Opto-Electrochemical Imaging of Ionic Species Using Optical and Redox Reporters

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Visualizing non-redox active ions in solution is challenging with currently available principles. Electrochemical scanning probe techniques are too slow for mapping concentration gradients over large areas, particularly for dynamic systems. Optical sensors often suffer from slow response times, lack of full reversibility, and pH cross-sensitivity, which diminish their suitability for chemical imaging applications. To overcome these limitations, we have developed an opto-electrochemical system capable of visualizing ionic species that are both optically and electrochemically silent. The technique is coined *Voltammetric Ion Transfer Microscopy* (VITM), which operates on the principle of optical transduction of ion transfer processes between two immiscible phases, driven by dynamic electrochemistry. This is achieved by confining a redox probe ($TEMPO^{\bullet}$) and an optical reporter (lipophilic rhodamine) within a thin ion-selective membrane on the surface of an electrode [1]. The fluorescent reporter is unquenched by the oxidation of $TEMPO^{\bullet}$ into $TEMPO^{+}$, which is coupled with the expulsion of a cationic species from the polymeric film to maintain charge neutrality [2]. The energy barrier for transferring the cation depends on its activity in solution, which is reflected in the electrochemical peak potentials. We use an integrated flow cell to visualize a heterogeneous ion distribution in two confluent solution streams, for which a single potential sweep at the electrode gives an averaged peak potential for all the ion transfer processes across the membrane (see Fig. 1a), with no information about the spatial distribution. By rapidly acquiring images during the potential scan, we identify the potential at which the fluorescence change is the largest for each pixel in the image stack. This enables the construction of a detailed ion concentration map of the solution, as shown in Fig. 1b for the model ion tetraethylammonium (TEA^{+}).

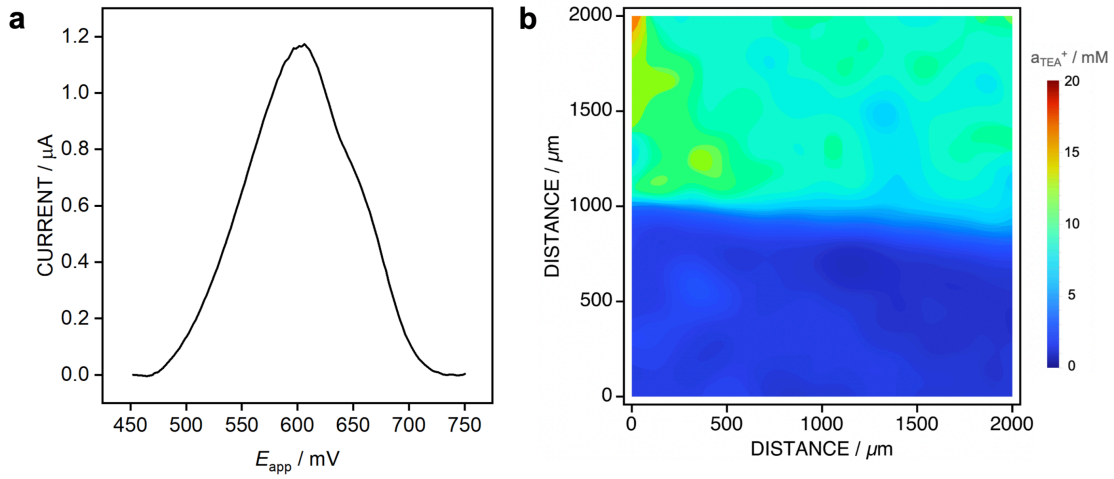

Figure 1. a) Voltammogram of two confluent TEA^{+} solutions (1 and 10 mM); **b)** corresponding TEA^{+} activity map.

[1] G. J. Mattos, N. Yu. Tiuftiakov, E. Bakker, *Electrochem. Comm.*, **2023**, *157*, 107603.
[2] P. Zhu, J.-P. Clamme, A. A. Deniz, *Biophysical Journal* **2005**, *89* (5), L37–L39.