

AC-SECM Metal Ion Imaging

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Detecting metal ions qualitatively and quantitatively using electrochemical techniques is well known. Ion selective electrodes (ISE) and voltammetric techniques are the predominant methods for detecting metal ions. (Pesavento et al., 2009) ISEs have many advantages such as their nondestructive nature and selectivity. However, ISEs are not available for every metal, and this limits the use of ISEs. (Batley et al., 2004, Pesavento et al., 2009) On the other hand, voltammetric techniques can disturb the existing equilibrium in the medium. Due to advantages such as sensitivity and low detection limits for most metal ions, ISEs are the top choice for the detection of metal ions. (Pesavento et al., 2009, Bakker et al., 2006)

Detection of metal ions can be helpful in understanding the chemical nature of a surface. In addition, mapping of metal ions can be used to understand the behavior of metal ions in biological systems. Maintaining the same level of accuracy throughout the detection period and producing minimum disturbance to the system are two main requirements for mapping techniques. Voltammetric and amperometric techniques can be used continuously with the same level of accuracy; however, these methods are not free of disturbance (consumption of analyte and electrolysis products). Non-amperometric methods, such as AC-SECM (alternative current scanning electrochemical microscopy) coupled with a modified electrode, can be used to detect ions without disturbing the system.

As metal ions chelate with the modified layer, the double-layer capacitance will change, and this change can be detected using impedance spectroscopy (Burke et al., 2008) or other AC current based electrochemical techniques. Since chelation is a reversible process, the chelation level is dynamic and fluctuates with respect to the free metal ion concentration of the system. Chelation of transition metal ions such as Cu(II) and Fe(III) have been reported previously with aniline. (Jacques et al., 2007) SECM ultra microelectrodes (UME) modified with aniline were used to test this hypothesis. UMEs modified with nitrobenzene were reduced electrochemically to produce aniline-modified UMEs. (Allongue et al., 1997)

Different transition metal wire-embedded substrates were used as the scanning surfaces for preliminary studies. Metal ion detection was performed using a 7 μm -carbon fiber UME modified with aniline. A solution of 0.05 M H_2SO_4 was used as the electrolyte for AC-SECM experiments. Corrosion at the embedded metal wire can be controlled by an applied potential to the substrate. Line scans were performed over the embedded metal wire soon after the substrate was given a potential pulse. A decrease in the AC current response is observed in the line scans performed using aniline-modified UMEs with Cu and Ni substrates. In these scans, a short potential pulse given just before the scan produced enough metal ions to register an AC current decrease. The magnitude of the AC current decrease increased with pulse potential. No current decrease is observed for a Pb-wire embedded substrate. This confirms

the ability of aniline-modified UMEs to detect some transition metal ions. The estimated level of detection based on these results is in the limit of $10 \mu\text{mol dm}^{-3}$.

To confirm this further, another set of experiments were performed using the same metal-wire embedded substrates. Metal ion production and detection were performed separately from each other. The produced metal ions diffuse across the medium to the electrode. The calculated diffusion times and the experimental times taken by the metal ions to register a signal are compared to validate the results. A metal wire-embedded substrate can produce concentration waves of metal ions after each potential pulse, and the modified electrode placed nearby can detect the metal ions. The time taken by metal ions to reach the electrode was measured, and this delay between the potential pulse and the AC current pulse must be comparable with the calculated diffusion times for each metal ions. The time observed to register an AC current decrease matched the calculated diffusion times for both Ni(II) and Cu(II) ions.

To mimic an actual biological system with a localized metal ion concentrations, a micro-capillary ($150 \mu\text{m}$) embedded substrate was used to generate localized metal ions for AC-SECM mapping. A series of different $10 \mu\text{mol dm}^{-3}$ metal ion solutions were pumped with the rate of $10 \mu\text{L/s}$. Cu^{2+} and Ni^{2+} ions were used as the possible chelating metal ion species to test the imaging ability of the modified electrode. A non-chelating Ca^{2+} ion solution was used for the control imaging scan. All these experiments were repeated with nitrobenzene-modified UMEs to validate the chelating ability of aniline with transition metal ions. Aniline-modified UMEs successfully mapped both Ni(II) and Cu(II) ions. As observed in the line scan results, nitrobenzene failed to detect these transition metal ions. These AC-SECM scans with aniline-modified UMEs showed a chelation effect with Ni^{2+} and Cu^{2+} ($10 \mu\text{M}$) solutions. Unlike the transition metals, Ca^{2+} failed to produce a change to the aniline-modified layer on the UME. Based on all these results, we believe that AC-SECM can be used effectively to detect some transition metal ions using a modified UME.

Improving the selectivity of chelating modifiers on the UME towards target metal ions is an important goal. Mapping and tracking of metal ion movement in biological systems are other possible paths in developing these AC-SECM metal ion mapping techniques.

References

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