# Investigation of Dynamic Concentration Profiles Within Diffusion Layers Using Ultramicroelectrodes

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Using an ultramicroelectrode as a probe positioned near an other electrode, we established that electrochemical detection allows spatially resolved information at the micrometric scale, so that the composition of dynamic diffusion layers created in the vicinity of this electrode can be examined with adequate precision.[1,2]

This allowed to discuss experimentally to which extent the spontaneous hydrodynamics of the solution influences the currents and the building up of diffusion layers at microelectrodes. We have been able to propose and test a model which takes into account the convective mass transport (see figure).[3] By decreasing the concentration of the supporting electrolyte, we demonstrated the influence of migration on the mass transport by mapping the concentration profiles of charged species at the electrode interface.

This method is also appropriate to monitor and to investigate the concentration profiles resulting from particular electrochemical mechanisms at the micrometric scale, especially under situations which will be not observable through the measurement of the electrode current only.[4,5] In this case, the mapping of species generated at the electrode describes the effective dynamics at the interface and henceforth provides the required and determinant informations.

References

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[4] C. Amatore, S. Szunerits, L. Thouin and J.-S. Warkocz. *Electroanalysis*, *13*, 8-9, 2001, 646-652.

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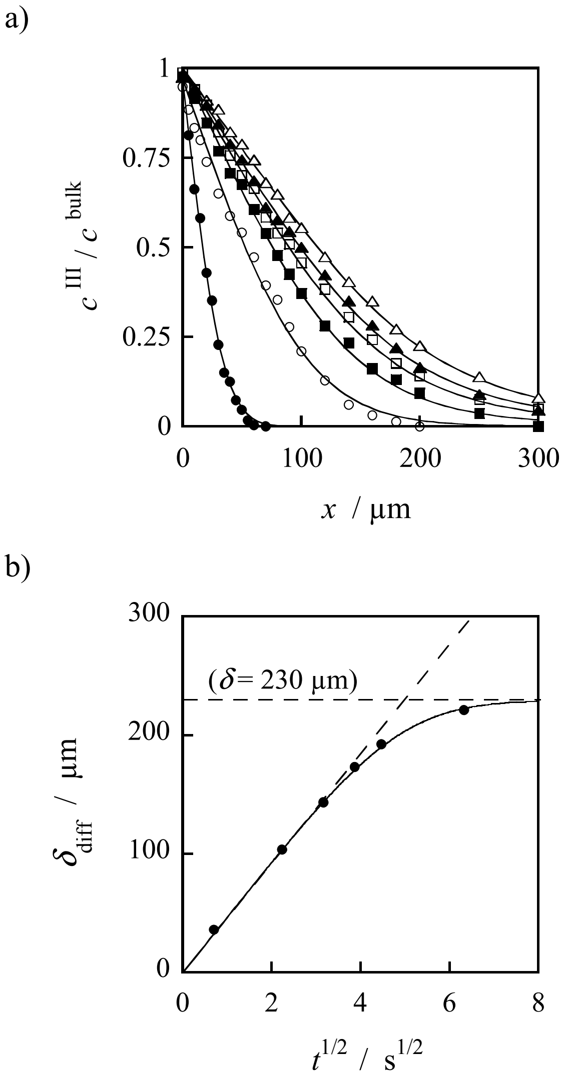

**Figure.** (a) Variations of the experimental concentration profiles (symbols) of $Fe(CN)_6^{3-}$ during the chronoamperometric oxidation of $Fe(CN)_6^{4-}$ (10 mM in aqueous 1 M KCl) for different values of the time duration of the experiment ($t$ = 0.5, 5, 10, 15, 20, 40 s). (b) Corresponding variations of the diffusion layer thickness $\delta_{diff}$ (symbols) from the data shown in (a). In (a,b), the solid lines represent the theoretical behavior predicted by the present model with $\delta$= 230 µm.