

Advances in the Direct Electrochemistry of Cytochrome C at Ionomer Coated Electrodes and at Nanoelectrodes Ensembles

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Since the first pioneering studies [1] on the electrochemistry of cytochrome c (Cyt C), many research groups tried to develop methods for observing the direct electrochemistry of Cyt C, with no promoter or mediator added. In the present work, two advanced electrode systems are examined for this goal. They are electrodes modified with the polyestersulfonated ionomer Eastman AQ 55, AQME [2-4], and nanoelectrodes ensembles, NEE [5-7].

At the AQME, the presence of the polyelectrolyte coating allows the observation of the direct electrochemistry of Cyt C in the $10\text{-}100\ \mu\text{M}$ range thanks to favourable electrostatic interactions between Cyt C and the ionomer. In particular, the study focused on the role of the permselectivity of the polymeric modifier in ruling the selectivity of electrocatalytic processes which take place at the modified electrode loaded with Cyt C. The reaction between reduced Cyt C and electroactive oxidants (substrates) dissolved in the solution phase is possible only for anionic oxidants (such as $\text{Fe}(\text{CN})_6^{3-}$, see Fig. 1) and not for cationic ones (e.g. the electrogenerated (ferricenylmethyl)trimethylammonium dication). Ionic interactions between the substrate and the polyanionic coating discriminate between the direct electrochemical reduction of the substrate and its electrocatalytic reduction by immobilised Cyt C, so that the modified electrode acts as an AND logic gate.

On the other hand, the possibility to study Cyt C electrochemistry at NEEs is also examined. Gold nanoelectrodes ensembles have been prepared by using an electroless plating method to deposit disk-shaped Au electrode elements (approx. diam. 40 nm) within the pores of a microporous polycarbonate template membrane. Due to the high density of electrode elements, the NEEs operate in the “total overlap” regime, and peak-shaped voltammograms are obtained. NEEs show enhanced electroanalytical detection limits, relative to a conventional “macro” electrode [6,7]. This is because the Faradaic current is proportional to the total geometric area of the NEE, while the background currents (double-layer charging and residual Faradaic currents) are proportional to the sum of the areas of the electrode elements in the NEE [5]. In order to prove whether the use of electrodes of nanoscopic dimensions could favor the direct electron transfer between Cyt C and the electrode surface, some experiments were performed using NEEs. As shown in Fig. 2, well resolved Cyt C voltammograms can be observed at NEEs. Data concerning the detailed analysis of the voltammograms will be presented and discussed. To our knowledge this is the first report showing the possibility to observe the direct electrochemistry of Cyt C at nanoelectrodes.

References

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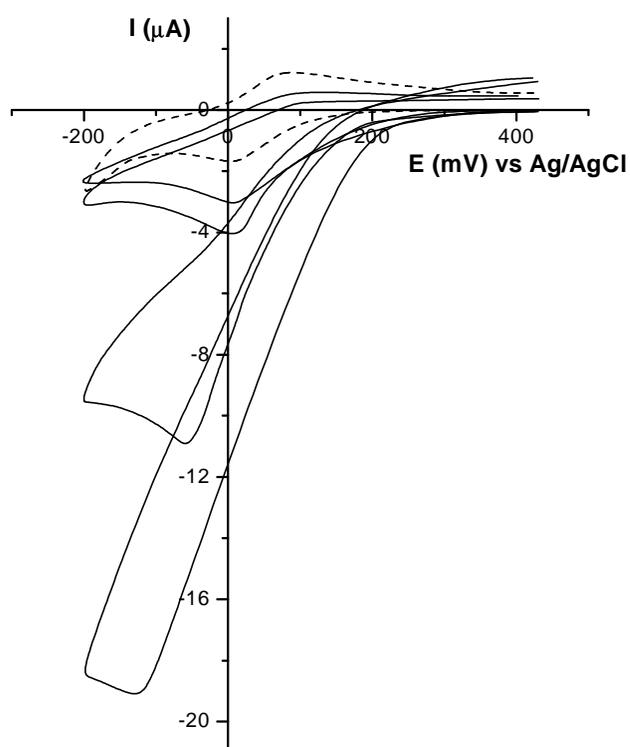


Figure 1: Cyclic voltammograms recorded at AQME/Cyt C dipped in 25 mM phosphate buffer solution (pH 7) in absence (dotted line) and in presence (full lines) of increasing concentration of $\text{Fe}(\text{CN})_6^{3-}$: 10, 20, 100, 200 μM . Scan rate $20\ \text{mV s}^{-1}$.

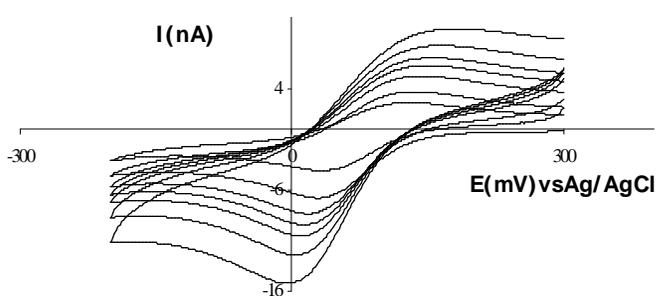


Figure 2. Cyclic voltammograms recorded at different scan rates (between 2 and $50\ \text{mV s}^{-1}$) at a NEE (total geometric area $0.07\ \text{cm}^2$, average nanodiscs diameter 40 nm) in μM Cyt C solution.