Electroactivation of Modified Carbon Paste Electrodes in the Presence of Phase Transfer Catalysts

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Carbon paste has been widely used in the preparation of modified electrodes particularly in combination with biocatalysts (e.g. enzymes). Such electrodes offer the advantages of versatile bulk modification, fast response, renewability and a low background current. The ease of fabrication and the control of modifiers loading (organic and inorganic molecules, enzymes, cofactors or mediators) have been valuable for electrochemical studies and analytical applications of modified carbon paste electrodes.

Electroactive cations such as metallic or organometallic species can be adsorbed or incorporated in zeolite frameworks and their charge-transfer reactions can be studied by electrochemistry when integrated in carbon paste electrodes. The zeolite Y (faujasite) can easily be exchanged with the ferricinium cation that has been extensively used, in solution or fixed at the surface of the electrodes, as an electron transfer mediator for the electrooxidation of many substrates (e.g. glucose) with enzymes (e.g. glucose oxidase).

The aim of the present study is to show up a new electrochemical behavior of zeolite modified carbon paste electrode when electrochemically activated in the presence of phase transfer catalysts. The benefit of improving the analytical performances of the activated electrodes in bielectrochemistry is also shown.

Modified carbon paste electrode (A) was prepared by mixing carbon powder with zeolite Y-FcH and paraffin oil. Electrode (B) was prepared by mixing carbon powder with paraffin oil in which a given amount of FcH was dissolved. Electrochemical behaviors of (A) and (B), in the absence and the presence of glucose and glucose oxidase, were compared. In phosphate buffer (A) and (B) show identical reversible voltammograms. Figure 1 shows the responses of (A) and (B) to the electrocatalytic oxidation of glucose by glucose oxidase. For the same experimental conditions (A) always showed higher catalytic peak than (B). This result indicates that the zeolite boost up the enzymatic mediated oxidation.

A new behavior of (A) was observed when a negative working potential was applied for a few seconds in phosphate buffer solutions containing transfer phase catalysts. The hight and the shape of the cyclic voltammetry signal were changed indicating an activation of the electrode surface (figure 2). The activation coupled with the catalytic electron transfer reaction for the enzymatic oxidation of glucose via mediator ($Fc\text{-}H^+$) induces, a drastic increase in the sensitivity of the modified electrode (figure 3). It also highly increases the apparent Michaëlis constant of the enzymatic reaction and expands the linear range of biosensors using the activated modified electrode. Similar but smaller activation was observed for (B).

To our knowledge this work presents the first example of electrochemical activation of the surface of modified electrode by the means of phase transfer catalysis. This activation could be useful for electrochemical studies of organic and biological molecules as well as for the preparation of sensitive amperometric biosensors.

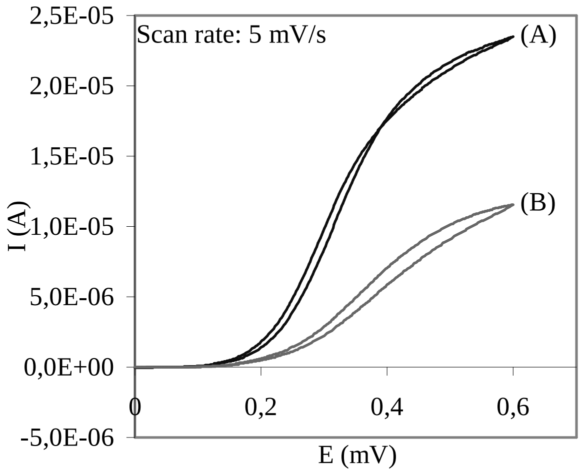

Fig. 1- Catalytic peaks for electrodes (A) and (B) in phosphate buffer containing 50g/L glucose and 750 UI/mL glucose oxidase.

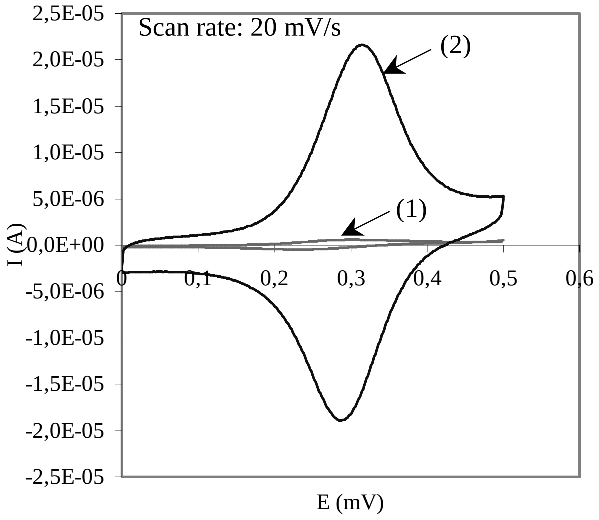

Fig. 2 - Effect of the activation on a Y-FcH modified carbon paste electrode (A). (1) Before activation. (2) After activation.

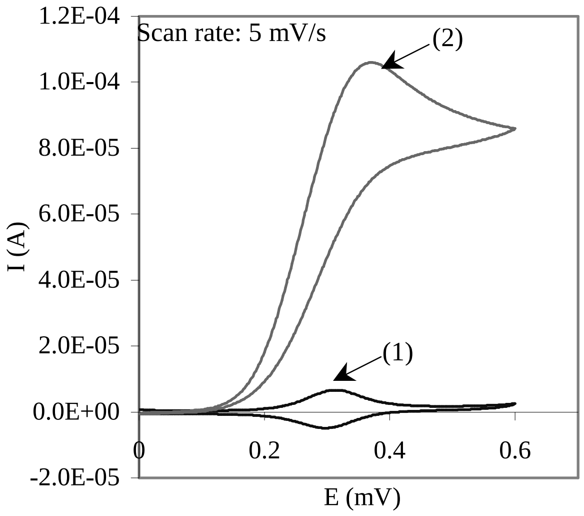

Fig. 3- Cyclic voltammetry of the activated electrode (A) in the absence (1) and the presence (2) of 50g/L glucose and 750 UI/mL glucose oxidase in phosphate buffer.