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Interplay between the potential waveform and diffusion layer dynamics determines the time-response of voltammetric detection in microchannels

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ABSTRACT

The diffusion layer is a critical factor affecting the temporal response of electrochemical devices. In this article, we have investigated the effect of the relaxation of the diffusion layer during the potentiodynamic sensing of ferrocenemethanol (FcMeOH) in microchannels and compared these results to amperometry. First, the effect of the relaxation of the diffusion layer is described, both theoretically and experimentally. Then, chronoamperometric and voltammetric measurements were considered, and the rate of current increase as a plug of FcMeOH is injected into the device was studied for both cases. It was found that, for the oxidation of FcMeOH, the waveform maximising the duration of the anodic phase provided an improved response for potentiodynamic methods, even though amperometry was always found to show the best results. This was further established by extracting the impulse response and modulation transfer functions, which characterize the time and frequency responses, respectively, of the fluidic/electrochemical system. These findings can help designing potential waveforms improving the time response of the device, in systems where high temporal resolution is needed. This is particularly appropriate to bioelectrochemical analyses, where release and uptake phenomena can occur on the millisecond timescale.

1. Introduction

Electrochemical methods are strong candidates for on-chip chemical analysis [1–3]. Indeed, contrary to many analytical techniques, electrochemical sensors are highly amenable to miniaturization and can be easily batch-produced with standard microfabrication techniques [4–6]. They are also attractive solutions for cheap, hand-held measurement systems applicable for instance to point-of-care diagnostics [7,8]. However, the specificity of electrochemical sensing, where the reaction actually induces a gradient of analyte established at the electrode following Fick's laws, requires a careful characterization of the detection system, especially if it is embedded into a microfluidic circuit. Indeed, several reports have highlighted the specific behaviour of electrochemistry in microchannels [9–13], where the mass transport characteristics are radically different from the ones encountered in traditional conditions of electrochemistry [14–16]. The fast time response and sensitivity of electrochemical sensors is one of their most attractive features, allowing for example the detection of neuronal transmission [17–22] or single molecules [23,24]. The effects of convection and diffusion on the temporal behaviour of electrochemical sensors therefore have to be studied carefully for these devices.

Amperometry (AMP) is considered as one of the electrochemical methods providing the highest time response. In contrast, cyclic voltammetry (CV), or other potentiodynamic techniques, are popular because of its improved chemical resolution, allowing for the simultaneous quantitation of different analytes. In a previous report [25], we have compared the response of AMP and CV to the injections of a plug of 1 mM ferrocenemethanol (FcMeOH) in a microfluidic system. This redox probe was used because of its fast electron transfer [11,26,27], guaranteeing that the observations will arise from mass transport rather than secondary reactions (adsorption, formation of chemical bonds, etc). In addition, its oxidation occurs at a potential where the results will not be distorted by oxygen reduction (oxygen is technically hard to remove from poly-dimethylsiloxane (PDMS) chips). This system (Fig. 1A) featured a fluidic chip allowing the injection of two different streams of liquid (typically, buffer and analyte), which are then mixed through several serpentines (channel height: 100 μm), before entering a sensing chamber (Ø

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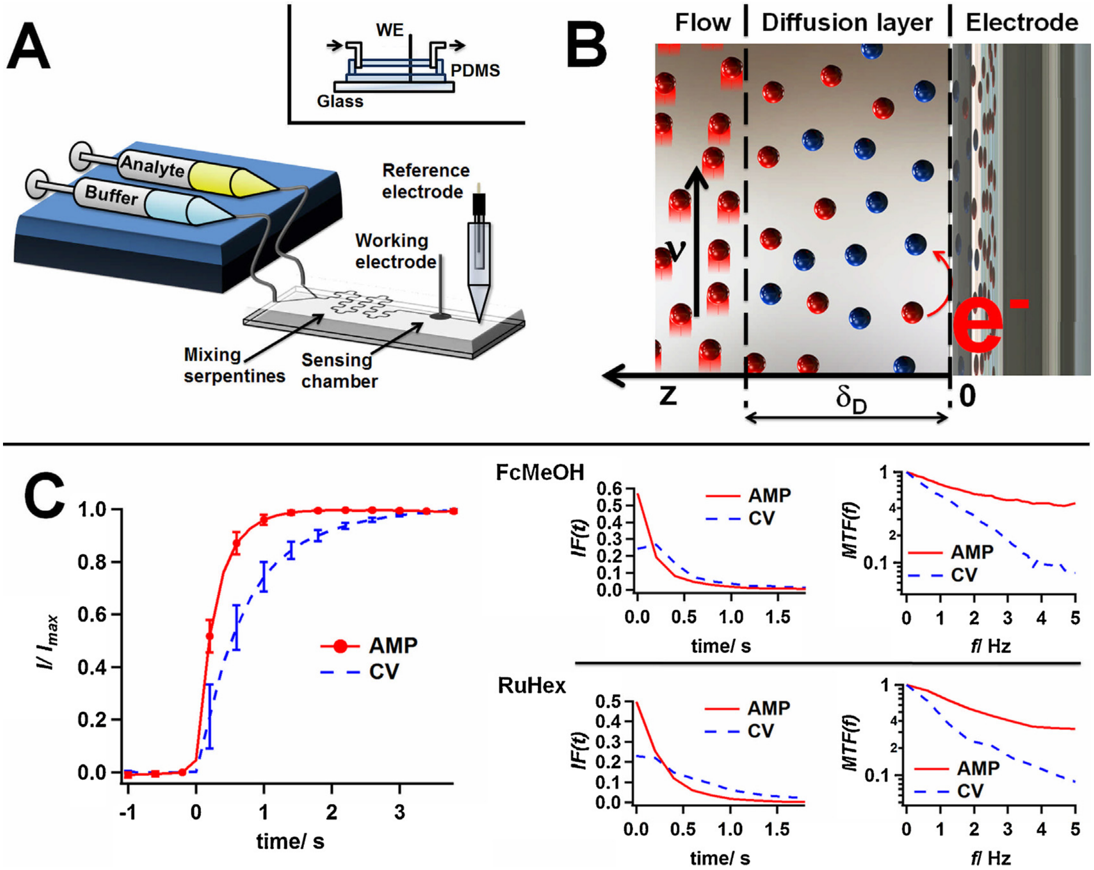

Fig. 1. Evidence for diffusive relaxation during electrochemical detection using an electrochemical/microfluidic chip. A) Schematic of the experimental setup, showing the two syringes actuated by a pump injecting specific flow profiles into the electrochemical/fluidic chip, having a section of mixing serpentines, a Pt working electrode, and an Ag|AgCl reference electrode completing the electrochemical setup. The insert is a simplified cross section view of the chip, showing the inlet and outlet, as well as the working electrode WE positioned across the sensing chamber, orthogonally to the plane of the chip. B) Scheme of the dynamics of the diffusion layer generated at the surface of the electrode during electroanalysis, as explained in the text. The reaction is here presented by the analyte (the red molecule) being oxidised or reduced into its conjugated form (the blue molecule). C) Comparison of AMP (N = 4 repeats, ±SD) and CV (N = 4 repeats, ± SD) detection of a 4 s step of 1 mM RuHex in aerated PBS injected into the device at 10 μl s^{-1}. The left part shows the normalised currents, underlining the delayed response of CV. The right part shows the impulse response functions (IF) and the modulation transfer functions (MTFs) associated to the AMP and CV detections of FcMeOH (from ref. [25], N = 7 repeats for AMP and N = 8 repeats for CV) and RuHex in similar conditions (4 s step of 1 mM of analyte in aerated PBS injected into the device at 10 μl s^{-1}).

1 mm). This chamber contained a Pt working electrode (WE) positioned along its vertical axis. The system is completed with an aqueous Ag|AgCl (3 M KCl) reference electrode (RE). The small size of the microchannels induced a high solution resistance, and the expected iR drop in this two-electrode configuration is in the 1-10 mV range. Furthermore, the faradaic currents observed during the experiments are ~100 nA, and in principle could induce a polarization of the reference electrode. This polarization is however expected to be limited because of the large effective surface of the chlorinated silver wire, with respect to the area of the WE, thus resulting in a lower current density at the surface of the RE. Furthermore, in all the experiments, the current of interest was measured in the diffusion-limited regime, and the applied overpotential was high enough not to be hindered by small variations due to an eventual iR drop or electrode polarization. The Reynolds' number in the microchannels section of the chip is ~100 at the highest flow rate considered (10 μl s^{-1}). In all the cases considered previously for the detection of plugs of FcMeOH in microchannels [25], the CV response was delayed over the AMP traces. As FcMeOH was found to show outer-sphere properties in our system, with a fast electron transfer, this delay was attributed to mass transport, more precisely to the relaxation of the diffusion layer in response to the observed concentration changes [28,29].

During electrochemical detection, the system establishes a diffusion layer of thickness δ_D in a region immediately adjacent to the electrode (for $0 \leq z \leq \delta_D$). Following a common approximation [30], if the system is positioned in a stream of fluid of flow rate ν, this region is characterised by the absence of any significant convection, which allows the establishment of the diffusion layer, in agreement with the Prandtl's hypothesis [31], as shown in Fig. 1B. On the other hand, for $z > \delta_D$, the fluid is well-mixed by the convection field, and the analyte concentration can be approximated as uniform. Even though it is possible, for the sake of clarity, to assume that there are only two discrete regions, one where diffusive transport controls the flux of analyte, and another one where convection dominates, and that the Prandtl's viscous boundary layer can be identified to the diffusion layer, the actual system is more complex. In our system, the Schmidt number Sc, the ratio of the kinematic viscosity to the diffusion coefficient, is high (>10^4), and the viscous boundary layer is expected to be much thicker than the diffusion layer, by a factor approximated with $Sc^{1/3}$ [32], which means in our device that the viscous boundary layer is at least 10 times thicker than the diffusion layer. In a linear approximation of the fluid velocity at the vicinity of the wall, the velocity at the edge of the diffusion layer would be, at best, a tenth of the maximal velocity in the chamber. This is in agreement with distinct domains where mass transport is respectively controlled