

**NPL REPORT
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**Electrochemical Scanning
Probe Microscopy –
An Overview**

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SUMMARY

Electrochemical scanning probe microscopy (SPM) has evolved from its initial inception in about 1989 to encompass a range of techniques providing unique information on the reactivity of surfaces, molecular and ionic diffusion, the kinetics of dynamic processes, and topographical imaging at a highly localised scale ranging from nm to μm . Electrochemical-SPM includes scanning electrochemical microscopy, electrochemical atomic force microscopy (AFM), electrochemical scanning tunnelling microscopy (STM), scanning vibrating electrode technique, scanning Kelvin probe, scanning Kelvin probe force microscopy, and scanning ion conductance microscopy. Investigations using these varied techniques include molecular imaging, kinetics of enzyme catalysis, kinetics of homogeneous reactions and of heterogeneous reaction (corrosion, catalysis), imaging of molecular transport through pores in polymer and biological membranes, quantification of fluxes through pores, imaging in thin-liquid layers, charge transfer at immiscible liquid-liquid interfaces, micro- and nano-patterning, electrochemical switching of molecular wires, and sensors. The range of innovative applications has continued to expand as the potential of electrochemical-SPM has become increasingly recognised. This overview describes the principle of the techniques and highlights the many exciting applications and the innovative ways that the technique has been adapted. Future developments envisage smaller probes and the combination of electrochemical scanning probe microscopy with complementary techniques such as near-field scanning optical microscopy (NSOM). NPL has only recently started to explore the application of electrochemical-SPM techniques. It is essential that expertise in this field is developed in support of measurements in materials, biological systems, and analytical chemistry. Currently, there are no measurement standards in electrochemical-SPM and NPL could play a key role in supporting their development.

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1 INTRODUCTION

While measurement techniques to characterise surface morphology, mechanical properties and chemistry at the micro to nano-scale are comparatively well established though under progressive evolution, measurement techniques to investigate the reactivity of surfaces, the kinetics of dynamic processes, and diffusion on a highly localised scale are still relatively in their infancy. Scanning micro- and nano-probe electrochemistry provides the basis for such local characterisation and is undergoing a rapid transition as it adapts to the many possibilities offered by developments in probe technology and associated instrumentation. The first papers on the fundamentals of electrochemical scanning probe microscopy (SPM) date from about 1989 and integrated test systems have become commercially available only since 1999.

The range of possible applications and the potential insights derived from electrochemical-SPM are remarkable and relate to the capability for imaging and for quantification of local kinetics and transport. Investigations include molecular imaging, kinetics of enzyme catalysis, kinetics of homogeneous reactions and of heterogeneous reaction (corrosion, catalysis), imaging of molecular transport through pores in polymer and biological membranes, quantification of fluxes through pores, charge transfer at immiscible liquid-liquid interfaces, micro- and nano-patterning, electrochemical switching of molecular wires, and sensors. The range of innovative applications has continued to expand as the potential of electrochemical-SPM has become increasingly recognised.

The purpose of this overview is to describe the principles of electrochemical-SPM, the innovative manner in which the principles have been adapted to fit varied measurement requirements, and to highlight the many exciting applications of the technique. In so doing, it is hoped to stimulate NPL scientists to consider its utilisation as a complementary research tool in the varied research projects within NPL. In the latter context, preliminary work on cell membrane transport is already underway and systems are being established for immediate application to the study of corrosion and catalysis but also as an underpinning tool in the Materials area.

The electrochemical-SPM techniques include scanning electrochemical microscopy (SECM), electrochemical-AFM, electrochemical-STM, scanning vibrating electrode technique (SVET), scanning Kelvin probe (SKP) and scanning Kelvin probe force microscope (SKPFM), and scanning ion conductance microscope (SICM). Most emphasis will be given to SECM because of the unique capabilities in characterisation of activity. In concluding the review, possible future directions will be highlighted.

The primary reference sources for this overview are the excellent books edited by Bard and Mirkin on SECM¹ and by Unwin on Instrumentation and Electroanalytical Chemistry². The main thrust in the present report is to distil the key features from these publications and related published literature with the emphasis on highlighting the capability and potential of the technique. These texts should be consulted for more detailed information and insight.

2 SCANNING ELECTROCHEMICAL MICROSCOPY

2.1 BACKGROUND

The technique evolved initially from the use of ultramicroelectrodes (UMEs) in voltammetry³⁻⁶, and a preliminary description of an UME is appropriate. The UME is an electrode with a very small radius, ranging from a few nm to 25 μm , mounted in an insulating sheath, as illustrated for a microdisc in Figure 1. For the UME the current in the diffusion-limiting regime is given by $4nFDca$ where n is the number of electrons involved in the reaction process, F is Faraday's constant, D is the diffusion coefficient, c is the concentration of the reacting species in the bulk solution and a is the electrode radius. Importantly, the flux under diffusion conditions can be approximated by Dc/a , and since a is small the flux can be quite large indeed. Thus, activation control can be studied over a wider range of potentials and the limiting diffusion current will be less sensitive to convection. Furthermore, the current at a small disc reaches steady-state in the order of a^2/D . Hence, in scanning mode, the UME can be considered effectively as reflecting steady-state conditions. Since the total current is small (pA to nA) by virtue of the small radius, resistive drops in solutions are not usually significant.

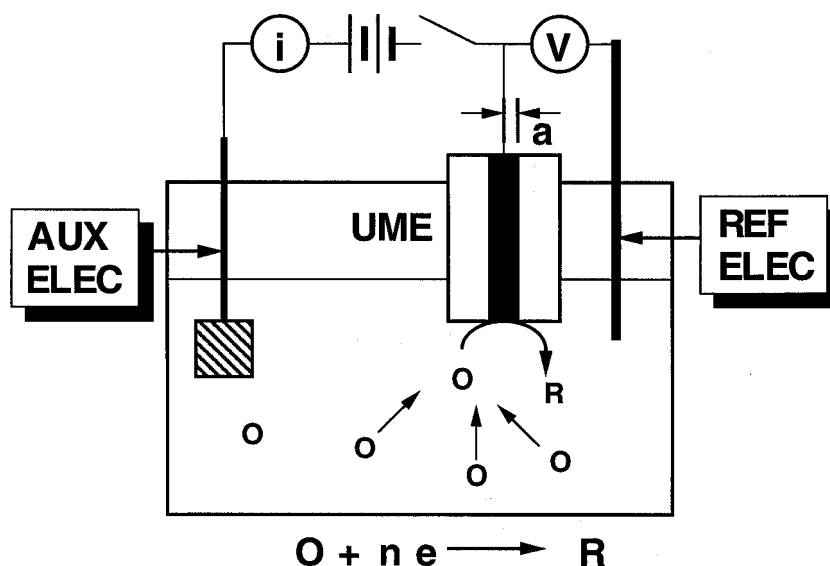


Figure 1 Schematic diagram of a cell for ultramicroelectrode voltammetry (after Bard⁷).

2.2 MODES OF OPERATION

When applied to the study of behaviour at interfaces, the UME can be considered as a scanning electrochemical microscope and can be used in different modes. Feedback mode and collection-generation represent the most common modes. These usually involve steady-state measurement but monitoring the current as a function of time (transient mode) can give information on rates of change, e.g. of local solution chemistry. The UME can be used also to induce local changes in solution composition in order to disturb the substrate reactions or adsorption at that locality, e.g. by a local increase in pH by reduction of water on the UME tip. This approach can be taken

further by inducing solution chemistry changes that lead to localised etching of certain surfaces (fabrication mode). The spatial and vertical resolution cannot be generalised as it is intrinsically linked to the size of the active tip. Conventional UMEs in SECM mode would generally give micron size resolution (typically 0.1 μm to 10 μm) but the resolution is improved considerably with nanometer-sized electrodes.

2.2.1 Feedback mode

The feedback mode can be illustrated by Figure 2.

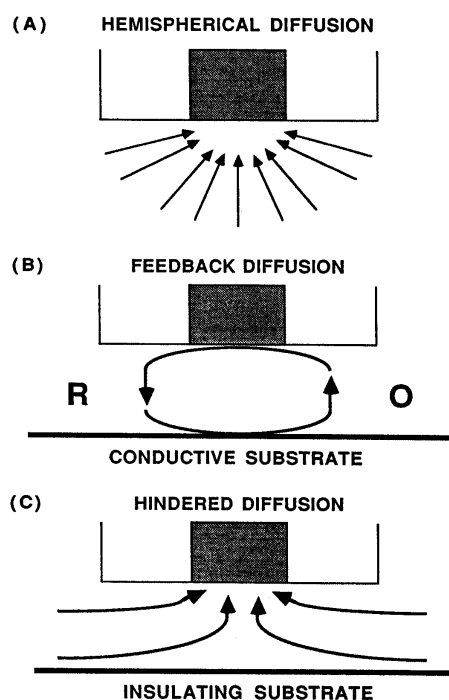


Figure 2 Basic principles of SECM; (A) far from the substrate, diffusion leads to a steady-state current, $i_{T\infty}$, (B) near a conductive surface, feedback diffusion leads to $i_T > i_{T\infty}$, (C) near an insulating surface, hindered diffusion leads to $i_T < i_{T\infty}$ (after Bard⁷).

Far from the substrate surface, with an applied electrode potential to the UME designed to give a diffusion-limiting current for reduction of species O, hemispherical diffusion to the surface is established. Now as the UME approaches the substrate, some shielding of diffusion of O to the UME from the bulk solution will be expected. This will prevail when the substrate is insulating and is often referred to as negative feedback. However, for an electrically conducting substrate (e.g. Pt), it is possible for the product of the reaction, R, to be oxidised by the substrate so long as the electrode potential of the substrate is more noble than the reversible potential for that concentration of R. This will lead to a regeneration of the reactant, O, at the UME.

The oxidant is still reduced under diffusion-limiting conditions (i.e. the concentration at the UME surface is so small as to be considered zero) by sustaining a very negative potential at the UME. However, the gap is now so small that the effective diffusion layer thickness is smaller than in (A), where the electrode is remote from the substrate,

and the current is then higher. Implicitly, this requires that the substrate is not only conducting but that the kinetics of oxidation of R are sufficiently fast so that transport to the UME is the slow step. As the gap is reduced the loss of reaction product to the bulk solution will also be minimised. Hence the current relative to the remote position will gradually increase with decreasing gap. In the limit, as the spacing goes to zero, electron tunnelling may ensue and the current will increase more markedly. The measurement of the current as a function of separation distance is referred to as the approach curve (Figure 3). The characteristics of these curves for a well-defined redox system can be used to determine the separation between probe tip and substrate using the measured current ratio and the UME radius.

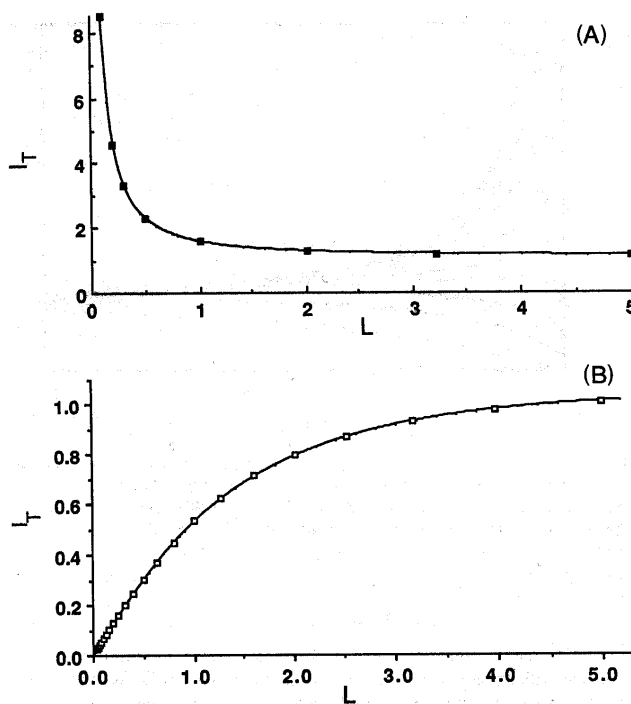


Figure 3 Diffusion controlled steady state current ($i_T / i_{T\infty}$) measured at UME as a function of dimensionless distance (distance of tip from substrate divided by UME tip radius) from the substrate; (a) conducting substrate, (B) insulating substrate. These are commonly referred to as approach curves (after Bard⁷).

2.2.2 Collection-generation modes

Under collection-generation conditions the potential of the UME and of the substrate are individually controlled. There are then two modes of operation: tip-generation/substrate-collection mode (TG/SC) and substrate-generation/tip-collection mode (SG/TC). In the TG/SC mode, the species is generated electrochemically at the UME tip at a set potential and then reacts with the substrate held at a separate controlled potential. This is a little similar to the positive feedback mode above but here the substrate potential is controlled and the net current in the substrate can then be measured. Since the substrate is usually much larger than the tip the substrate reaction is essentially 100% efficient, provided the product of the tip reaction is stable in the measurement time-scale. In the SG/TC mode, the tip is designed to measure the products of reaction from the substrate. By scanning the surface in the x-y plane it is

then possible to map out regions of activity. A scan in the z-direction, away from the substrate, will give insight as to the concentration profile, though consideration must be given to the impact of the measuring probe itself (see later).

2.3 TEST SYSTEM DESCRIPTION

2.3.1 Main features

The primary components of the scanning electrochemical microscope are shown in Figure 4. A 3-D motorised stage allows movement in the x, y and z planes at a controlled rate and should be designed such that the lateral position error is $0.2a$ or less and the vertical position error $0.002a$ or less. A video microscope is useful for monitoring the position of the tip during the approach and at other stages of the experiment in following the position of the probe relative to the scanned surface. The bipotentiostat is used in collection-generation modes as it allows simultaneous control of the potential of the two working electrodes (tip and substrate). However, two potentiostats can be adapted for that purpose, with one in floating mode.

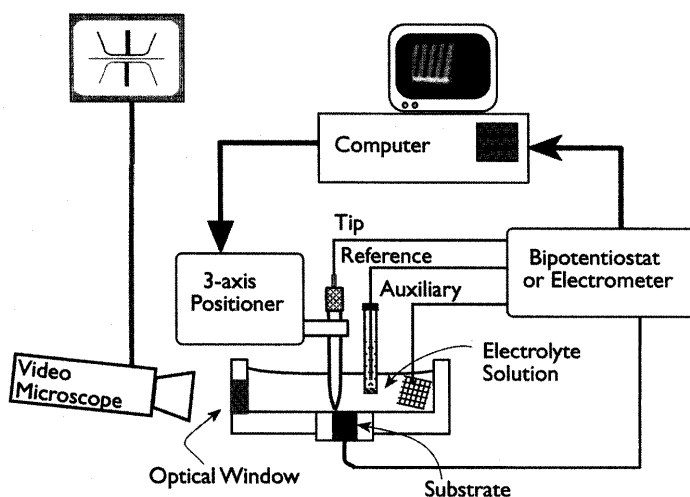


Figure 4 SECM test system set-up (after Wipf⁸).

2.3.2 Test cell

The test cell can be configured to suit the application but should be constructed with material inert in the test fluid. Examples of typical cells are shown in Figure 5. The first, with the electrodes inserted through the cover allows gas flow in principle but it is doubtful that control would be adequate and it would be more effective to have the 3-D stage etc. in a chamber. Figure 5b has the feature of a window for viewing whilst 5c is a very simple throw-away type of containment. Since the current passing is usually very small the solution volume need not be large, as uncontrolled solution chemistry changes will be small. However, if the substrate is corroding, solution chemistry changes during the course of the test may affect the result and it is convenient then to pump solution through at a rate sufficient to replenish the solution but not perturb the measurement.

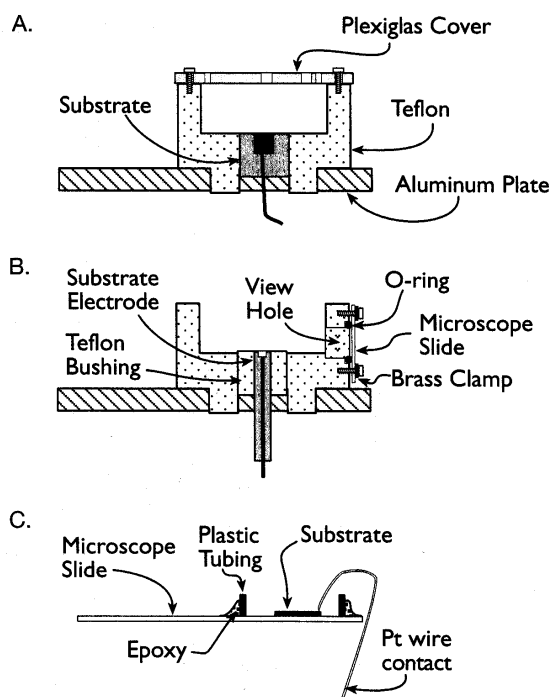


Figure 5 Examples of SECM test cells (after Wipf⁸).

2.3.3 SECM tips

2.3.3.1 UME

There is a wide range of possibilities for SECM tips but the more common forms are illustrated in Figure 6.

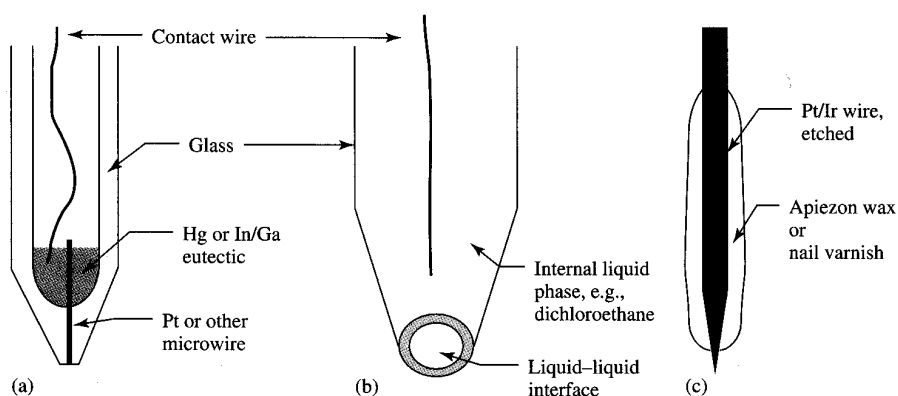


Figure 6 Examples of SECM tips (a) microdisc, (b) micropipette, (c) etched metal wire (after Horrocks⁹).

Figure 6a is typical of a conventional voltammetric UME with metal wire or carbon fibre heat-sealed in a glass capillary and the end polished to expose the cross section of the wire. The diameter of the wire would be determined by availability but $0.3\ \mu\text{m}$ is possible for Pt wires. The micropipette UME finds use in liquid-liquid interfacial measurements whilst the etched metal wire can be adopted for penetration of soft interfacial films.

2.3.3.2 AFM-SECM tips

An AFM tip (or STM tip) can be adapted to act as an electrochemically active probe so that it functions as a high resolution UME and surface topography probe. Figure 7 shows an example of an AFM tip, fabricated from metal microwires of Pt and similar¹⁰. It is essential that an insulating coating be applied such that only the very tip of the AFM is exposed. An alternative preparatory approach is to sputter coat a conducting layer onto the conventional Si AFM cantilever and then apply the insulating coating in such a way as to leave the tip-only active. In some cases a nitride layer has been used as the insulating layer and focused ion-beam machining used to generate the active region (Kranz et al¹¹).

The principle of application for AFM-SECM and SECM with more conventional UMEs is similar; there are just differences in the resolution and the degree of shielding due to the smaller tip. In particular, feedback mode as described below will be different. Interestingly, the AFM tip can be used to characterise or image the topography and electrochemical activity of a conventional UME with tip diameter of 10 μm . Warwick University have explored the use of carbon nanotubes attached to a coated AFM tip as a high-resolution sensor.

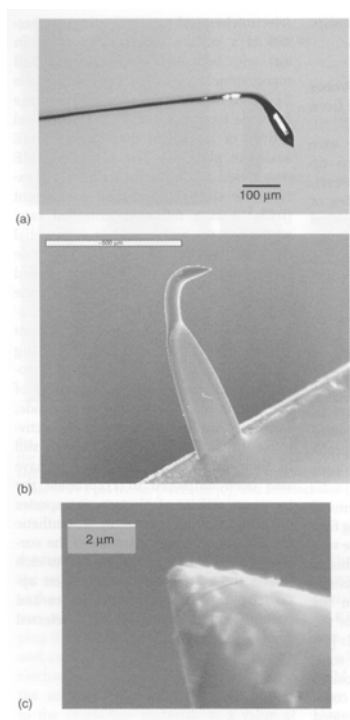


Figure 7 Example of AFM tip for AFM-SECM (after Macpherson¹⁰).

2.4 APPLICATIONS OF SECM

There is a wide range of applications for SECM that take advantage of the specific characteristics of SECM and the variety of modes in which it might be operated. In summary, the scanning electrochemical microscope can give spatial and rate information when acting as a detector of species produced by homogenous reaction in

solution or heterogeneous reaction at a substrate, or by diffusion through a membrane of some description. In the latter case, use of ion-selective electrodes instead of the UME can give a measure of diffusion of cations such as K^+ . By applying a current to the UME, the local characteristics of the system can be altered in a controlled way; e.g. modifying the solution chemistry to influence the substrate. Another feature of SECM is the ability to characterise processes in a thin liquid layer formed in moist air. The following examples demonstrate the diverse and remarkably innovative nature of the applications based on these primary features.

2.4.1 Chemical imaging of heterogeneous reaction kinetics

The SECM can be used in principle to detect and quantify differences in reaction rates at different locations on a substrate surface. In essence, the electrode is working in a collection or detection mode in which the products of reactions are oxidised or reduced or an ion-selective electrode used to monitor changes in ion concentration reflecting the local reaction rate. The application to heterogeneous reactions in general is described in detail elsewhere¹. Here we will give a couple of examples typifying the principles.

2.4.1.1 Corrosion

For corroding systems in collection mode the trick is to select a suitable redox mediator for which one of the species reacts with the product of dissolution and the other is oxidised or reduced at the UME. An example is shown for dissolution of a MnS inclusion with iodide/triiodide redox mediator in Figure 8.

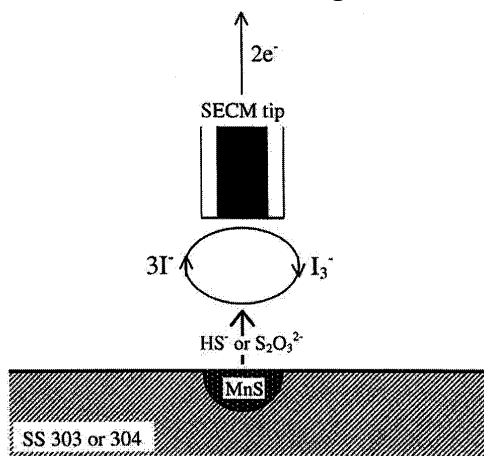


Figure 8 SECM characterisation of the kinetics of MnS dissolution (after Paik et al¹²).

The triiodide ion reacts with HS^- or $S_2O_3^{2-}$ to generate the iodide ion, which is then oxidised back to the triiodide ion at the electrode. The potential of the UME is set to a value at which the oxidation current is diffusion-limited. The current measured reflects the extent of reaction with the sulphide species and hence gives a measure of the dissolution rate. Of course, in this case, by converting the products of dissolution so rapidly, there is no opportunity for a build-up of species and there is the possibility of generating species (here elemental sulphur) that might then affect the reactions on the adjacent metal surface. Hence, care in the application of such mediators is required.

A complementary application of redox mediators in corrosion studies is the non-destructive detection of pitting precursor sites on oxide-covered electrodes. An example is Ti covered with TiO_2 . Exposed to a solution of bromide ions (or indeed iodide or ferrocyanide ions) anodic polarisation of the Ti/ TiO_2 at a constant sweep rate results in oxidation of these ions at electroactive sites, shown subsequently to be the sites of pitting attack when polarised to a more noble potential. The bromine generated at these electroactive sites is then reduced at the UME. By traversing the surface, the location of the active sites is then imaged^{13,14}.

Imaging of active corrosion can be obtained by oxidation of the product of the reaction directly, i.e. without a mediator. Wipf¹⁵ applied this to a 304 stainless steel in low chloride solution under pitting corrosion conditions. In essence the UME was oxidising ferrous ions from the active pit to ferric ions. Such a test should be conducted in deaerated solution as ferrous ions readily react with oxygen in solution to generate ferric ions. The current measured in aerated solution would underestimate the true magnitude of the dissolution current in that circumstance. Whether aerated or deaerated, the possibility of subsequent uncontrolled reduction of ferric ions on the substrate must be considered.

There is a converse situation when the consumption of the product of reaction results in steeper concentration gradients and the possibility that the probe then enhances the dissolution rate.

2.4.1.2 Adsorption-desorption

In the above section, the emphasis was on the probe acting as a monitor/detector but not disturbing the reaction process. In studying adsorption-desorption processes at surfaces the probe can be used to perturb the equilibrium and obtain information on adsorption-desorption kinetics and surface diffusion as the system responds to the disturbance. A demonstrative example is the adsorption of hydrogen ions on a metal oxide as described by Macpherson and Unwin¹⁶ and exemplified in Figure 9. The UME tip is located at a distance of about one tip radius from the surface. The system is allowed to come to equilibrium in the test solution with no current flowing in the UME. The potential of the UME is then stepped to a value at which the H^+ ions are consumed at a diffusion-limiting rate. The reaction depletes the concentration of hydrogen ions in the solution in the gap between the UME and substrate resulting in desorption of hydrogen ions from the surface in order to maintain equilibrium. There is now a surface gradient in adsorbed hydrogen ion concentration and so surface diffusion is activated. Using appropriate mass continuity equation, the time variation of the current measured at the UME can be analysed, in principle, to give quantitative information on the rates of desorption, adsorption and surface diffusion. Short-time variation in the current is considered to reflect mainly adsorption/desorption kinetics and long-time variation of the current gives insight with regard to the significance of surface diffusion and the diffusion coefficient.

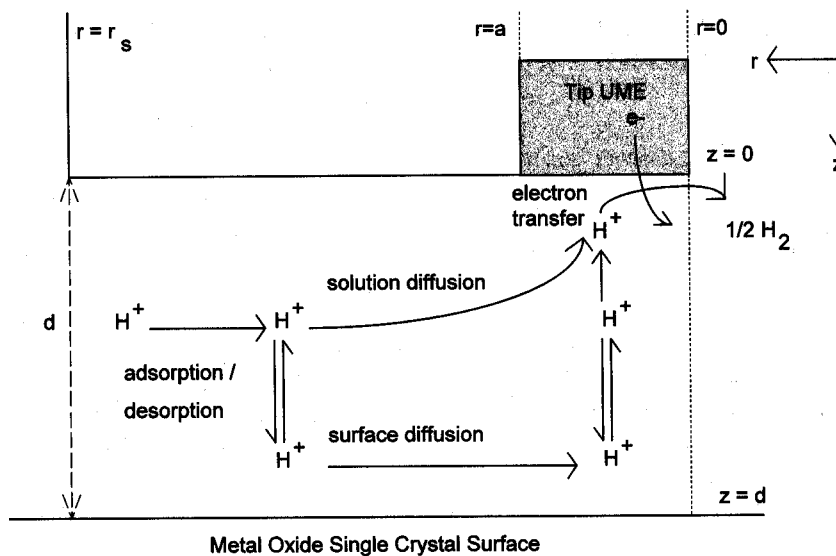


Figure 9 Application of UME for measuring kinetics of adsorption-desorption and surface diffusion (after Macpherson and Unwin¹⁶).

2.4.2 Topographical imaging

In the feedback mode the current measured will be sensitive to the distance from the surface. This feature can be used to obtain a topographical image of the surface by scanning in the x-y plane at constant height whilst monitoring the current or similarly by controlling the current constant and determining the distance from the surface, in both cases using a reference current-distance curve for the system. Some examples are indicated in subsequent sections. In generating such maps care is needed to ensure that extraneous factors such as locally active regions do not contribute to the current; e.g. giving the impression of a recess in the surface if using negative feedback mode..

2.4.3 Transport through membranes

SECM offers an opportunity for discrete measurement of transport through individual pores in a porous membrane in contrast to the spatially averaged fluxes commonly measured¹⁷. The SECM is rastered across the sample at constant height and held at a potential corresponding to diffusion-limiting oxidation or reduction of the electroactive donor species (Figure 10).

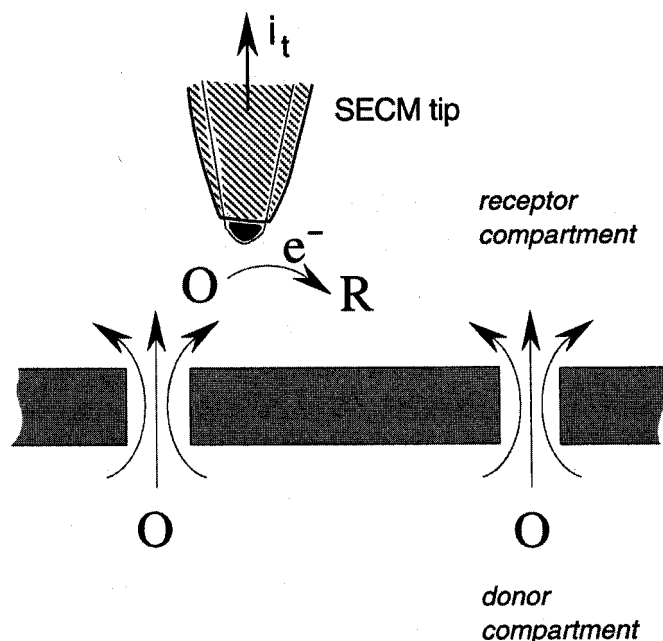


Figure 10 SECM measurement of localised molecular flux through a porous membrane. The diffusion-limited current associated with reduction of O gives a measure of molecular flux. Scanning over the surface will give an image of transport through the pores (after Bath et al¹⁷).

The magnitude of the current will reflect the local concentration of the transported species, which in turn will be proportion to the flux through the pore. Thus, an image of the distribution of flux of species is obtained, whether induced by diffusion, migration or convection through the pore. Importantly, the transport of the species from the mouth of the pore into the receptor compartment is dominated by diffusion, allowing application of relatively simple analysis based on Fick's laws of diffusion. Hemispherical isoconcentration contours of the species develop from the microscopic pore, regardless of the real shape of the pore mouth. The latter can only be resolved if the probe is positioned at a distance from the surface much smaller than the size scale of the pore.

Since the measurement of the concentration of the diffusing species by its nature consumes it, it is important to demonstrate that the result is independent of the application of the UME. The probe should be as small in active area as possible, the underlying assumption being that the local concentration at a distance from the surface is maintained by diffusion at a rate significantly higher than the diffusion-limited consumption at the UME. This is intuitively evident when the UME radius is much smaller than the pore radius. In many cases this may not apply and then the detection process affects directly the flux through the pore. This can be demonstrated by numerical analysis of the transport and reaction equations as illustrated by Figure 11.

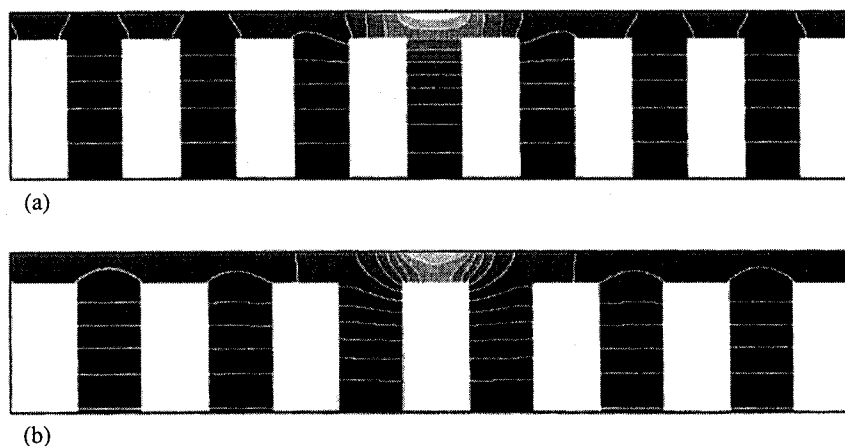


Figure 11 Theoretical prediction of the distribution of species in a model porous structure with the UME positioned directly above pore opening (a), and positioned between pores (b). The isoconcentration contours highlight the impact of species consumption by the UME in steepening the concentration gradients in the pore in (a) with some partial blocking also in position (b) (after Nugues and Denuault¹⁷).

In (a) the probe is situated above the opening of a pore and the increased concentration gradient within the pores, shown by contrast of the contour lines with distant neighbours, highlights the perturbation of the flux in the pore. The species is drawn through faster. Positioning the probe between pores is considered to have a partial blocking effect because now the inactive sheath of the UME is restricting diffusion away from the pore. These effects are inevitable as the probe approaches the pore mouth. Hence, use of a very small UME and measurement at greater distances from the surface are both effective in minimising the impact although there is a loss of image resolution in the latter case. It is suggested^{17, 18} that the perturbation of the concentration profile is negligibly small when the tip-to-surface distance is greater than about one tip radius from the surface. Clearly, measurement as a function of distance from the surface should be undertaken and the measurements compared with predictions from solution of hemispherical diffusion. However, where pores are in close proximity or when the membrane is semi-permeable, interpretation is more challenging as illustrated by the overlapping contours in Figure 12. Then, close proximity to the pore mouth is more critical if the individual flux is to be resolved.

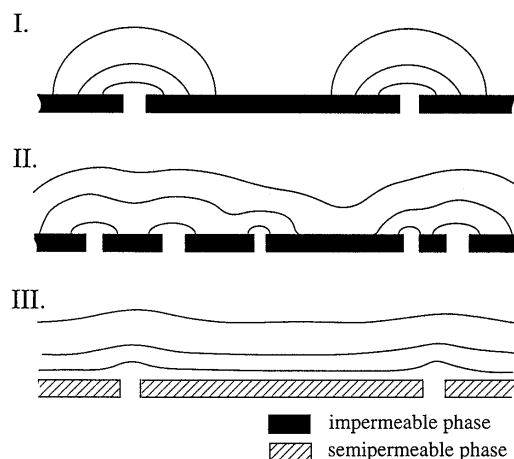


Figure 12 Isoconcentration contours above porous membranes. Transport through membranes I and II occurs exclusively through the pores in an otherwise impermeable membrane. In membrane II, transport occurs through the semi-permeable membrane also (after Bath et al¹⁷).

Bath et al suggest several strategies for imaging membrane structures and quantifying the flux of species as shown in Figure 13.

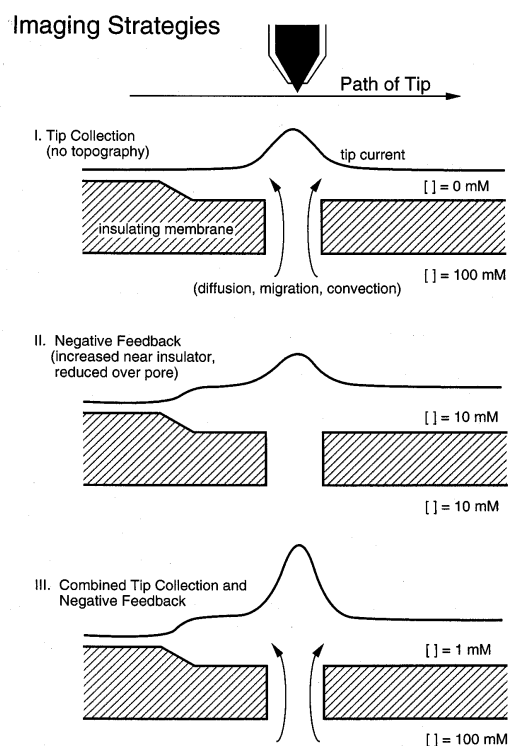


Figure 13 Possible imaging modes for SECM analysis of porous membranes – see text (after Bath et al¹⁷).

The first is as just described. The second reflects the situation where the species concentration is the same on either side of the membrane. The probe is rastered above the surface at a fixed height, but progressively decreasing after each scan, and the

diffusion-hindering effect (negative feedback) of the electrode close to the surface is used to image the pores and adjacent topography. Controlled modulation of an external driving force for transport between the two compartments during imaging can allow decoupling of topographical and pore flux components of the measured UME current. In the final mode, the concentration of the reacting species is lower in the receptor compartment but non-zero. Thence, information on topography and local flux can be obtained.

In these modes, the SECM has been used to investigate transport through synthetic porous membranes and through biological membranes. An example of the latter is characterisation of transport of a redox species through cartilage, the flux induced by osmotic pressure. The level of both spatial and quantitative information is highlighted in Figure 14. The first figure simply illustrates the measured diffusion current, relative to the value remote from the sample and the second the conversion of the data into a calculated flux.

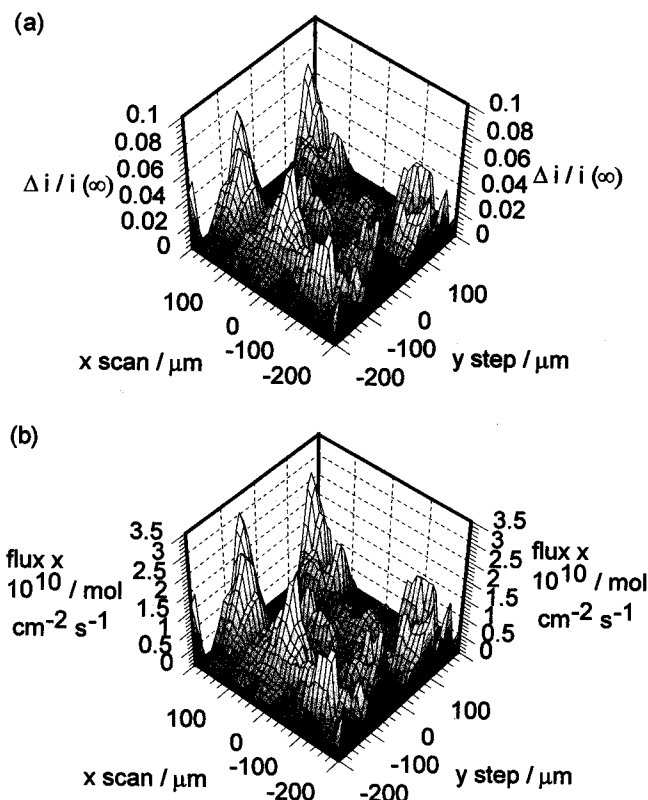


Figure 14 (a) SECM image of sample of cartilage where there are equal concentration of species ($0.01\text{ M Ru(NH}_3)_6\text{Cl}_3$ and 0.2 M KNO_3) on each side of the sample with the flux induced by applied osmotic pressure across the sample; (b) Corresponding interfacial flux image (after Macpherson et al¹⁹).

The SECM has been used also to study potassium ion transport through lipids. Lipids are a diverse group of biological substances made up primarily or exclusively of nonpolar groups that form the basic components of biological membranes. Potassium ion transfer plays a key role in “information” exchange. The potassium ions can be detected using an ion-sensitive microprobe²⁰.

Molecular transport across skin has been studied using hairless mouse skin¹⁷ as part of an investigation into transdermal transport of drugs using the principle of iontophoresis. A potential difference is placed between two electrodes placed in contact with the skin with the drug molecule, ion or neutral molecule, contained in a solution beneath one electrode. In the SECM experiment, the skin forms the membrane between the donor and receptor compartments and a species such as $\text{Fe}(\text{CN})_6^{4-}$ is placed in the donor compartment with 0.1 M NaCl as the supporting electrolyte in both compartments. An iontophoretic current is driven across the membrane and the $\text{Fe}(\text{CN})_6^{4-}$ is oxidised at the UME. By scanning across the surface it is shown that the transport is highly localised, occurring through discrete pores in the skin associated with hair follicles. With appropriate analysis, the pore radius and the flux could be determined. Such information gives insight into the ability to deliver drugs through the skin at well-defined and controlled rates.

2.4.4 Liquid-liquid interfaces

Charge transfer across immiscible electrolyte solutions (ITIES) is important in solvent extraction in hydrometallurgy, in drug delivery, in electrocatalysis and in sensors²¹. The conventional electrochemical approach is to apply a potential between electrodes located in each liquid and the current flowing between the auxiliary electrodes in each fluid is then measured. The difficulty is the resistive potential drop across the interface and the uncertainty in the details of the charge transfer process, i.e. ion transfer or electron transfer. Using SECM, common ions are added to each liquid but with different concentrations in each. This imbalance in concentration creates a “natural” potential difference between the two fluids and this provides the driving force for charge transfer. Because the SECM can be located at a very local region of the surface and probe the interface directly, it can be used to distinguish ion transfer and electron transfer and to gain information on the controlling kinetics of exchange. In addition, resistive potential drop and double-layer charging effects are minimised. The principle is commonly demonstrated as in Figure 15.

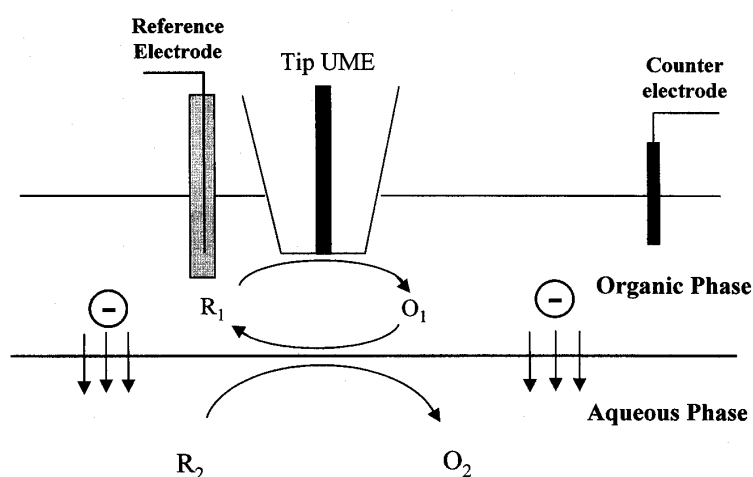
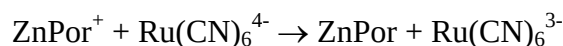


Figure 15 Schematic illustration of the feedback mode SECM measurement of the kinetics of electron exchange between organic and aqueous species (after Mirkin and Tsionsky²¹).

In the organic phase the reduced species R_1 is oxidised to O_1 at the UME. At the interface with the aqueous phase O_1 then reacts with R_2 to regenerate R_1 with the reaction product O_2 . This results in a electron transfer with the balancing exchange of ions dominated by transfer of the supporting common ion. This common description may be more easily conceptualised by a specific example



Here, the Ru(CN)_6^{4-} anion (R_2) in the aqueous phase gives up an electron at the interface to regenerate ZnPor (the reduced species R_1) in the organic phase but without any significant mass exchange of the reacting species between the two liquids, just a net electron transfer, balanced by the net common-ion transfer.

In these measurements, the UME is set at a potential at which the oxidation of R_1 is diffusion-limited and is essentially working in tip-collection mode. The current measured reflects the rate controlling process and may include contributions from diffusion of the organic phase mediator species in the gap between the UME and the interface, transport of the aqueous mediator to the interface, electron transfer, and transfer of the common ion. In principle these can be isolated; e.g, by use of high concentrations of common ion relative to reactants, excess of mediator species in the aqueous phase to limit the impact of consumption, and minimisation of the UME tip diameter.

In such studies it is important that the interface between the fluids is well-defined and its position can be determined. Typically, an approach curve would be obtained using a conducting aqueous phase with a suitable redox anion but with the non-aqueous phase containing no electroactive species. The latter acts as an insulator, and the approach curve then shows a very discrete transition in the current at the interface. It can be deduced in this case that the interface is sharp on the nanometer scale. However, there are different perspectives on the nature of the interfacial electron transfer process as highlighted in Figure 16. A significant potential drop occurs in the models represented by Figures 16a and 16b, the distinction being whether an ion-free layer exists as in (b) or a sharp transition as in (a). In contrast, the potential drop will be small in the model of Figure 16c because the electron transfer occurs *within* a mixed solvent layer rather than *across* the interfacial layer with the associated steep potential gradient. Such differences can be distinguished by SECM and the evidence suggests that the reactants do not penetrate the boundary.

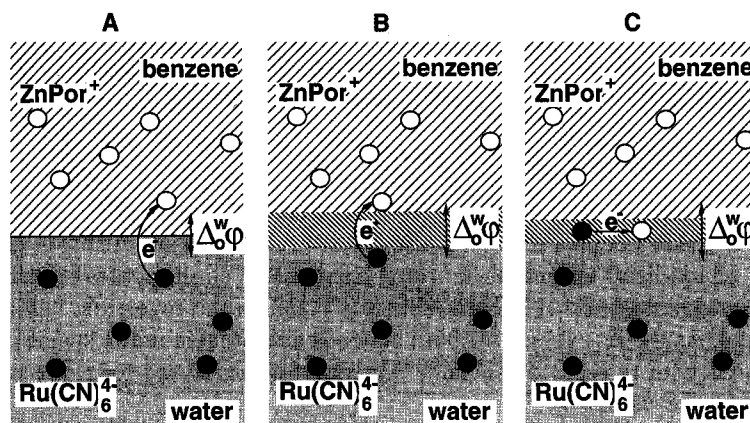


Figure 16 Different models of interfacial electron transfer between aqueous and organic phase – see text (after Mirkin and Tsionsky²¹).

In the context of understanding interfacial reactions, a “spacer” can be used in the form of a molecular monolayer. Typically this might be a lipid that dissolves in the organic phase and forms a monolayer film at the interface with the water. The orientation is such that the hydrophilic head group is immersed in water, while the hydrophobic tail remains in the organic phase. Such a monolayer will affect ion and electron transfer in different ways. Here, electron transfer occurs by tunnelling through the monolayer. The primary concern in such work is with continuity of the molecular layer and avoidance of pin-holes. It is considered²¹ that investigation of such monolayers provides a useful analogue for some biological membranes.

2.4.5 Characterisation of biological systems

Some examples have been described in the section on membranes. Wider applicability is now assessed.

2.4.5.1 Physical imaging

Physical imaging of biomolecules can be considered as topographical imaging on a molecular scale. Both positive and negative feedback approaches have been used. There has been debate^{22,23} as to whether STM imaging of biomolecules on a non-conducting substrate reflects tunnelling pathways in the biomolecule and on the mica surface or ion migration in a thin water layer formed on the biomolecule and the support, as suggested in Figure 17.

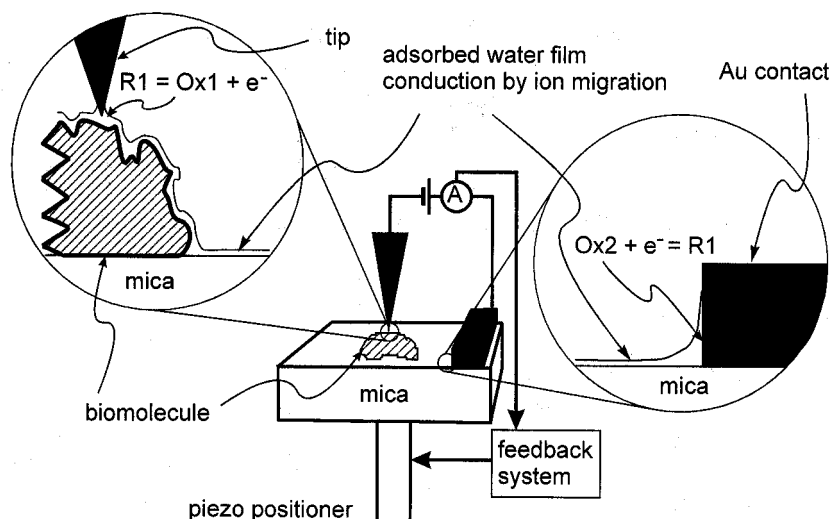


Figure 17 Mechanism of image formation with an STM-like apparatus of biomolecules on insulating supports. (after Fan and Bard²²).

Unwittingly, the STM was considered²² to be acting as a SECM, the bias voltage driving Faradaic reactions at the tip and Au contact. In fixed current scanning mode, the tip height would then generate the image of the adsorbed biomolecule but the current flow would be electrolytic rather than tunnelling. This interpretation is highly debated and needs to be confirmed.

Positive feedback in which the current is enhanced by the regeneration of the reactant consumed by the UME can be used if a layer of biomolecules is placed on a conducting sample. The biomolecules act as inhibitors to electron transfer limiting the positive feedback relative to the uncovered electrode. However, the extent of detailed information that can be deduced is limited.

2.4.5.2 Chemical activity imaging

Imaging of chemical activity is far more informative because it gives insight into the functionality of the biomolecules. Here, the imaging can represent characterisation of the kinetics of reactions and the distribution of activity of biomolecules located on a substrate. This is illustrated in generation-collection and in feedback mode in Figure 18.

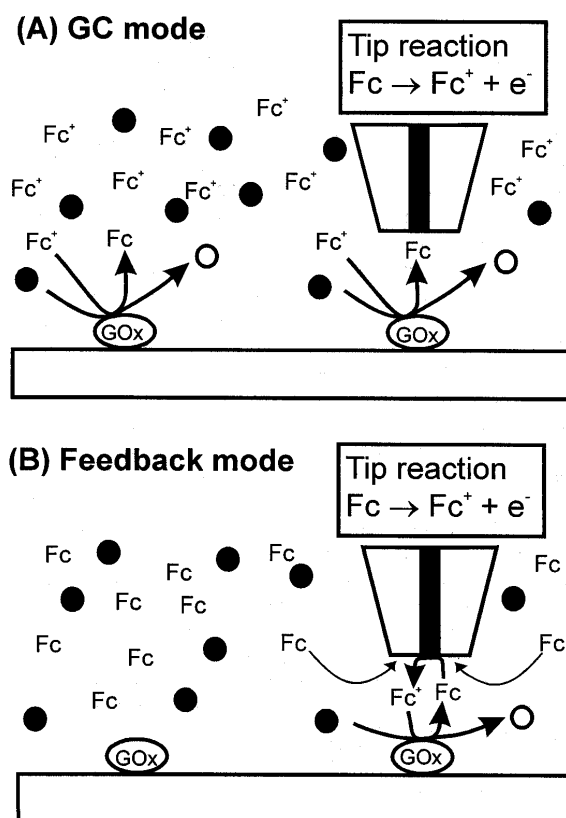


Figure 18 Schematic illustration of the difference between (A) generation-collection mode and (B) feedback mode detection of immobilised enzyme activity. Here • represents glucose and O is gluconolactone (after Horrocks and Wittstock²⁴).

An enzyme, glucose oxidase, is catalysing the transformation of glucose to gluconolactone. A redox mediator, ferrocene monocarboxylic acid (Fc) is used. Fc^+ serves as an effective artificial electron acceptor for this enzyme, sustaining the catalytic cycle (the natural one, oxygen is deliberately excluded). Thus, the kinetics of generation of the oxidised state reflects the kinetics of reaction. In generation-collection mode, the bulk solution contains the cation. This accepts electrons from the enzyme and the product Fc diffuses to the UME and is then oxidised back to the cation, the current reflecting the reaction kinetics. In feedback mode, the bulk solution contains the neutral ferrocene molecule. This is oxidised at the UME to generate the electron acceptor cation. When the tip is scanned above the sample with the enzyme located, enhanced reaction occurs because the ferrocene molecule is re-generated and is then oxidised in the feedback mode.

In feedback mode, there is an interdependence of tip and specimen reactions but in generation-collection mode, the tip acts as a passive sensor. Care must be taken in the latter mode to ensure that no reversible reactions occur, by ensuring a sufficient distance from the specimen or by applying a constant potential sufficiently removed from the reversible potential.

In more general applications the generation-collection mode involves rastering the tip across the specimens to produce a map of local concentration of species generated or

consumed at the specimen. In that sense, it is similar to more common use of the method, the only distinction being the biochemical nature of the reactions and the innovative configuration and chemistry for the application. The tip of the electrode is selected to determine the particular analyte. It is most commonly Pt but carbon fibre tips are used for neurotransmitters, Sb for hydrogen ions. The key aspect of the SECM is the positioning technology.

Imaging single biomolecules with STM-SECM has already been referred to with respect to Figure 17, as has imaging of immobilised enzymatically active layers above. There are challenges in extending the technique to imaging the activity of other biomolecules such as antibodies, DNA and so on because there is no continuous transformation of a reagent and thus no flux to play with. In principle, selectively binding an enzyme label and using the reaction processes exemplified above may overcome this. It would not be the first technique to use; fluorescence or SEM might be more readily adopted. However, it offers very sensitive detection, the molecule is not removed from solution and it does not depend on the optical properties of the specimen surface. Immobilised antibodies have indeed been imaged using SECM²⁵.

SECM has been applied also to physiology and cell biology. This has included mapping the topography of a leaf and the rate of photosynthetic oxygen production at chloroplasts *in vivo*²⁴. Resorption of bone by specialised cells known as osteoclasts has also been studied enabling determination of the rate of resorption. Such studies are important in understanding osteoporosis. The application of the latter is illustrated in Figure 19.

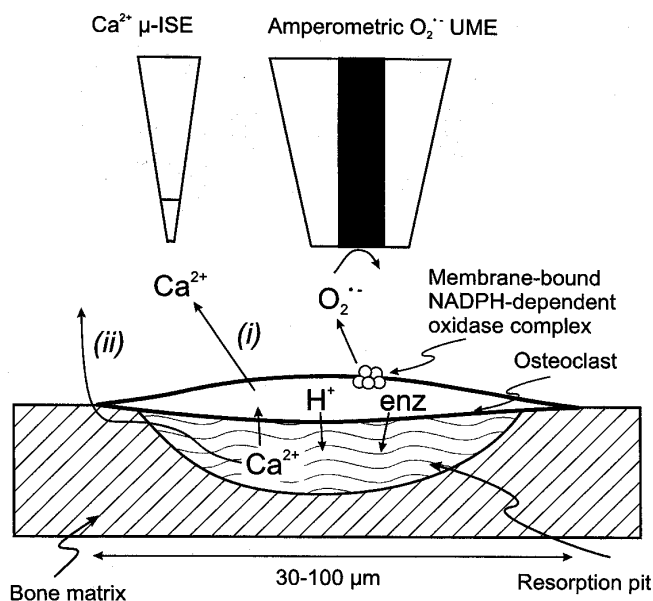
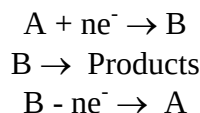


Figure 19 Illustration of the processes involved in osteoclastic resorption of bone. Two SECM tips, a potentiometric Ca^{2+} sensor and an amperometric superoxide anion sensor are shown. The osteoclast resorbs bone through secretion of protons and hydrolytic enzymes, enz, which breaks down the bone matrix. The disposal of Ca^{2+} released may occur through intracellular (i) or extracellular pathways (ii) (after Horrocks and Wittstock²⁴).

2.4.6 Homogenous reactions

The SECM can be used to study the kinetics of homogeneous reactions provided the reactions are coupled with an electrochemical reaction process²⁶. By using a suitably small UME short-lived intermediates can be identified.

The simplest example can be represented by:



Where A is reduced to B, which then decomposes with the residual B oxidised back to A.

The principle of the application of SECM is the measurement at one electrode of the fraction of the species B electrogenerated at the other electrode that survives transfer. Between the electrodes, the species is being lost by homogenous reaction, in this case decomposition, within the diffusion time determined by the spacing of the electrodes. This is exemplified in Figure 20.

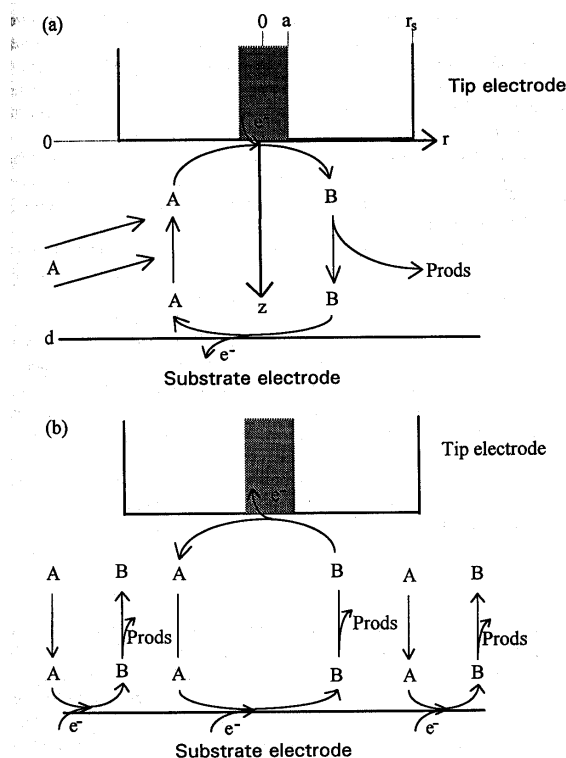


Figure 20 Principles of the feedback (TG/SC) modes in (a) and the ST/TC modes in (b) for measuring follow-up chemical reaction of electrogenerated species (after Unwin²⁶).

Here, in Figure 20a, the UME generates species B at a diffusion-controlled rate (dependent on the concentration of species A), which then diffuses to the substrate electrode (and to the bulk but to a very limited extent) decomposing as it transfers.

Species A is regenerated and diffuses to the UME tip, thereby enhancing the current at the tip in positive feedback mode. This diffusion-limited tip current reflects the regeneration kinetics at the substrate from which can be deduced the kinetics of decomposition. In this description, the conductor substrate simply acts as a base for reconverting B to A under diffusion control with no directly applied potential. An alternative approach is to directly bias the potential and measure the diffusion-limited oxidation of B as in tip-generation/substrate collection mode. In this case a bipotentiostat is required. Figure 20b illustrates this alternative approach using the substrate-generation/tip collection mode.

The advantage of SECM is the ability to study high mass transport rates by controlling the spacing and tip size thus enabling determination of the kinetics of rapid homogeneous reactions. Tip-generator/substrate collection mode is considered the most powerful in that context. Novel developments include the microjet electrode as shown in Figure 21, which allows the study of even higher rate constants in chemical reaction-electron transfer systems. Flow velocities are of the order of tens of meters per second. As a side issue, this may be considered simply as a miniaturised impinging jet system for studying erosion processes, eg. adhesion of inhibitors.

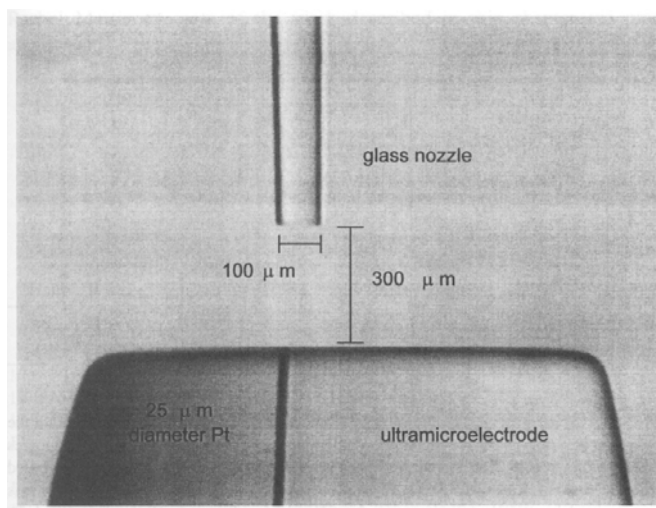


Figure 21 Micrograph of a microjet in which solution impinges at high velocity onto a UME disc (after Unwin²⁶).

2.4.7 Micro- and nano-patterning

The local nature of the electron transfer when the UME is brought close to a surface led to its application as a tool for surface modification, including metal deposition, etching, and the patterning of surfaces by enzymes. The UME is used in direct mode with the substrate as the auxiliary electrode, or in feedback mode, with the substrate unbiased and the mediator used to determine process at the substrate (Figure 22). Mandler²⁷ has described a range of possible applications. Here, a couple of examples using the feedback mode are illustrated.

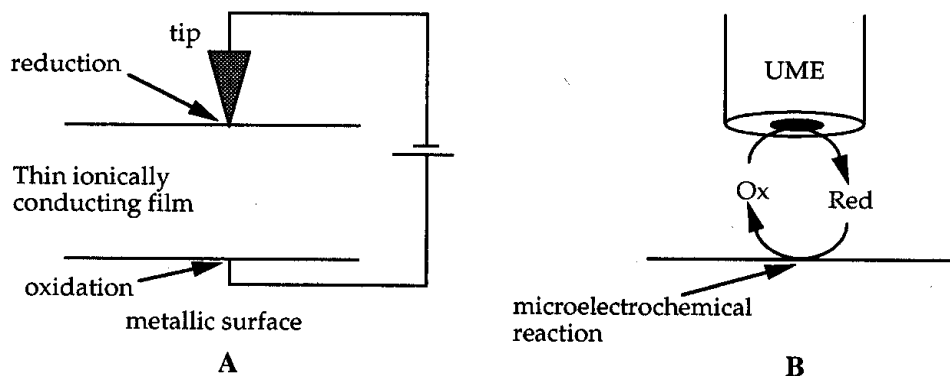


Figure 22 Schematic representation of the direct (A) and feedback (B) modes of the SECM (after Mandler²⁷).

The first example is “microwriting” of gold patterns with the SECM as shown in Figures 23 and 24. Here, a gold UME is dissolved anodically in bromide or chloride solution close to the substrate, which is negatively biased. The gold-halide ion is then reduced to gold at the substrate. The chloride (or bromide) ions are then regenerated and diffuse back to the UME to complete the feedback loop.

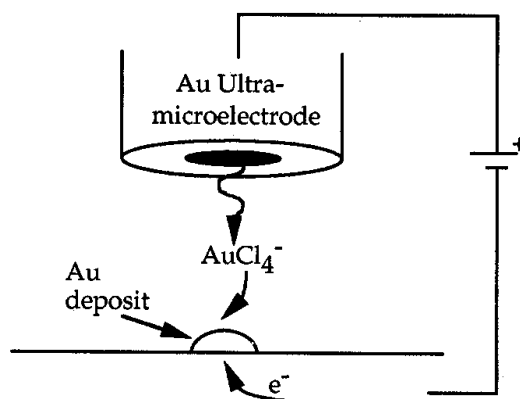


Figure 23 Schematic representation of the system for “microwriting” of gold patterns with the SECM (after Mandler²⁷).

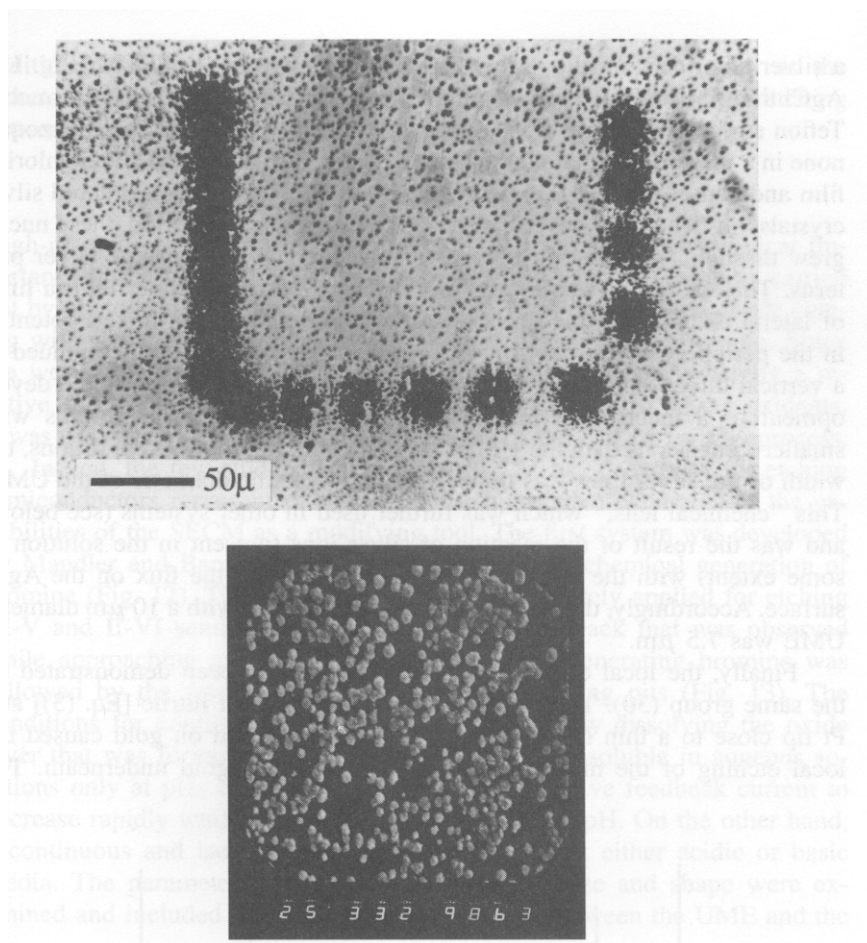


Figure 24 Top: A scanning electron micrograph of gold particles deposited on indium tin oxide substrate. Bottom: a higher resolution image showing individual gold particles of average size $1.0 \pm 0.1 \mu\text{m}$ (after Mandler²⁷).

The feedback mode can be used for semiconductor etching. Here, the bromide-bromine redox couple is used with the GaAs wafer etched by the strong oxidant (Figures 25 and 26). The bromine is regenerated by oxidation of bromide ions diffusing to the UME in the feedback loop.

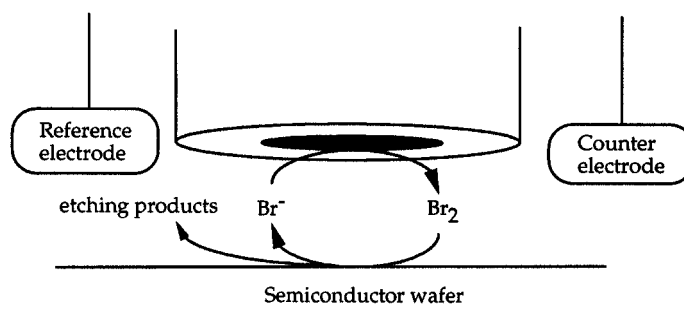


Figure 25 Processes in SEMC etching of semiconductor in feedback mode (after Mandler²⁷).

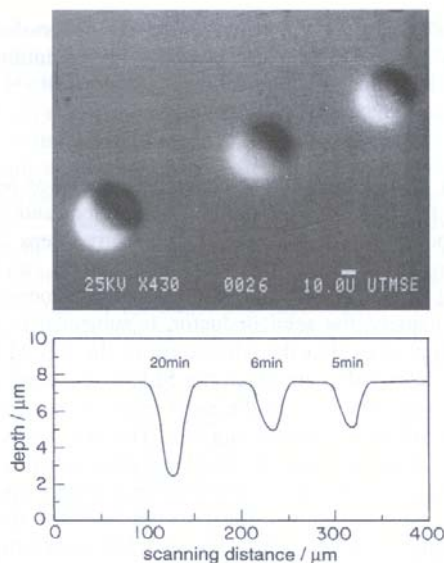


Figure 26 SEM image and profiles of etching pits on GaAs induced by a 25 μm Pt UME (biased at 1.0 V SCE) above the surface in a 0.02 M HBr/0.1 M HCl solution for different durations (after Mandler and Bard²⁸).

An alternative approach to etching, applicable to some substrates, is to induce local chemistry changes that result in dissolution of the substrate. An example is dissolution of an ionic crystal in an initially saturated solution of its solute ions. The latter is depleted by reaction at the UME, thereby inducing local dissolution.

3 ELECTROCHEMICAL-AFM

The atomic force microscope with a modified tip can be used at a high resolution SECM, the range of applications for which has been described above. Here, we focus on the intrinsic feature of the AFM, its capability for measuring the force between the sharp tip and the substrate and the application in that mode to electrochemical and corrosion measurement. The principles of AFM are illustrated in Figure 27. As Macpherson notes, the AFM can image any surface whereas the STM is constrained to (semi) conducting surfaces.

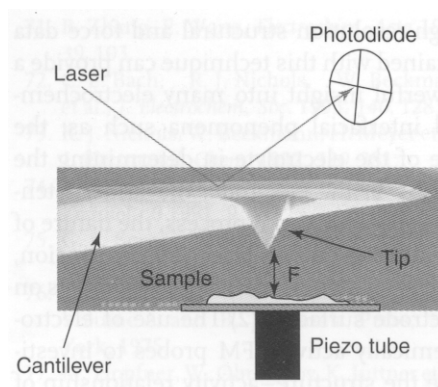


Figure 27 Illustration of basic concept of AFM tip. A force-sensing cantilever deflects in response to the force between the tip and substrate as the tip scans across the surface (after Macpherson¹⁰).

Some examples of imaging with AFM will now be described. Understanding of the role of ionic adsorbates such as halide ions is important in many electrochemical and corrosion processes. The AFM can be used to image adsorbed bromide ions and iodide ions on silver revealing the adsorbed “lattice” structure as shown in Figure 28. Here, in (a) a hexagonal structure is observed in a fluoride solution consistent with structure of the Ag(111) surface. In bromide solutions at sufficiently high potential, an adsorbed Br^- lattice structure can be discerned (b) whilst in I^- solutions, an adsorbed ion lattice structure was observed at all potentials (d).

Bromide and iodide ions are strongly adsorbed on the silver surface. In contrast, the more electronegative ions, chloride and fluoride, are highly solvated, the surface interaction is weaker and no evidence for adsorption has been observed.

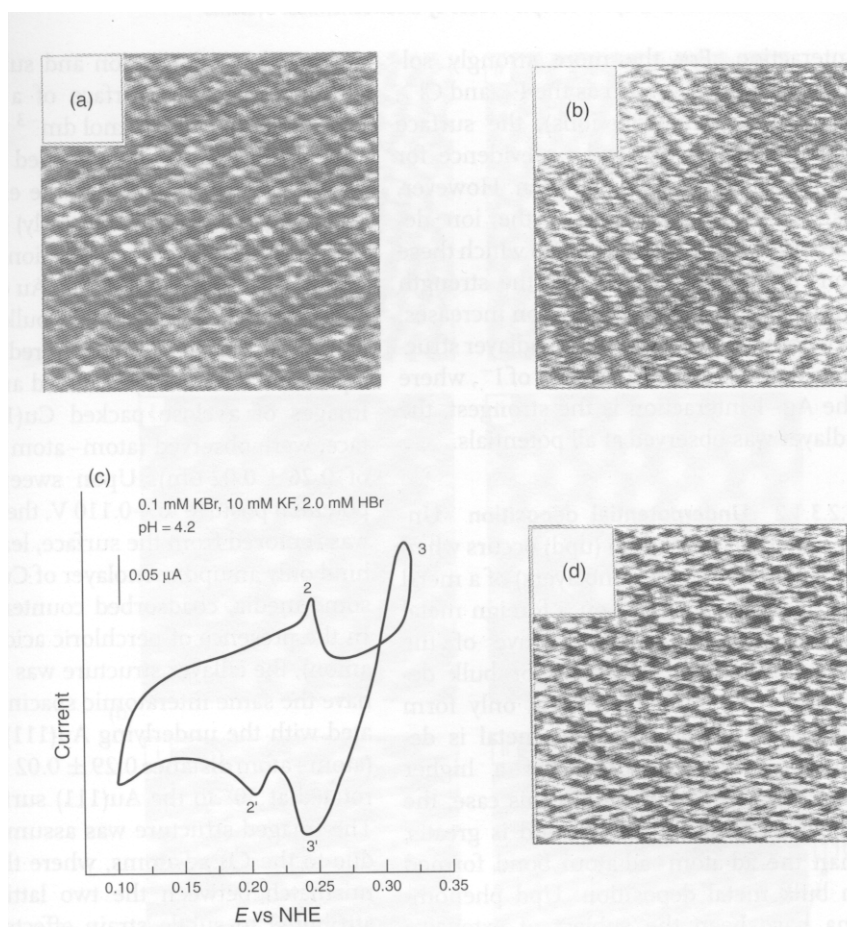


Figure 28 AFM study of halide adsorption on Ag(111). Images are 6 nm x 6nm (a) and 8 nm x 8 nm in (c) and (d) – see text (after Sneddon and Giwirth²⁹).

Underpotential deposition can also be studied. Underpotential deposition occurs when monolayers of the metal are deposited by cathodic reduction of the cation at a potential more positive than the reversible potential. The structure of the adlayer is strongly affected by co-deposition of anions and this can be readily imaged by AFM. In corrosion studies, the AFM is essentially detecting changes in local surface topography due to dissolution of the metal or particles, such as inclusions or intermetallics (reference 30 provides an example among many). Used in combination with techniques

for micro-pH measurement or fluorescence spectroscopy it can provide insight into the initial stages of attack. Another application of AFM described by Macpherson¹⁰ is the study of the time evolution of self-assembling monolayers, enabling insight into the kinetics and mechanism of adsorption. These monolayers “offer a highly ordered structure, are stable, and can be functionalised to offer a rich chemistry of functional end groups” (e.g. n-alkanethiols adsorbed on gold – see Section 8)

In addition to topographical imaging, the force-measuring capability of the AFM as the tip approaches the surface and then retracts can give information on the elasticity, charge and adhesive properties of the surface. Approach curve measurements have been used to probe the diffuse double layer at an electrode surface with nanometer resolution. The conceptual image of the double layer is shown in Figure 29 and consists of an inner Helmholtz layer containing solvent molecules and other species (ions or molecules) that are specifically adsorbed. The outer Helmholtz layer reflects the closest approach of solvated ions (non-specifically adsorbed). The thickness of the layer depends on the characteristics of the solution (see below) but can be as small as 1 nm.

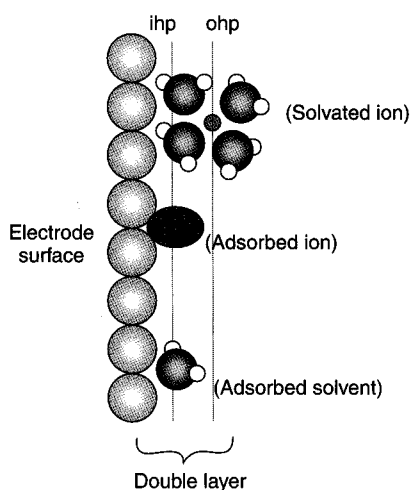


Figure 29 Schematic illustration of electric double layer at the electrode-electrolyte interface (after Macpherson¹⁰).

Such measurements have been carried out with a silica sphere attached to the tip as the geometry is then well-defined, in contrast to the uncertainty in geometry at the apex of conventional pyramidal tips at the 10 nm range. An example of the force measured in the approach mode for a gold substrate in chloride solutions at pH 5.5 with varying applied potential is shown in Figure 30. Under the solution conditions, the silica probe surface had a negative charge. For a negative electrode potential, the interaction force was repulsive indicating that the substrate surface was also negatively charged. Under these conditions, the concentration of K^+ ions increases and that of chloride decreases in the vicinity of the electrode, creating repulsion between the positive double-layers of the silica probe and the gold surface. This generates an upward deflection of the probe and a force registered as positive on the AFM. In more dilute solutions the double layer is considered to be less compressed and thus the force interaction is localised in the latter case (Figure 30).

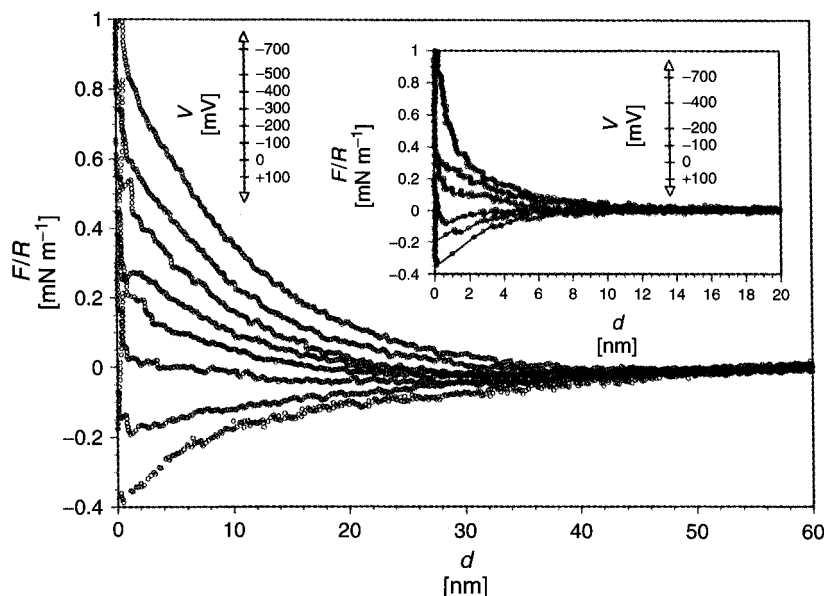


Figure 30 Force between a silica sphere and gold electrode in aqueous solution of 1×10^{-3} M KCl and 1×10^{-2} M KCl (inset) at pH 5.5 as a function of applied potential. Electrostatic repulsion decreases as the electrode potential increases from -700 to 100 mV (after Hiller et al³¹).

The substrate need not be metallic. Force-curve measurements have been used to characterise the charge of a conducting polymer film in aqueous media.

Retraction force measurement gives an indication of the adhesive properties of the surface. Here, chemically modified tips have been developed that allow measurement of intermolecular interaction.

The more conventional use of AFM for measuring topographical details has been explored extensively, for example in corrosion studies where the early stages of material removal can be imaged on a fine scale or in deposition measurements. In the latter case, contact often disturbs the surface and tapping mode is preferred as the effect is minimised (Hyde et al³²). There is an issue of whether the probe causes shielding of mass transport and affects the process that is being investigated. That should always be assessed though in the study by Hyde et al it is claimed to be relatively insignificant.

4 ELECTROCHEMICAL-STM

An overview of electrochemical-STM has been undertaken by Moffat³³. The scanning tunnelling microscope uses an atomically sharp probe tip to map contours of the local density of electronic states on the surface. A bias voltage is applied between the tip and the substrate leading to a tunnelling current of a few nA at a substrate-tip distance of a few nm. The electron tunnelling process falls off exponentially with distance enabling very high (sub-Angstrom) vertical resolution and distance control. The technique is used in constant current or constant height mode as shown in Figure 31. The first uses negative feedback to adjust the z-piezo voltage to maintain a set tunnelling conductance and is referred to as constant current imaging. The variation of the tip position in the z-

direction as the tip is scanned in the x-y plane reflects the contours of constant current density yielding information on topography and on atomic structure. The scan rate depends on the current measurement bandwidth and the speed at which the height adjustment is driven. In constant height mode, scanning can be more rapid as only the tunnelling current fluctuations are measured. In general, the use of STM requires atomically flat surfaces usually of a single crystal.

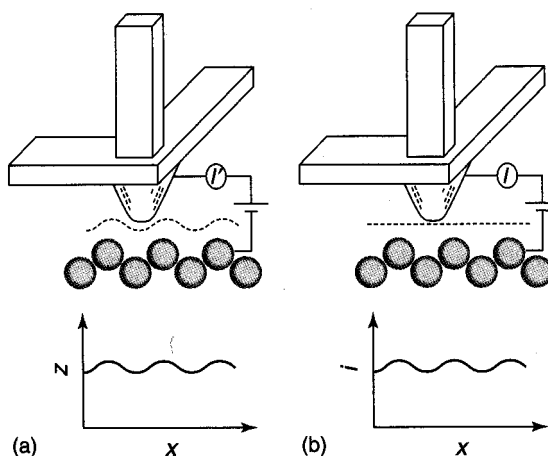


Figure 31 Schematic representation of constant current (a) and constant height (b) modes of STM operation (after Hansma and Tersoff³⁴).

In electrochemical-STM, the tip and substrate potentials are controlled independently relative to a reference electrode using a bipotentiostat. The advantage that electrochemistry offers is the ability to adjust precisely the Fermi levels of both the substrate and tip independently of each other. Test may be conducted with the tip potential, relative to the reference electrode, constant and the substrate potential changed. Alternatively, a constant bias voltage could be applied between the tip and the substrate with the electrode potential of the substrate varied.

Under constant current mode, the set current is maintained by a combination of electron tunnelling and the Faradaic process at the tip. The latter is minimised by coating the probe with an insulating layer with only the very tip exposed (similar to procedures for SECM-AFM), by careful choice of tip potential to limit the Faradaic kinetics, and by controlling the tip-substrate separation, since tunnelling only occurs at separation distances below a few nm. Imaging in STM mode has been applied to specifically adsorbed ions as the solvated ions are unlikely to exist in the junction during atomically resolved imaging (see discussion above on double layer). Specific ion adsorption will alter the local density of states and the surface dipole. Figure 32 shows an example of an image of adsorbed chloride on Cu(111) and the transition from this imaging of the anions to the underlying substrate as the tunnelling resistance is decreased³⁵. Fourier transformation can yield information on the geometry of the adsorption site.

Other applications include investigation of the influence of adsorbed ions on surface reconstruction and growth of clusters in metal deposition³⁶. A key feature is the capability for in-situ real-time measurement with atomic resolution.

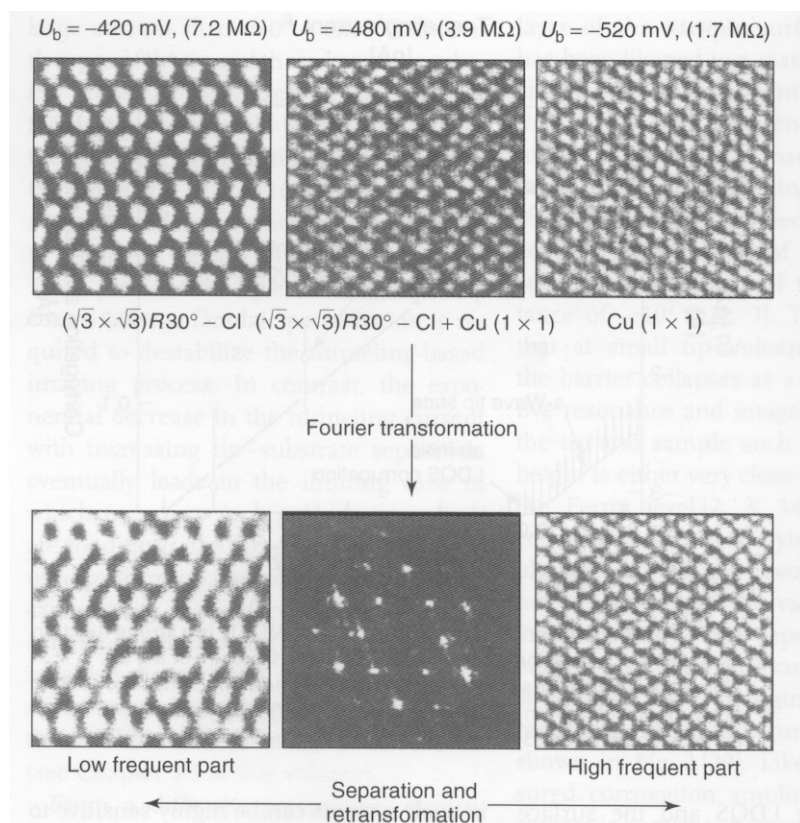


Figure 32 STM images of Cu(111) in 10 mM HCl showing the dependence of image formation on the tunnel conductance (after Broekmann et al³⁵).

5 SCANNING VIBRATING ELECTRODE TECHNIQUE

The scanning vibrating probe electrode measures the potential drop generated by current flow in a small volume of solution by vibrating Pt-Ir tipped microelectrodes between two virtual points in the electrolyte at a defined distance from the surface³⁷. The difference in potential is then amplified and the probe position moved to the next measurement point along a line. By scanning over the surface at constant height a map of the current flowing can be deduced in principle following analysis of the potential drop distribution using Laplace's equation.

In corrosion of metals, this will reflect the distribution of current associated with anodic and cathodic current at the metal surface but with decreasing resolution of local anodic and cathodic processes with distance from the surface and with increasing conductivity of the solution. For the latter reason, relatively low conductivity solutions may be necessary for some systems, sufficient to generate distinguishable potential gradients in solution.

The test system comprises of two microelectrodes mounted on a support and connected to a 3-D stage to control position and distance from the surface. The amplitude of vibration is typically 20 μm with a typical frequency (this varies according to the manufacturer) of around 600 Hz and 200 Hz respectively parallel and normal to the sample surface. A reference sample in terms of a small gold disc with an applied current of known magnitude is used as a calibration to derive a quantitative measure of the current magnitude. An example of a voltage-displacement scan across a carbon steel

weld is given in Figure 33, in this case indicating an anodic weld metal³⁸. The conversion of these voltage maps to quantitative surface current density maps requires careful analysis. Also, scanning on a macroscale can be slow compared with the rate of change of surface current densities so that the results can be deceptive, certainly following short-term exposure where rapid changes are often occurring. Moving the probe too rapidly also stirs the solution locally. The assumption of a uniform conductivity in the solution may be invalid, indeed it may not be known close to the surface. Hence, the quantitative interpretation needs to be considered carefully but it has been an effective tool in characterising welds, defects in coatings and so on.

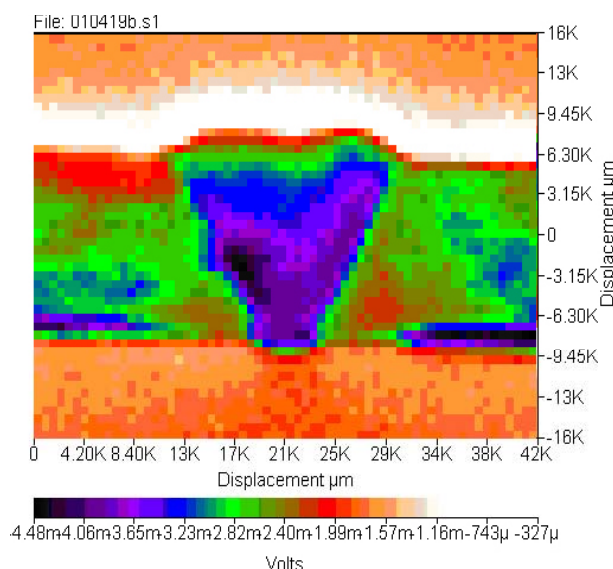


Figure 33 SVET map of carbon steel weld in ASTM seawater diluted by factor of ten showing anodic weld metal (Nimmo et al³⁸).

Novel applications include the combination of the microdroplet technique³⁹ for studying corrosion on a local area of a substrate with SVET or SECM measurement⁴⁰. An example of the set-up for the former is shown in Figure 34.

The micro-electrochemical set-up consists of a microcapillary, fixed like an objective lens in an optical microscope, containing the electrolyte, a reference electrode and a counter electrode if polarisation is required. The outer perimeter at the bottom of the capillary is sealed to achieve a very small solution volume. The tip of the capillary can be as small as 1 μm and can be positioned discretely at specific microstructural sites (Figure 35).

The SVET tip is inserted into the small volume to provide information on local variations of current and resolve galvanic coupling. The localisation of the wetting limits the influence of adjacent material, which could otherwise be a factor in investigating coupling when using conventional SVET or SECM.

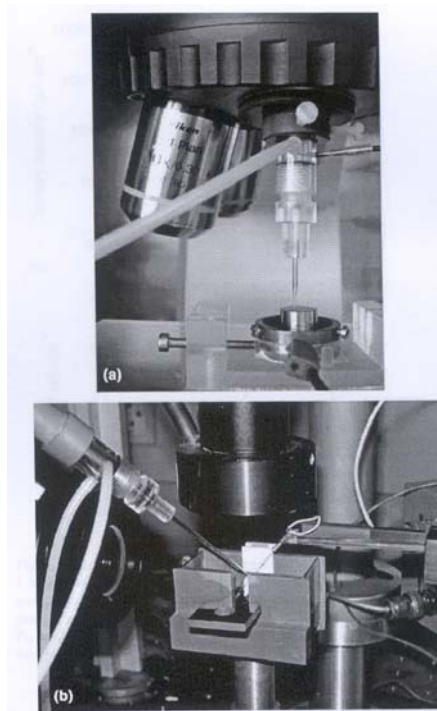


Figure 34 Set-up for local electrochemical measurements using the electrochemical microcell (a) and in combination with SVET (b) (after Krawiec⁴⁰).

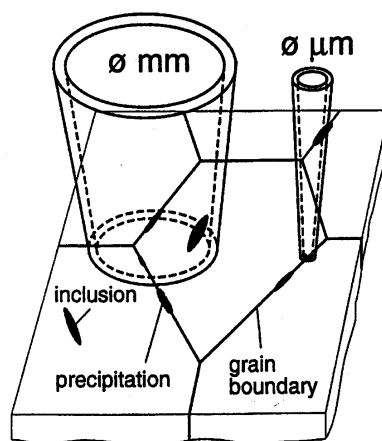


Figure 35 Schematic of microcapillary set-up for exploring specific microstructural features (after Schreyer et al³⁹).

6 SCANNING KELVIN PROBE (SKP) AND SCANNING KELVIN PROBE FORCE MICROSCOPY (SKPFM)

The Kelvin probe is a non-contact vibrating capacitor technique that measures the contact potential difference between an electrically conducting vibrating probe and an electrically conductive or partially conductive specimen. The contact potential difference arises from the difference in work function, or for non-metals the difference in surface potential, between the probe and specimen. The principle dates from the work of Kelvin⁴¹.

The SKP has a multiplicity of applications where the work function is affected by surface condition. It has applications in corrosion⁴²⁻⁴⁶, semiconductor doping⁴⁷, biological systems^{48,49} (e.g. detecting and discriminating immobilised DNA⁴⁹), catalysis⁵⁰, and organic monolayers⁵¹.

The theoretical principles have been discussed most recently by McMurray and Williams⁴². Here, we will focus primarily on metals. When the probe and specimen are electrically connected (externally, as probe and specimen do not contact), electrons will flow from the metal with the lower work function into that with the higher work function until their Fermi levels equalize. A Volta (outer) potential difference (ΔV) will become established between the metal surfaces (Figure 36), which under ideal conditions in vacuum would be determined by the difference in work functions. An electrical charge will be stored between the electrodes. If a periodic variation in the probe-specimen spacing is applied (small compared to the spacing) by vibrating the probe an alternating current will flow. The value of ΔV is then determined by nulling the current; i.e. adjusting the bias or backing potential in Figure 36 until the current flowing is zero. ΔV is then given by $-E$.

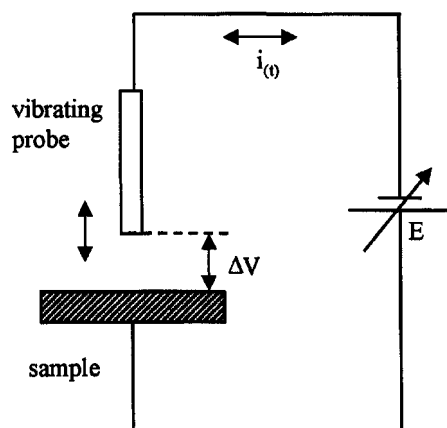


Figure 36 Schematic illustration of the principles of the SKP (after McMurray and Williams⁴²).

The standard scanning Kelvin probe microscope has a spatial resolution for potential measurement of about 100 μm with a sensitivity to potential measurement in the mV range. The advantage of the scanning Kelvin probe force microscope lies in its enhanced lateral detection limit, which can be at least 0.1 μm ⁴³. The principle is the same, with the AFM cantilever tip (metallic tip such as Pt-Ir) oscillated and the current then nulled by adding a DC voltage that balances the field as described above.

In electrochemical and corrosion studies, the probe does not touch the electrolyte, remaining in air; otherwise, Faradaic processes would arise since the probe and specimen are electrically connected. Thus, exposure is limited to adsorbed water, thin liquid layers and droplets. The technique has had a dramatic impact in the characterisation of atmospheric corrosion, corrosion under intermittent exposure conditions, and corrosion damage in coatings. The impact derives from the linear relationship between the corrosion potential and the Volta potential first demonstrated

by Stratmann et al⁴⁴⁻⁴⁶. An example from later work by Guillaumin et al⁴³ is shown in Figure 37.

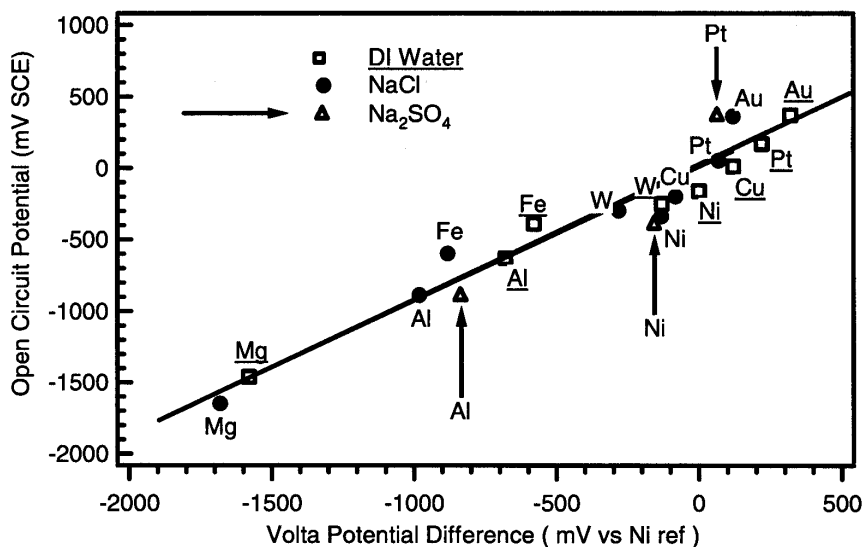


Figure 37 Comparison of the potential measured in air by SKPFM (after exposure) with open circuit potential (free corrosion potential) measured in solution: in deionised water (squares and underlined symbols), in 0.5 M NaCl and in Na₂SO₄ (after Guillaumin et al⁴³).

Thus, for the first time in atmospheric corrosion it was possible to undertake corrosion potential mapping in real time, allowing distinctions between active and inactive areas and between anodic and cathodic zones on the surface and under coatings. With the higher resolution of the SKPFM variations in local microchemistry and microstructure can be identified as highlighted by Figure 38.

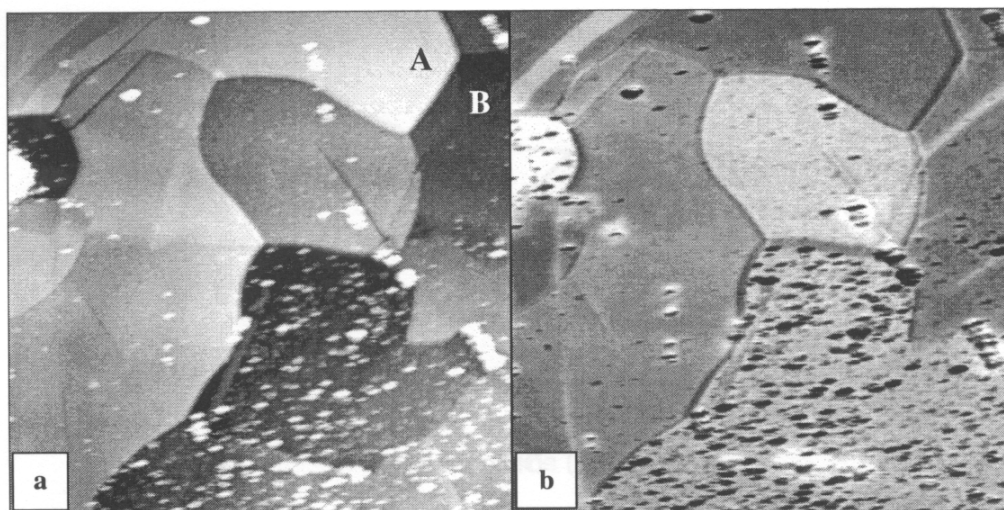


Figure 38 Comparison of (a) 2D AFM topographic image (100 μm x 100 μm and gray scale range of 800 nm) and (b) Volta potential difference distribution of the same area with a gray scale image of 0.5 V. The material is pure magnesium (after Guillaumin et al⁴³).

The tip-specimen distance is important. The Volta (outer) potential difference is constant at distances from about 100 nm to microns⁴³. However, for distances less than 100 nm, the measured potential becomes dominated by adsorbed species and typically varies with separation distance. At close proximity to the surface, the potential difference is related to oriented dipoles in the interphase region, the arrangement of which is equivalent to charge separation⁴³.

7 SCANNING ION CONDUCTANCE MICROSCOPY

Scanning ion conductance microscopy⁵²⁻⁵⁶ is a relatively novel technique that provides a new approach to bio-imaging of live cells. Topographic information, pore structure/ion channel characterization and cell volume measurement can be obtained in real time, allowing monitoring of dynamic changes.

Prater et al⁵³ give an excellent description of the function of the scanning ion conductance microscope as depicted in Figure 39. The description is so lucid that it makes sense to reproduce verbatim where appropriate.

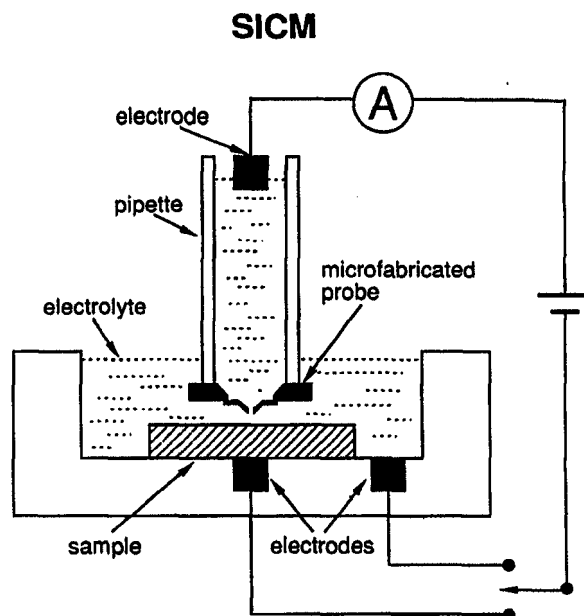


Figure 39 Schematic of the SICM (after Prater et al⁵³).

An aperture mounted on a glass capillary is filled with electrolyte. Typical aperture diameters of 200 nm have been used but micropipette tip diameters as small as 10 nm have been reported. The resolution is intrinsically related to the aperture diameter. Such glass micropipettes tend to be fragile and Prater et al have demonstrated the use of an end-cap for a glass capillary based on fabricating a hollow tip in the center of a silicon membrane. "The assembly is placed in a bath of electrolyte and positioned over the sample. A bias voltage is applied to the electrode inside the glass capillary and ions flow through the aperture to one of the two electrodes in the electrolyte bath. The ionic current is measured and used as the feedback signal for standard scanning probe microscope control electronics. The two electrodes in the bath allow the SICM to function in one of two modes: one that is sensitive only to topography and the second mode sensitive to the flow of ions through pores in a sample. In the first mode, the

electrode to the side of sample is grounded and ions flow from the aperture, over the sample, and to the grounded electrode. If the aperture is positioned so that its distance from the surface is on the same order of its diameter, the amount of current flowing from the aperture is reduced as surface features block the current flow. The sample is moved up and down on a piezo-electric translator under feedback control to keep the current constant while the sample is scanned under the tip. The vertical motion of the piezo-electric translator follows the topography of the sample. The voltage applied to the vertical axis of the piezo-electric translator is plotted as a function of position to form an image.

The second mode of operation is sensitive to ionic flow through pores in the sample. In this case the electrode directly under the sample is grounded and the ionic current flows through the aperture into the pores of the sample. The aperture is scanned across the sample without adjusting its vertical position and the current flowing through the aperture is measured as a function of position to form an image. The amount of current will increase as the aperture is brought directly over a pore. Thus, an image obtained in this mode is a map of the pores that carry the current through the sample. If the sample surface is rough, its topography also modulates the current, making the resulting image a combination of information about topography and ionic current flow through pores. In critical applications, an image formed in this mode could have topographic contributions removed by comparing it to an image taken in the topographic mode.” It is possible to actually touch the micropipette or nanopipette onto the surface to locate ion channels on a cell surface. The distinctive feature is that these can be live cells. The SICM technique has similarities to the application of SECM as described in Section 2.4.3. An example of the application for topographical imaging using a 100 nm aperture scanning nanopipette is shown in Figure 40.

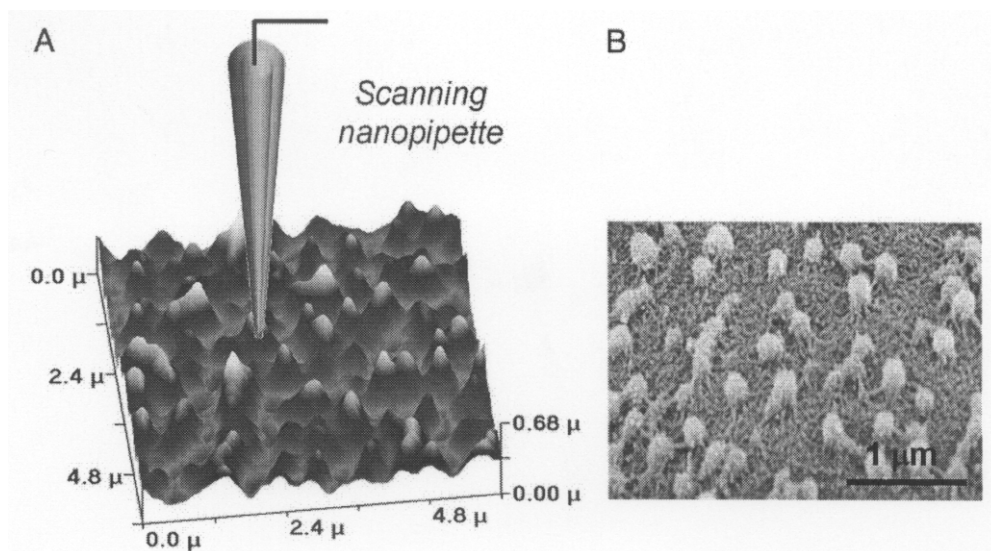


Figure 40 SICM (A) and SECM (B) image of microvillar structures in *Xenopus* kidney epithelial A6 cells (after Gorelik et al⁵⁶).

8 FUTURE DIRECTIONS

There will always be a drive towards smaller probes in order to explore to finer and finer detail the characteristics of reaction in relation to the detailed atomic or molecular structure of the substrate. An AFM tip with a carbon nanotube attached as the sensor is already being applied⁵⁷. There are limitations as closer proximity to the surface requires more careful preparation and positioning. Approach curves should be measured to ensure that they conform to theoretical predictions for the configuration.

However, perhaps the most significant advance will be the combination of techniques to explore local behaviour as suggested by Bard⁵⁸. AFM-SECM gives combined force and activity measurement but the incorporation of near-field scanning optical microscopy (NSOM) using optical fibres with light only through the tip can enable SECM and photoelectrochemical measurements⁵⁹. Electrogenerated chemiluminescence (ECL) with SECM has also been proposed as a possible exploratory tool for optical imaging. Light generated at ultramicroelectrodes can be accomplished either by radical ion annihilation (in aprotic solvents) or by a co-reactant route (also applicable in aqueous solutions). The quartz crystal microbalance can be used to monitor mass changes and link to SECM determination of species generated on a substrate.

Little work has been done on the application of SECM to study of the gas-liquid interface. However, Slevin et al⁶⁰ have developed an inverted tip that can approach an interface from below (Figure 41).

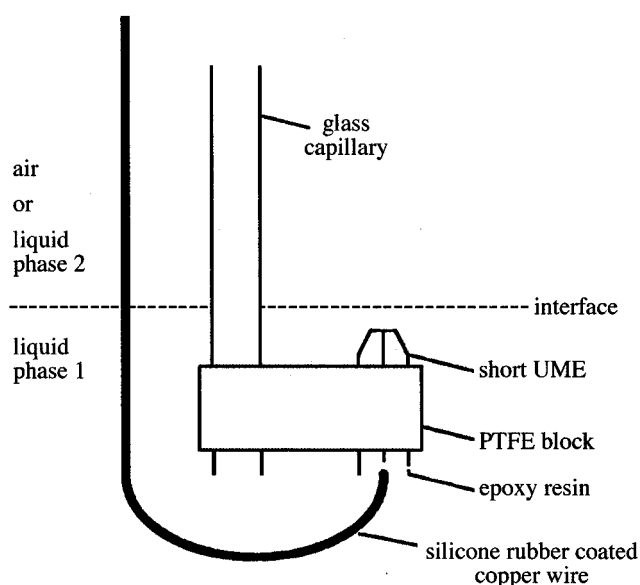


Figure 41 Inverted tip configuration of the UME for investigating the liquid-gas interface. The glass capillary is connected to the piezo positioners and the insulated copper wire makes contact to the tip (after Slevin et al⁶⁰).

This set-up allows can be used to measure transfers of species such as oxygen across the electrolyte-air interface.

Other novel applications include measurement of the conductivity of single molecular wires^{61,62}. An illustration of the spontaneous formation of individual molecular connections between a gold STM tip and a gold-coated substrate are shown in Figure 42.

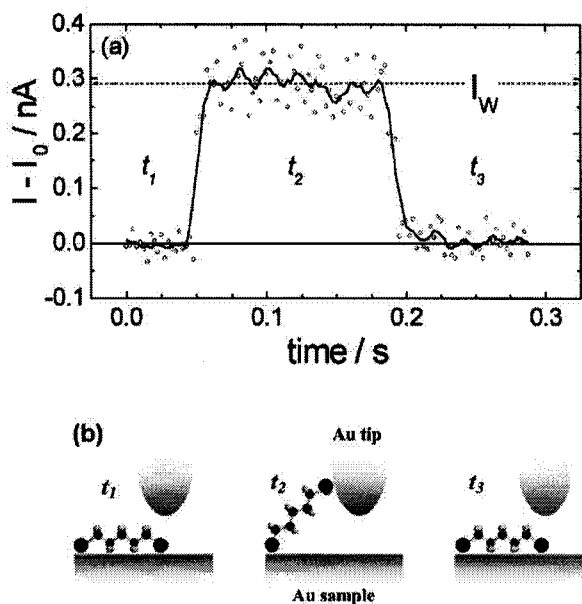


Figure 42 Typical current jumps on Au(111) covered with a small surface concentration of 1,8-octanedithiol reflecting spontaneous formation of a molecular wire between tip and substrate (after Haiss et al⁶¹).

The conductivity of the wire can be determined and it is similar to that in an electrolyte.

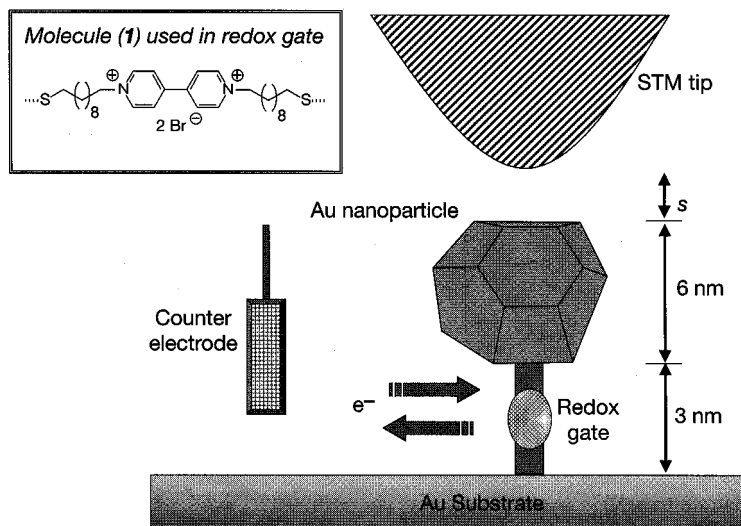


Figure 43 Schematic representation of a nanoscale redox switch (after Gittins et al⁶³).

The distinctive feature of use in an electrolyte is that it is then possible to alter the conductivity of certain molecules that have an electrochemically active moiety in the alkyl chain by varying the applied potential. An example of such a moiety is

bipyridinium, which can be reversibly reduced between its bication and cation radical states. The change in electronic structure of the molecule can be considered to constitute a nanoscale redox switch (Figure 43)⁶³.

An AFM-based cantilever stress sensor has been used to obtain in-situ information about processes occurring at the solid-liquid interface in an electrochemical environment with submonolayer sensitivity (Brunt et al⁶⁴).

Electrochemical-STM can be used to deposit a single catalyst particle of known morphology on a substrate allowing detailed study⁶⁵. More extensive arrays could be developed in principle using SECM techniques (essentially depositing Pt from a Pt⁴⁺ containing solution by pulsing the voltage). The activity of the probes in different media can then be explored by complementary SECM techniques.

A possible future development, if more on a wish-list basis at the moment, is to be able to image surface reconstruction directly using very fast video recording techniques.

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10 REFERENCES

1. A.J. Bard and M. V. Mirkin (eds), Scanning Electrochemical Microscopy, Marcel Dekker, New York, 2001
2. P. Unwin (ed), Instrumentation and Electroanalytical Chemistry, Volume 3 of Encyclopaedia of Electrochemistry, A.J. Bard and M. Stratmann *eds), Wiley-VCH, Weiheim, 2003.
3. R.C. Engstrom, W. Weber, D.J. Wunder et al, Anal. Chem., 58 (1986) 844-848.
4. R.G. Wightman and D.O. Wipf in Electroanalytical Chemistry, Ed. A.J. Bard, Marcel Dekker, New York, 1988, Vol. 15, pp 267-353.
5. A.J. Bard and L. R. Faulkner, Electrochemical Methods, John Wiley and Sons, New York, 1980.
6. A.J. Bard, F.-R. F. Fan and J. Kwak et al, Anal. Chem., 61 (1989) 132-138.
7. A.J. Bard, Reference 1, pp 1-16.
8. D.O. Wipf, Reference, pp 17-74.
9. B.R. Horrocks, Reference 2, pp 444-490.
10. J. V. Macpherson, Reference 2, pp 415-443.
11. C. Kranz, G. Friedbacher, B. Mizaikoff, A. Lugstein, J. Smoliner and E. Bertagnolli, Ana. Chem. 73 (2001) 2491-2500.
12. C.H. Paik, H.S. White and R.C. Alkire, J. Electrochem. Soc., 147 (2000), 4120-4124.
13. N. Casillas, S.J. Chalersbois, W.H. Smyrl and H.S. White, J. Electrochem. Soc., 140 (1993) L142.
14. N. Casillas, S.J. Chalersbois, W.H. Smyrl and H.S. White, J. Electrochem. Soc., 141 (1994) 636.

15. D.O. Wipf, Colloids and Surfaces A, 93 (1994) 251-261.
16. J.V. Macpherson and P. Unwin, Reference 1, pp 521-592.
17. B.D. Bath, H.S. White and E.R. Scott, Reference 1, pp 343-395.
18. S. Nugues and G. Denuault, J. Electroanal. Chem., 408 (1996) 125.
19. J.V. Macpherson, D.O'Hare, P.R. Unwin and C.P. Winlove, Biophys. J., 73 (1997), 2771.
20. S. Ameiya and A.J. Bard, Anal. Chem., 72 (2000) 4940-4948.
21. M.V. Mirkin and M. Tsionsky, Reference 1, 299-342.
22. F-R.F. Fan and A.J. Bard, Science, 270 (1995) 1849-1851.
23. R. Guckenberger and M. Heim, Response to reference 22, Science 270(1995) 1851-1852.
24. B.R. Horrocks and G. Wittstock, Reference 1, pp 445-519.
25. G. Wittstock, K.J. Yu, H.B. Halsall, T.H. Ridgway and W.R. Heineman, Anal. Chem., 67 (1995) 3578-3582.
26. P.R. Unwin, Reference 1, pp 241-298.
27. D. Mandler, Reference 1, pp 593-627.
28. D. Mandler and A.J. Bard, J. Electrochem. Soc., 137 (1990) 2468.
29. D.D. Sneddon and A.A. Giwirth, Surf. Sci., 343 (1995) 185.
30. E. Schmidt-Reider, X. Q. Tong, J.P.G. Farr and M. Aindow, British Corrosion J., 31 (1996) 139-145.
31. A.C. Hillier, S. Kim and A.J. Bard, J. Phys. Chem., 100 (1996), 18808.
32. M. Hyde, R. Jacobs and R. G. Compton, J. Phys. Chem, 106 (2002) 11075-11080.
33. T.P. Moffat, Reference 2, pp 393-414.
34. P.K. Hansma and J. Tersoff, J. App. Phys. 61 (1987) R1.
35. P. Broekmann et al, J. Electroanal. Chem., 467 (1999) 307.
36. G. Staikov and W.J. Lorenz, Electrochemical Nanotechnology, Eds. W. J. Lorenz and W. Plieth, Wiley-VCH, pp13-26.
37. H.S. Isaacs, Corros. Sci., 28 (1988) 547-558.
38. W. Nimmo, A.J. Griffiths, L.Orkney, A.Mensah and A. Turnbull, Br. Corros.J., 37 (2002) 193.182-
39. A. Schreyer, T. Suter, L. Eng and H. Bohni, Electrochemical Nanotechnology, Eds. W. J. Lorenz and W. Plieth, Wiley-VCH, 1999, pp 199-214.
40. H. Krawiec. V. Vignal and R. Oltra, Electrochemistry Communications, 6 (2004) 655-660.
41. L. Kelvin, Phil. Mag and J. Sci., 46 (1898) 46.
42. H.N. McMurray and G. Williams, J. Appl. Phys., 91 (2002) 1673-1679.
43. V. Guillaumin, P. Schmutz and G.S. Frankel, J. Electrochem. Soc., 148 (2001) 163-173.
44. M. Stratmann, Ber. Bunsenges. Phys. Chem. 94 (1990) 626.
45. M. Stratmann and H. Streckel, Corros. Sci., 30 (1990) 715.
46. S. Yee, R.A. Oriani and M. Stratmann, J. Electrochem. Soc., 138 (1991) 55.
47. G. Koley and M.G. Spenser, J. Appl. Phys., 90 (2001) 337.
48. W.F. Heinz and J.H. Hoh, Biophys. J., 76 (1999) 528
49. D. C. Hansen, K. M. Hansen, T.L. Ferrell and T. G. Thundat, Discrimination of biomolecular conformation using the scanning Kelvin probe technique, MRS Fall meeting, December 2-6, Boston, MA, 2002.
50. C.G. Vayenas, S. Bebelis and S. Ladas, Nature (London), 345 (1990) 625.
51. M. Pfeiffer, K. Leo and N. Karl, J. Appl. Phys., 80 (1996) 6880.
52. P.K. Hansma, B. Drake, O. Marti, S.A. Gould and C.B. Prater, Science, 243 (1989) 641.

53. C.B. Prater, P.K. Hansma, M. Tortones and C. F. Quate, *Rev. Sci. Instrum.*, 62 (1991), 2634-2638.
54. Y. E. Korchev, J. Gorelik, M.J. Lab, E. V. Sviderskaya, C. L. Johnston, C.R. Coombes, I. Vodyanoy and C. R.W. Edwards, *Biophys.J*, 78 (200) 451-457.
55. Y. E. Korchev, Y. A. Negulyaev, C.R.W. Edwards, I. Vodyanoy and M.J. Lab, *Nature Cell Biology*, 2 (200) 616-619.
56. J. Gorelik et al, *PNAS*, 100 (2003) 5819-5822.
57. J.V. Macpherson, University of Warwick, Private communication, 2004.
58. A.J. Bard, Reference 1, 629-638.
59. G. Shi, L.F. Garfias-Mesias and W.H. Smyrl, *J. Electrochem. Soc.* 143 (1998) 3011.
60. C.J. Slevin, S. Ryley, D.J. Walton and P.R. Unwin, *Langmuir*, 14 (1998) 5331.
61. W. Haiss, R. J. Nichols, H. v Zalinge, S.J. Higgins, D. Bethell and D. J. Schiffrin, *Phys.Chem.Chem.Phys.*, 1 (2004) 1-9.
62. W. Haiss, H. v Zalinge, H. Hobenreich, D. Bethell, D. J. Schiffrin, S.J. Higgins and R.J. Nichols, *Langmuir*, 20 (2004) 7694-7702.
63. D.L. Gittins, D. Bethell, D.J. Schiffrin and R.J. Nichols, *Nature*, 408 (2000), 67-69.
64. T.A.Brun, E.D. Chabala, T. Rayment, S.J. O'Shea and M.E. Welland, *Electrochemical Nanotechnology*, Eds. W. J. Lorenz and W. Plieth, Wiley-VCH, 1999, pp 87-100.
65. U. Stimming and R. Vogel, *Electrochemical Nanotechnology*, Eds. W. J. Lorenz and W. Plieth, Wiley-VCH, 1999, pp 73-86.