VOLTAMMETRIC ELECTROCHEMICAL DETECTION OF CONCENTRATION CHANGES IN A MICROFLUIDIC CHIP IS DELAYED IN COMPARISON TO AMPEROMETRY

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ABSTRACT

The time responses of two electrochemical methods, amperometry (AMP) and cyclic voltammetry (CV), used in a microchannel to detect the concentration variations of an outer-sphere redox species were compared. Overall, our results show that the temporal resolution of AMP is superior to the one of CV. As no secondary reaction (formation of chemical bounds, adsorption, *etc.*) can hinder the detection, this phenomenon was attributed to the instability of the diffusion layer in CV, filtering off the fast frequency components of the detected signal. This fact can have implications to improve electrochemical detection in microchannels, especially at fast flow rates.

KEYWORDS: Electrochemical detection, diffusion layer, amperometry, voltammetry

INTRODUCTION

Electrochemical methods are powerful alternatives to the usual analytical techniques used in microfluidic systems. Both amperometry (AMP) and cyclic voltammetry (CV) are used in literature: the main characteristic of CV is that the electrode potential is constantly cycled over a user-defined range, leading to constant changes in the analyte concentration profile in the vicinity of the electrode, while the potential remains constant for AMP.

Here, we investigate the time response of an electrode incorporated into a microfluidic channel to variations in analyte concentration of the outer-sphere redox probe ferrocenemethanol (FcMeOH). Our experimental data show that the temporal resolution of CV is not as good as for AMP, as CV cannot properly detect fast concentration transients. This delay has been previously observed in the case of dopamine detection, and attributed to analyte adsorption on the electrode [1,2]. In contrast, FcMeOH is an outer-sphere redox species, and adsorption is not expected to happen during the reaction, hence ensuring that the observed delay effectively arises from diffusive/convective phenomena, rather than being of purely chemical origin.
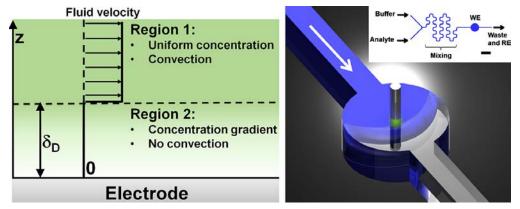

Figure 1: Left- Schematic of our simple diffusion layer model. The concentration gradient is indicated by the green color, the shape of the convection field is not significant. Right- Graphical representation of the principle of the electrochemical chip, where the electrode is exposed to changing concentration profiles. The insert shows the layout of the chip, with the working (WE) and reference (RE) electrodes (the bar shows 1 mm).

THEORY

During electrochemical detection, a diffusion layer, of thickness δ_D, is established as the analyte of interest is consumed at the electrode. If, additionally, this electrode is now exposed to a flow, the diffusion layer is actually constrained by the flow, and, in first approximation, 2 regions appear, characterized by their distance z to the electrode surface (Figure 1, left). If $z > \delta_D$, the convection field ensures that the solution is well-mixed, and the analyte solution is uniform. However, for $\delta_D > z > 0$, the effect of convection is assumed to be negligible, because of buffer viscosity, thus allowing the establishment of the diffusion layer. The diffusion layer can be characterized by its relaxation time τ_D:

$$\tau_D = \frac{\delta_D^{\,2}}{2D} \tag{1}$$

where D is the diffusion coefficient of the analyte [3]. This value describes the transient response of the diffusion layer to modifications of the system. In the case of CV, where the potential is constantly modified, thus altering the diffusion layer, it is expected that the effect of τ_D will hinder the capability of the system to accurately measure fast changes in concentrations. In this case, the diffusion layer can indeed be shown to induce, both qualitatively and quantitatively, a Resistor Capacitor (RC) circuit-like delay, thus hindering the temporal accuracy of the measurements.

EXPERIMENTAL

Our chip is built in polydimethylsiloxane, using standard soft lithographic methods. A Pt working microelectrode, made of a Ø51 µm Pt wire, is inserted into the detection chamber with a syringe needle (Figure 1, right). The system is completed with an Ag|AgCl reference electrode. The Pt electrode can be exposed to solutions of FcMeOH of different concentration and flowing at different velocities, using the two inlets and the mixing serpentines. The layout of the chip is shown in the insert of Figure 1, right. The flows are controlled with a Nemesys programmable syringe pump (Cetoni, Korbussen, Germany).

RESULTS AND DISCUSSION

The chip is used to expose the electrode to different concentration profiles, for instance a sawtooth, a sine and a step, as shown in Figure 2. In the case of the sawtooth waveform, the delayed response of CV is observed on the fast, decaying part of the signal, but not on the slower rising part. Similarly, only a minor delay is seen for the sine, because of the slow concentration transients, but the temporal resolution appears to be much higher for AMP in the case of the step. Overall, these observations already show the delayed response of the CV method over AMP, especially for fast concentration transients. Because of the specific nature of CV sensing, were the potential is constantly cycled, this voltammetric delay was attributed to the relaxation dynamics of the diffusion layer [3].
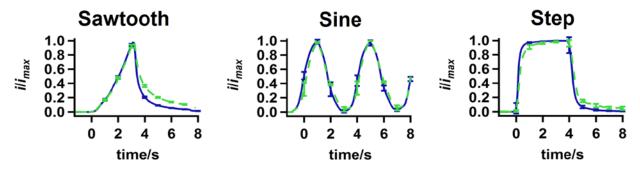

Figure 2: Detection of different concentration waveforms (flow rate: 10 µl s^{-1}) showing the faster response of AMP over CV (solid line: AMP; dashed line: CV).

To investigate further this phenomenon, steps of 1 mM FcMeOH were injected in the chip at different flow rates (0.5, 1, 5 and 10 µl s^{-1}, data not shown). The CV delay increases with the flow rate, hence hinting a frequency-dependent behavior. To evaluate this, the modulation transfer function (MTF) of the system is computed from the experimental data for both AMP and CV and for different flow rates (Figure 3). This function shows the ability of the system to resolve signal variations at a certain frequency [4]. The MTFs are largely similar at low flow rates, but the magnitude of the MTF associated to AMP is higher than the one of CV, thus showing its increased temporal resolution.
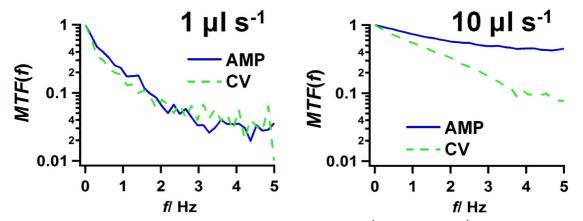

Figure 3: MTF computed from the experimental data (left- 1 µl s^{-1}; right- 10 µl s^{-1}) for AMP (solid lines) and CV (dashed lines). At high flow rate, the MTF for AMP shows a higher magnitude, indicating hence a better time resolution for the analyte detection.

CONCLUSION

The delayed response of CV over AMP has been characterized. Although this phenomenon has been previously attributed to analyte adsorption, we showed that the diffusion/relaxation layer plays an important role and that its formation/regeneration needs to be taken into account, when detecting fast electrochemical signals [5].

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