaborated by cathodic sputtering of a graphite target in an Ar-N_2 active plasma for varying nitrogen contents, determined by XPS ($0.06 \leq x \leq 0.39$). The EIS method was used either in solutions containing only supporting electrolyte Na_2SO_4 0.5 M, or in KCl 0.5 M solutions containing ferri-ferrocyanide species (10^{-2} M). In the latter case, charge transfer was studied as function of different potential excursions. The charge transfer resistance R_{ct} was shown to depend strongly on this protocol:

-When the potential was moved from positive values (after some hold time at that value) to negative ones, R_{ct} displayed a marked maximum around the rest potential. Conversely, when the potential was moved from the negative to the positive side, R_{ct} was nearly unchanged or showed a slight decreased around the rest potential. It was concluded that cathodic electrochemical pretreatment increases the reactivity of those material in a similar way as most of the results found for BDD materials.

In the case of blocking electrode conditions, the interfacial capacitance was found to depend on the nitrogen content in the film, on the electrode potential and on pH. The capacitance showed in all cases a more or less marked maximum. Its value was higher in the acidic pH range and also for N% contents around 30% in the sputtering gas. This maximum disappeared both at low or high ($\sim 40\%$) nitrogen contents. The maximum was shifted towards cathodic potentials with the pH increase in a non-Nernstian way. This effect could be simulated by considering the film surface as formed of imines and amines both presumably acting as Brönsted bases and therefore showing a surface charge depending both on pH and potential.

Acknowledgements: USP-COFECUB.