

Spatially Resolved Optical Ion Sensing with Voltammetric Ion Transfer Microscopy: Fundamentals and Applications

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Ion concentration gradients are fundamental for numerous chemical, biological and environmental processes and techniques capable of spatially resolved ion detection are essential to obtain a deeper understanding of such heterogeneous systems. However, well-established methodologies of chemical imaging typically suffer from long acquisition times, limiting their applicability to dynamic systems. To address this limitation, our group has recently developed a new approach, termed Voltammetric Ion Transfer Microscopy (VITM), enabling the acquisitions of millions of spatially resolved concentration within seconds.¹ The imaging platform consists of a planar electrode coated with a thin ion-selective membrane (ISM) incorporating a redox probe, a lipophilic derivative of the stable radical TEMPO, and a lipophilic rhodamine fluorophore as optical reporter.^{2,3} The radical form of TEMPO may quench the fluorescence of the dye, allowing for a direct correlation between electrochemical and optical signals.⁴ The conversion of lip-TEMPO between its radical and cationic forms using dynamic electrochemistry induces ion transfer between the aqueous and organic phases to preserve membrane electroneutrality while simultaneously modulating the fluorescence intensity (Figure 1a). This contribution considers some limitations of the system and extends its scope of applicability. Specifically, we report on the incorporation of a new ammonium ionophore in the membrane, which enables the selective imaging of ammonium ions in chemical and biochemical gradients.

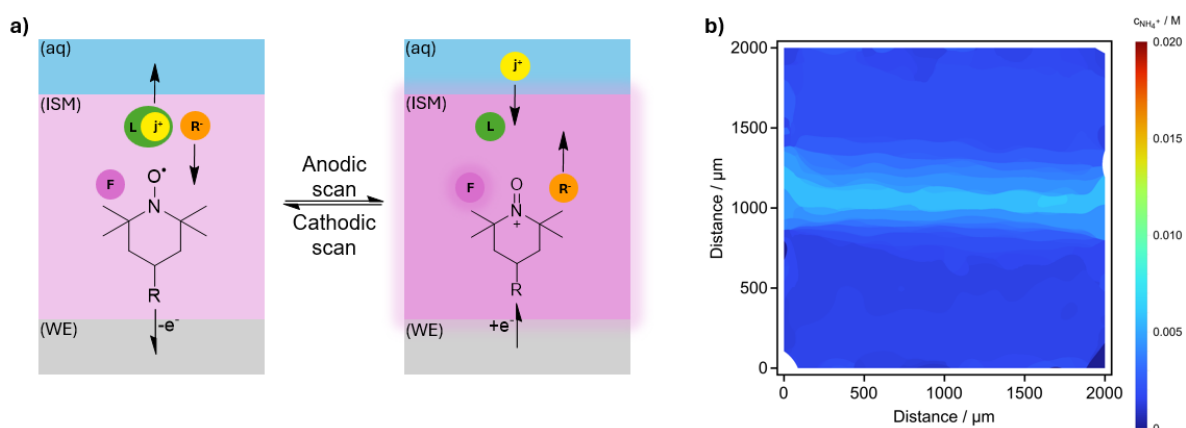


Figure 1. a) Ion transfer mechanism and related fluorescence intensity change of the fluorophore (F). R-represents a cation exchanger, j⁺ a generic cation and L an ionophore. **b)** Ammonium concentration density plot. Solutions of urease (top) and urea (bottom) flow over the membrane from left to right. Ammonium is produced along the central portion of the image where the two solutions meet and enzyme turnover occurs.

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