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## Modification of Carbon Electrode with Pyridine

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The modification of surface by reduction of diazonium salts attracted a lot of interest in the past decade. This method, easy and rapid, is very attractive because several molecules can be used to form a covalent attachment between aryl groups bearing a desired functionality and different substrates.

The procedure developed by Pinson et al.<sup>1</sup> is the following. An aromatic amine is transformed into a diazonium by a standard diazotization procedure. A solution containing the diazonium salt is used to modify electrode by electrochemical reduction. In fact, from an aryl diazonium, it is possible to generate the corresponding radical at the electrode surface and create a covalent bound according to Scheme 1.

Pyridine is a simple heterocyclic organic compound. The nitrogen atom on pyridine features a basic lone pair of electrons not delocalized. Pyridine is a weak base which nucleus is aromatic. The pKa of the conjugate acid is 5.25.

To investigate the behaviour of the immobilized pyridine group, glassy carbon was used as substrate. Cost, versatility and low electrical resistance of glassy carbon are properties which make it a useful electrode for electrochemistry. This material is well known, well characterized and its modification by reduction of in-situ generated diazonium salt is convenient<sup>2</sup>. That is why it will be our substrate for this study.

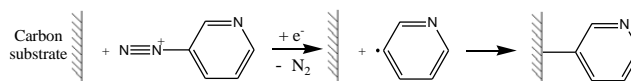
A covalent bond between glassy carbon and pyridine could be obtained from an aryl diazonium by electroreduction of its diazonium salt<sup>3</sup>. A first advantage is that pyridine molecule is at the electrode surface and that could facilitate interfacial electron transfer.

In this work, a covalent bond between glassy carbon and pyridine was obtained in two steps at ambient temperature in aqueous media. Firstly, the diazonium cations were synthesized in the electrochemical cell by reaction of 3-aminopyridine with NaNO<sub>2</sub> in aqueous HCl. Secondly, glassy carbon electrodes were modified by electrochemical reduction of the *in situ* generated 3-aminopyridinium cations under several conditions. The effects of the glassy carbon electrode modification conditions like diazonium concentration and diazotization reaction time, grafting time and potential of potentiostatic reduction were investigated.

The resulting modified electrodes were characterized by cyclic voltammetry experiments, carried out in a 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> aqueous solution. This method has been used to confirm and to determine the barrier properties of the deposited layers as well to estimate the pKa of the immobilized pyridine. X-ray photoelectron spectroscopy (XPS) was used to evaluate the atomic concentrations of the species present at the glassy carbon electrode surface. Additional techniques will be used to determine the thickness and the morphology of the grafted layer.

Cyclic voltammetry experiments showed that the blocking effect of the grafted layer increases as the applied potential is made more negative and as well with an increase of the reduction time. It is possible to obtain a relative control of the layer thickness by changing the applied potential and the grafting time.

The evolution of the peak current as a function of the solution pH for the electrochemically modified electrodes in the solution containing Fe(CN)<sub>6</sub><sup>3-/4-</sup> as redox probes was investigated. Analyses revealed that the apparent pKa of the immobilized pyridine could be estimated at 5.3.



Scheme 1: Grafting reaction.

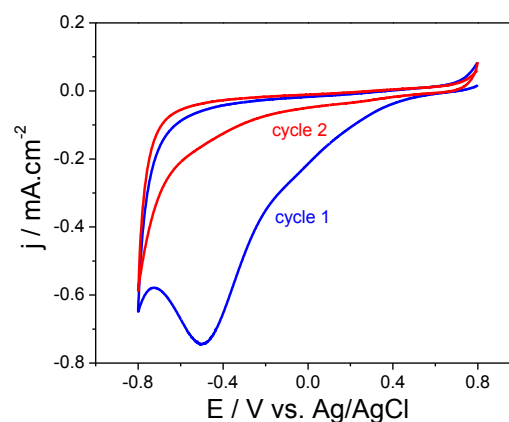


Figure 1: Cyclic voltammograms for the reduction of 5 mM of 3-aminopyridine in presence of 2 equivalents of NaNO<sub>2</sub> in 0.5 M HCl at a scan rate of 50 mV.s<sup>-1</sup>. The first two cycles are shown.

- (1) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J. M. *Journal of the American Chemical Society* **1992**, *114*, 5883.
- (2) Baranton, S.; Bélanger, D. *Journal of Physical Chemistry B* **2005**, *109*, 24401.
- (3) Yeşildag, A.; Ekinçi, D. *Electrochimica Acta* **2010**, *55*, 7000.