Diffusion at Double Microband Electrodes Operated Within a Thin Film Coating. Theory and Experimental Illustration.

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The diffusion transport of reversible redox species was investigated at microbands within a thin film coating. The effect of the film thickness onto the diffusion was studied theoretically and by numerical simulations both at single band (Fig. 1A) and double band microelectrodes operated in generator-collector mode (Fig. 1B). A quantitative evaluation of the currents were performed in the conformal space fitted to the geometry of the device and the diffusion equations were resolved by finite differences. According to the diffusion length of the species in this restricted volume, the theory and simulations showed that several diffusional regimes are expected which provide a way to estimate both the diffusion coefficient, the diffusion coefficient ratio between reactant and product and the concentration of the electroactive species incorporated in the film, but also to evaluate at the same time the film thickness. The experimental validity of the model was tested with a two-paired platinum microband assembly operating into an Nafion® micrometric film loaded with iron(III) in which the electrochemical reactions are the reduction of iron(III) at the generator (Fig. 2A) and the oxidation of electrogenerated iron(II) at the collector (Fig 2B). A good agreement was obtained between theory and experiments which shows that the chronoamperometric responses of such devices afford a possibility of monitoring the physical and geometrical properties of a polymer film in relation to its chemical environment.

References:
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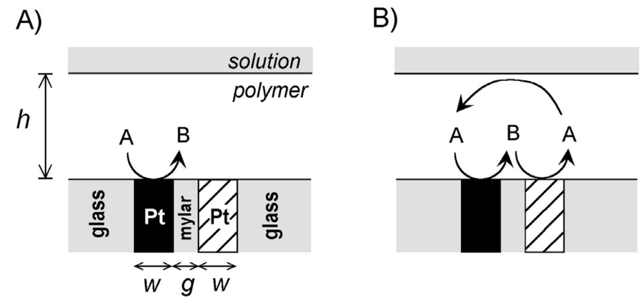

Figure 1: Schematic representations of the cross-section of the microbands assemblies (A) Single-band mode operation: only one electrode is connected (solid black). (B) Double-band mode showing the cross-talk between generator (solid black) and collector (hatched shade) electrodes. h is the thickness of the polymer film, w the width of each Pt microband and g that of the mylar insulating gap. Insulating materials (glass, mylar, bulk solution) are shown in solid gray, while the space available to diffusion is represented in white.

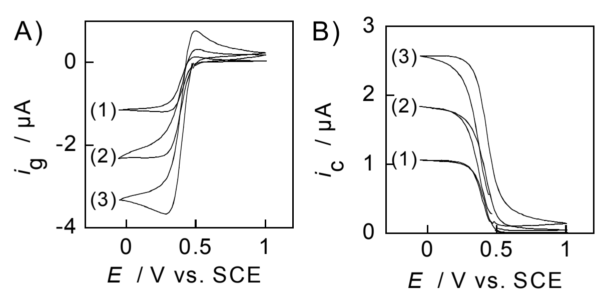

Figure 2: Cyclic voltammograms monitored at Fe^{III}-loaded Nafion®-coated microband assemblies ($w \sim 5$ µm, $l \sim 3.5$ mm, $g \sim 2.5$ µm) placed in a Fe^{III}–free 0.1 M H_2SO_4 aqueous solution. (A) generator current i_g (B) collector current i_c. In (A,B) estimated film thicknesses (1) $h = 3$, (2) 5 and (3) 11 µm; the generator potential was scanned at 5 mVs^{-1} while the collector potential was poised at 0.8V *vs.* SCE.