Electrochemical Sensors Based on the Interfacing of Nanoelectrodes Ensembles with Chemical Recognition Elements

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Nanoelectrodes ensembles (NEEs) are nanotech-based electroanalytical tools which can find application in a variety of fields ranging from sensors to electronics, from energy storage to magnetic materials [1].

The present communication deals with NEEs developed specifically for chemical sensing purposes. In particular, the possibility of interfacing NEEs with molecular recognition elements is examined.

The nature of the Faradaic currents observed at a NEE depends on the distance between the electrode elements and the timescale (scan rate) of the experiment [2,3].The commercially-available template membranes used to prepare the NEEs in this study have very high pore densities (in excess of 10^8 pores cm^{-2}) and rather small pore diameters (approx. 40 nm) so that they operate in the "total-overlap" response regime.

These NEEs show improved electroanalytical detection limits relative to conventional electrodes [4,5] because the Faradaic current is proportional to the total geometric area of the NEE, while the background currents (double-layer charging currents) are proportional to the sum of the areas of the electrode elements in the NEE.

The use of NEEs in micromolar cytochrome c (cyt c) solutions revealed the possibility to observe the direct electrochemistry of the protein, without the need of adding any promoter or mediator. Cyt c detection limits at NEEs are 1x 10^{-6} M for cyclic voltammetry and $5x10^{-8}$ M for differential pulse voltammetry (see Fig. 1). The main difference between the voltammetric signals recorded at NEEs in the absence and in the presence of the promoter 4,4'-bipyridyl was the more extended dynamic range obtained in the latter case.

NEEs can be modified by deposition of water soluble ion-exchange polymers such as polyester sulfonated cation exchangers [4]. A new method for the deposition and stabilization of thin film of polycationic poly-L-lysine on NEEs is presented.

Such a coating results particularly useful for developing electroanalytical- biosensing detection schemes based on the ion-exchange incorporation of anions. The anion can be an electroactive analyte such as in the case of electroactive dyes used in the food industry or a biocatalytic component such as enzymes of low isoelectric point. By this approach it is possible to take advantage both of the high sensitivity of NEEs and of the ion-exchange selectivity and preconcentration capabilities of the stabilized poly-L-lysine coating.

References

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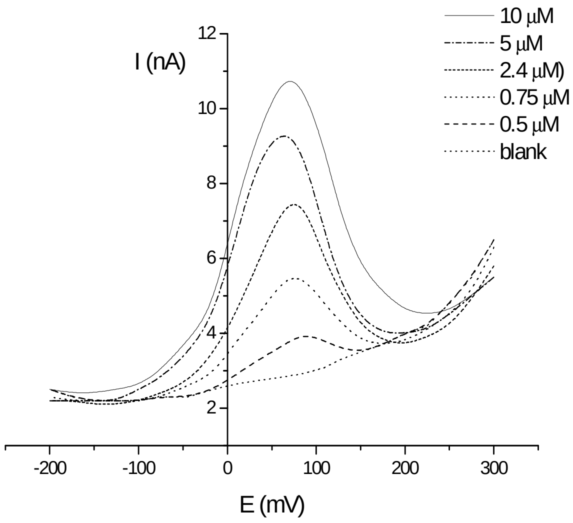

Figure 1. Differential pulse voltammograms recorded at a NEE in solutions containing increasing cyt c concentrations (indicated in the figure) in 10 mM phosphate buffer, pH 7.3.
DPV parameters: scan rate 5 mVs^{-1}, pulse height 25 mV, initial potential +300 mV and final potential -200