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Scanning Electrochemical Cell Microscopy: New Perspectives on Electrode Processes in Action

*Cameron L. Bentley, Minkyung Kang and Patrick R. Unwin**

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

*p.r.unwin@warwick.ac.uk

Abstract. Scanning electrochemical probe microscopy (SEPM) methods allow interfacial fluxes to be visualized at high spatial resolution and are consequently invaluable for understanding physicochemical processes at electrode/solution interfaces. This article highlights recent progress in scanning electrochemical cell microscopy (SECCM), a scanning-droplet based method that is able to visualize electrode activity free from topographical artefacts and, further, offers considerable versatility in terms of the range of interfaces and environments that can be studied. Advances in the speed and sensitivity of SECCM are highlighted, with applications as diverse as the creation of movies of electrochemical (electrocatalytic) processes in action to tracking the motion and activity of nanoparticles near electrode surfaces.

1. Introduction

Electrodes of practical importance are structurally heterogeneous on a wide range of length scales and even model electrodes (*e.g.*, single crystals) contain defects that may impact on the overall activity. Yet, in an age where nanoscience and electrochemistry are increasingly intertwined, there is an over-reliance in electrochemistry on macroscopic voltammetric techniques which are not well-suited to analyzing spatially-heterogeneous (non-uniform) electrochemical fluxes that determine the response of complex electrodes.

Scanning electrochemical probe microscopy (SEPM) methods provide a means of obtaining localized information and activity maps of electrode surfaces and the purpose of this brief review is to provide a status update on scanning electrochemical cell microscopy (SECCM), a meniscus-contact based SEPM. In comparison to the more widely-used scanning electrochemical microscopy (SECM) technique, SECCM offers a number of advantages including easy to make and characterize probes (see Section 2) that have a much more stable response than their SECM counterparts. Moreover, SECCM is designed to track the surface topography and map activity *simultaneously* and *directly*, which is still difficult to achieve in SECM. As SECCM has been described in a few earlier reviews [1-3], and the wealth of information the technique provides is well-illustrated by a recent review of sp² carbon materials [4], this article surveys recent work to demonstrate the versatility of the technique and highlights major advances that allow data to be acquired with unprecedented time resolution to open up new perspectives on electrochemistry, including movies of electrochemical processes *in-flux* and major novel insights on the interaction of nanoparticles (NPs) with surfaces.

2. SECCM: Experimental Setup and Working Principles

The instrumentation and working principles of SECCM using the double barrelled pipet format have been described in detail in a previous review [2]. In brief, as shown in Figure 1A, a potential bias (V_2) is applied between quasi-reference counter electrodes (QRCEs) placed in the barrels of a pulled theta-pipet probe (see Figure 1A, inset) to induce an ion conductance current (i_{dc}) across the liquid meniscus formed at the end of the pipet, and changes in i_{dc} are used as a feedback signal to position the probe at a set distance from the surface of interest. During operation, the probe is modulated sinusoidally normal to the surface of interest, and once contact between the meniscus cell and the surface has been established (the nanopipet itself does not contact the substrate), the ion current across the meniscus will show a periodic modulation (*ac* component, i_{ac}) at the same frequency of oscillation due to reversible deformation of the meniscus. It should be noted that although other feedback types can inform on the position of the probe over a conductive substrate (*i.e.*, surface current, as in the original single-channel scanning micropipet contact method [5-8]), the magnitude of i_{ac} informs on the status of the droplet (see Figure 1B), independent of the substrate conductivity, expanding the applications of SECCM to a variety of substrate materials, including insulators [9-11] and semiconductors [12, 13]. In addition, if the substrate material is a (semi)conductor, electrochemistry can be performed within the confined area contacted by the meniscus cell [2, 14].

By avoiding the need to fully immerse the substrate (as in SECM), SECCM opens up the possibility to work with a wide range of substrate materials, with electrodes ranging from polycrystalline metal foils (*i.e.*, “pseudo single crystal” approach [15-18]), photoactive materials (*e.g.*, semiconductors or polymers [19, 20]) and other unusual substrates (*e.g.*, transmission electron microscopy, TEM grids [21-23] or battery materials [6]). Beyond

electrode surfaces, it is worth noting that insulating materials can also be studied with this meniscus-based format, from the dissolution of crystals [10] to the titration of static charge [11].

Furthermore, combining spatially resolved electrochemical data from SECCM with information from other imaging and spectroscopic techniques [*e.g.*, electron microscopies, atomic force microscopy (AFM), electron back-scatter diffraction (EBSD) and/or Raman microscopy] applied to the same area in a *correlative multi-microscopy approach*, allows micro/nanoscale structure to be unequivocally related to function (*i.e.*, catalytic activity), which is the ultimate goal in materials science. Recent key studies demonstrating the versatility of SECCM are highlighted below.

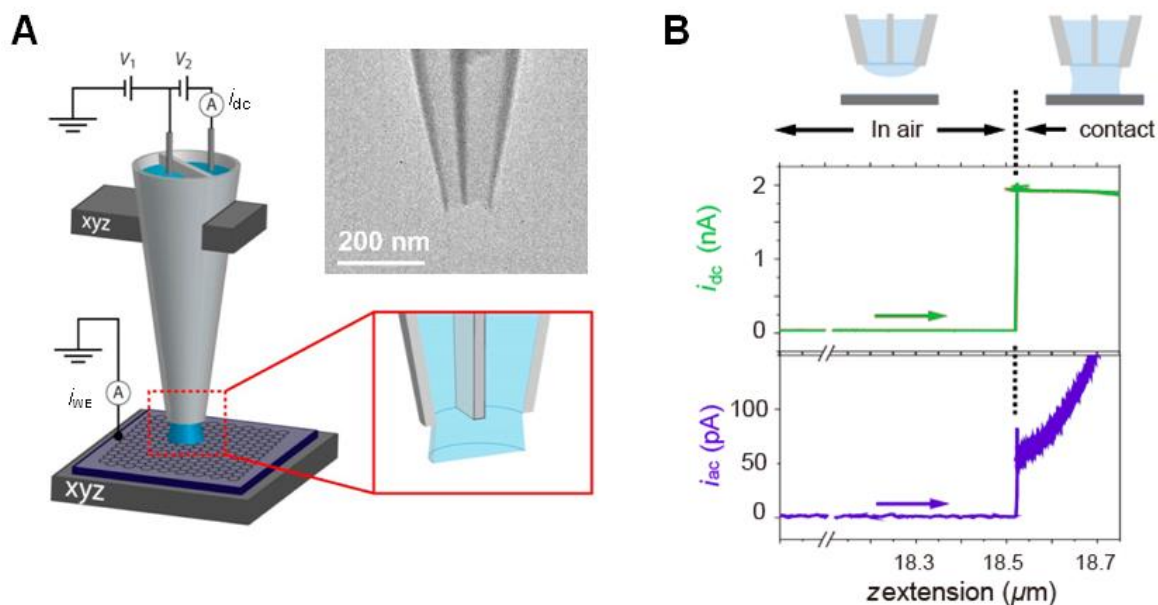


Figure 1. (A) Schematic of the scanning electrochemical cell microscopy (SECCM) setup, with a transmission electron microscopy (TEM) image of a double-barreled quartz nanopipet (radius, $r = 50$ nm) inset. (B) Approach curves of an SECCM probe with dc (i_{dc}) and ac (i_{ac}) ion conductance current plotted as a function as z extension towards the substrate. Shown above the plots are illustrations delineating three regions; in air, where no contact has been made with the substrate; jump-to-contact (dashed line); and contact. (A) was adapted with permission from ref 4. Copyright 2016 American Chemical Society.

3. Versatility in Experimental Setup

Unusual substrates. A particularly exciting substrate on which to perform SECCM is a TEM grid (see Figure 2A), as this allows direct characterization of deposited nanomaterials (*e.g.*, NPs) to resolve fully the relationship between structure and function. For example, using this approach, the initial stages of palladium electro-deposition was elucidated on a carbon TEM grid substrate, and a model for electrodeposition based on the nucleation of NPs that aggregate to form stable structures (aggregative growth mechanism) was proposed [21]. In a more recent study [23•], a chemical vapour deposition (CVD) grown graphene sheet was transferred by a polymer-free method to a TEM grid, and using SECCM, it was found that Cu-supported graphene exhibited stronger wettability than suspended graphene, as exemplified in Figure 2B.

Other unusual substrates investigated with SECCM include LiFePO_4 , a well-known Li-ion battery cathode material (heterogeneous activity was measured within individual NPs using the original single channel SECCM probe [5], which, as highlighted above, can be used if the surface of interest is entirely conducting [6]); and exfoliated graphene (*vide infra*) [24•], where the substrate comprises microscopic zones with very different properties (monolayer, bilayer, multilayer graphene etc.), and it would be extremely difficult to mask these off for investigation by conventional electrochemical techniques. Finally, the low electrochemical currents (typically pA to low nA) inherent to SECCM make it almost immune to the ohmic drop effects normally experienced during macroscopic electrochemical measurements with resistive materials such as semiconductors, making it ideal for the study of materials such as single wall carbon nanotube (SWCNT) ensembles [12] and boron-doped diamond [13].

Photoelectrochemistry. Correlating structure and function (*i.e.*, photoactivity) for photoactive electrode materials is generally challenging due to the requirements for sub-micron

spatial resolution and high signal-to-noise, as low conversion efficiencies typically result in sub-pA photocurrents. Through combination with photoillumination, SECCM (with environmental control, *vide infra*) has been shown to be a powerful technique in this application, demonstrated through high spatial resolution photoactivity mapping of thin film TiO₂ aggregates (adsorbed N719-dye, commonly used in the photoanodes of dye-sensitized solar cells, DSSCs) and *in situ* photoactivity (for the oxygen reduction reaction, ORR) measurements of an electropolymerized conjugated polymer [poly(3-hexylthiophene), P3HT] film on a transparent Au substrate [19]. Furthermore, in a follow up study [20], photo-SECCM was employed to screen P3HT films of varying thicknesses, revealing a correlation between film morphology (*i.e.*, structural disorder and thickness) and photoactivity.

Environmental control. As in conventional electrochemistry, controlling the environment can be crucial. In SECCM, when this is needed, it can be achieved using a custom-built environmental chamber (purged with Ar or N₂, see Figure 2C), which was first used in the study of triiodide (I₃⁻) reduction on Pt in an ionic liquid, where it was revealed that the kinetics of this commercially important reaction (I⁻/I₃⁻ is the most commonly used redox mediator system in DSSCs) are more facile on surfaces with the (110) orientation compared to the (100) orientation [16]. A similar approach (with flamed-annealed, and droplet-protected Pt substrates) was later employed to investigate the relationship between Pt crystallographic orientation and catalytic activity for the ORR [mixed (111) and (100) > mixed (110) and (100), see Figure 2D] and hydrazine oxidation [(111) > (100), *vide infra*] in aqueous media [17, 18]. SECCM scans can often be started within a few minutes of preparing a surface and one can check the fidelity of the scan response at similar types of surface site that are encountered at different points in the image [25, 26]. Most importantly, as with any high resolution measurement, one should carefully check – when possible – that measurements at the nanoscale map onto macroscale responses. This aspect is well-illustrated by studies of sp² carbon

electrode materials, where macroscopic kinetics measurements can be made within seconds of preparing a surface and compare very well with SECCM [4, 26].

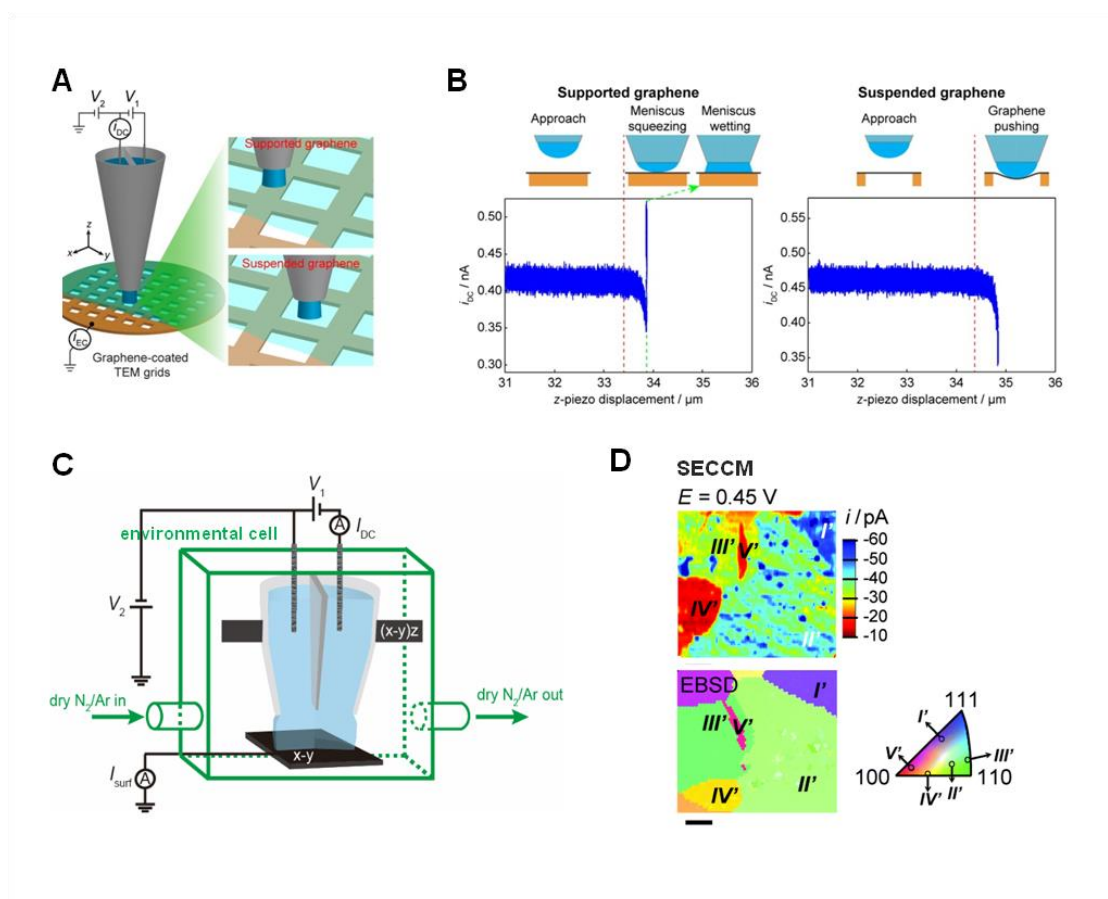


Figure 2. (A) Schematic of an SECCM pipet landing on supported and suspended parts of a graphene membrane over a Cu TEM grid (not to scale). (B) Typical approach curves demonstrating the change in i_{dc} against z -displacement over supported and suspended graphene. Dashed red and green lines indicate the position where the meniscus first contacted and wetted the graphene surface, respectively. (C) Schematic of the SECCM setup, placed in a custom-built environmental cell to control oxygen and moisture levels within the meniscus. (D) SECCM surface current image obtained at 0.45 V vs. the reversible hydrogen electrode (RHE) in 0.05 M H_2SO_4 and corresponding EBSD image of an area of a polycrystalline Pt electrode. Labels ‘I’, ‘II’, ‘III’ and ‘IV’ highlight four characteristic grains. The scale bar is 10 μm . (A) and (B) were adapted with permission from ref 23. Copyright 2016 American Chemical Society. (D) was reproduced from ref 17 with permission from the Royal Society of Chemistry.

4. Pushing the Limits: High Temporal and/or Spatial Resolution

As highlighted in a recent review [1], developments in the electronics for measuring small currents (*e.g.*, amplifiers, bipotentiostats), precise nano-positioning systems, operating interfaces (hardware and software, *vide infra*) and fabrication procedures (*e.g.*, multifunctional probes [11]) have radically advanced the speed, spatial resolution, functionality and sensitivity of SECCM and related SEPMs. Key studies demonstrating the high temporal and/or spatial resolution offered by SECCM, as well as the vast amount of information that can be obtained from a single electrochemical imaging experiment are highlighted below.

Single Nanoparticle Electrochemical Impacts (SNEI). Single NP measurements are a new frontier in electrochemistry [27]. Along with other nanopipet methods which are discussed elsewhere in this volume [28], SECCM techniques have been shown to have considerable attributes for the study of single NPs (*e.g.*, SNEI, see Figure 3A), owing to the flexibility in electrode size and material, as well as greatly enhanced signal/noise compared to alternative configurations [22, 29-32]. The importance of using a high bandwidth, high signal-to-noise measurement system was first highlighted in the study of the dynamic interaction between ruthenium oxide (RuO_x) NPs and highly-oriented pyrolytic graphite (HOPG) during the electrocatalytic oxidation H_2O_2 , where it was found that the NP impact frequency was orders of magnitude larger than could be accounted for by a single pass diffusive flux of NPs [30•], which was a concept that had dominated this field [33]. This work was the first to introduce the idea that a single NP could undergo multiple interactions with an electrode during impact studies. In a later study, the surface oxidation of single Au NPs (to form a monolayer of AuO_x) was shown to be a rapid process which can be used in NP sizing analysis and also suppresses the (electro)catalytic activity of the particles, effectively “switching off” the borohydride and hydrazine oxidation processes at highly oxidising potentials [31••]. Finally, contrary to

previous reports [34, 35], Ag NP stripping (dissolution) was shown to be a complex process, involving size-dependent ($r_{\text{NP}} = 5$ to 50 nm) partial dissolution based on various distinctive current-time ($I-t$) traces and the residence time of the NPs during impact with carbon or Au substrates (see Figure 3B) [32], which fits with optical measurements performed by Kanoufi and co-workers [36, 37]. This study again highlighted how the electrometer bandwidth could seriously affect measured signals and the resulting data analysis (see Figure 3B where the traces and data obtained with 2 electrometer time constants are compared).

High Speed Imaging. Using the SECCM platform with a spiral scanning pattern (see Figure 3C) and a frame rate approaching 4 seconds per image frame, a series of images containing ~16,500 pixels (obtained at a constant distance with different potentials applied to the substrate), with a pixel density of 1000 pixels μm^{-2} can be acquired and combined to build a movie of spatially resolved electrochemical (current) maps [1]. Using this approach, electrochemical images with nanoscale spatial resolution of individual nanomaterials are obtainable on a timescale of seconds, as demonstrated for the reduction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ on a SWCNT and the oxidation of water on iridium oxide (IrO_x) NPs adhered to an HOPG support. Interestingly, as shown in Figure 3D, the individual IrO_x NPs displayed different electrocatalytic activities as a function of overpotential, thought to be related to the morphologies of the individual clusters, demonstrating the power of this technique for elucidating structure-function (*i.e.*, catalytic activity) relationships [38••].

Voltammetric SECCM. Potential-sweep voltammetry is one of the most commonly used classical electrochemical techniques due to the wealth of information that can be obtained from a single experiment. In voltammetric SECCM, cyclic or linear-sweep voltammograms (CV or LSV, respectively) are recorded at each pixel, either after lateral movement of a defined length during meniscus contact (*i.e.*, constant distance mode [24•]) or at each hop after the probe approaches and the meniscus makes contact with the surface (*i.e.*, hopping mode [18,

39], see Figure 4A). Temporal and spatial resolution can be controlled through the voltammetric scan rate and hop distance, respectively, and each pixel provides a full (voltammetric) picture of electrochemical activity as well as topographical information. In-depth kinetic analysis can be performed through pixel-resolved Tafel analysis or finite element method (FEM) simulations and equipotential images or current “maps” can be constructed from spatially resolved current-potential (I - E) data and played back as movies.

LSV-SECCM was first applied in constant-distance mode (coupled with FEM simulations) to investigate the redox-dependent electrochemical activity of graphene and graphite step edges. These measurements established that the $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ process has very similar voltammetric characteristics (*i.e.*, wave-shape and $E_{1/4} - E_{3/4}$ values) at the basal surface and edges, but with an additional overpotential for the basal surface, which was explained through the local electronic structure (*i.e.*, local density of states) limiting the overall rate of electron-transfer near the intrinsic Fermi level of graphene [24•]. In later studies, a voltammetric hopping mode CV-SECCM regime (see Figure 4A) was adopted to investigate the electro-oxidation of hydrazine at polycrystalline Pt [18••] and blistered graphite substrates [39]. As previously alluded to, the electrocatalytic activity of Pt towards hydrazine oxidation shows a strong dependence on the surface crystallographic orientation, with grains having more (111) features showing higher activity (*i.e.*, higher currents and smaller Tafel slopes) than grains with (100) features, as shown in Figure 4B to D. Interestingly, it was also found that the presence of oxygen greatly suppressed the catalytic current on almost all grains (see Figure 4E), highlighting the importance of environmental control in hydrazine electrocatalysis [18••].

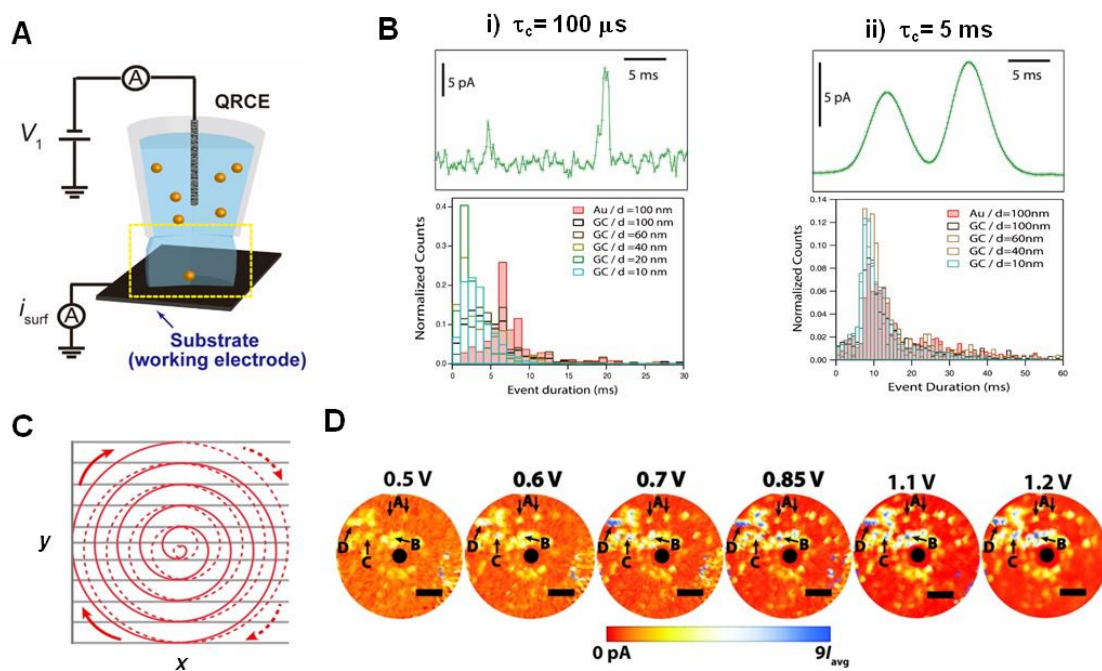


Figure 3. (A) Schematic showing the microdroplet electrochemical cell setup used in SNEI experiments. (B) $I-t$ traces (top) showing Ag NP stripping events obtained with two different electrometer time constants (τ_c), (i) $100\ \mu\text{s}$ and (ii) $5\ \text{ms}$. Histograms (bottom) of NP residence time obtained with Ag NPs of diameters ranging from 10 to 100 nm on glassy carbon (GC) and Au substrates. (C) Archimedes spiral scan pattern (red) for high-speed SECCM imaging, with the forward scan (solid line) and reverse scan (dashed line) compared with the conventional raster scan pattern (grey). (D) A series of electrochemical image frames obtained with high-speed SECCM imaging at different applied potentials (0.5 to 1.2 V vs. Ag/AgCl QRCE, 50 mM KCl) showing the electro-oxidation of water on individual IrO_x NPs adhered to an HOPG substrate. Individual IrO_x NPs are denoted as “A”, “B”, “C”, and “D” and the scale bar is $5\ \mu\text{m}$. (A) and (B) were adapted from ref 32 with permission from the Royal Society of Chemistry. (C) and (D) were adapted with permission from ref 38. Copyright 2015 American Chemical Society.

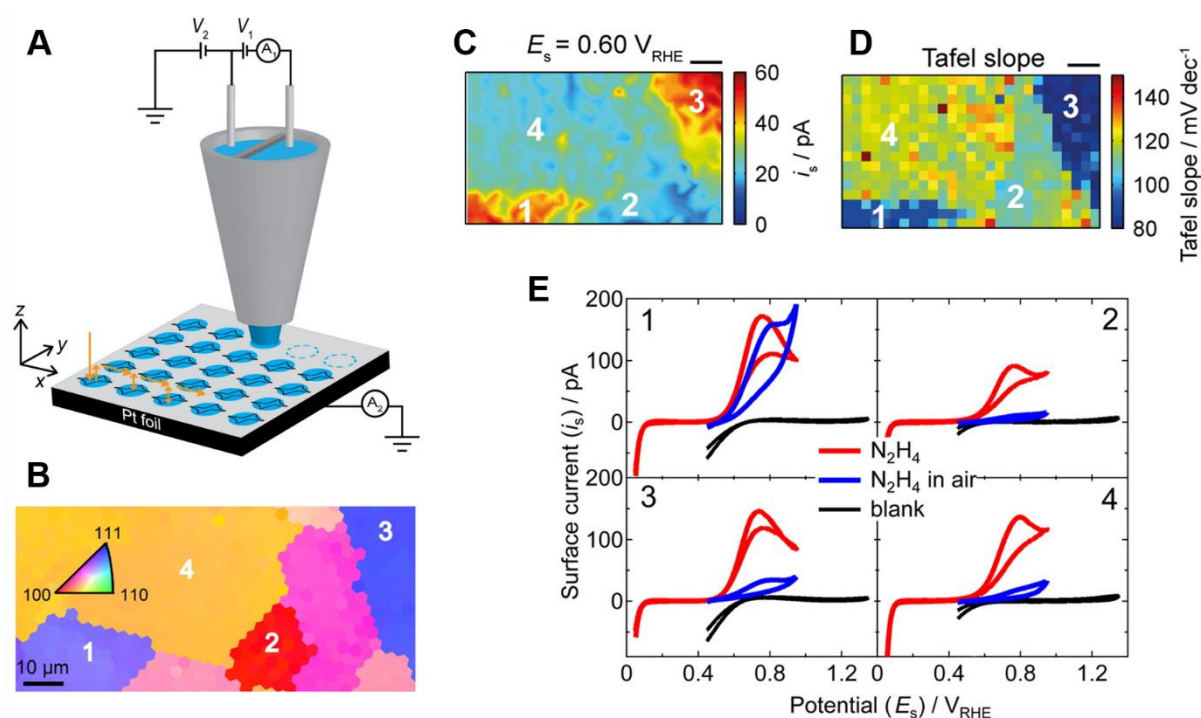


Figure 4. (A) Schematic of the voltammetric SECCM setup. The arrows show the movement of the nanopipet probe along the surface. (B) EBSD image, (C) equipotential image (current map) obtained at 0.60 V vs. RHE and (D) Tafel slope (determined in the potential range 0.45 to 0.65 V vs. RHE) map of the area of a polycrystalline Pt foil used in the hydrazine oxidation electrochemical imaging experiments. Labels “1”, “2”, “3” and “4” highlight four characteristic grains. The scale bar is 10 μm in all images. (E) Comparison of N_2H_4 oxidation in a deaerated environment (red), N_2H_4 oxidation in air (blue), and blank (in air, black), averaged CVs for different grain orientations (numbers indicated). All electrochemical experiments were recorded in a solution of 2 mM N_2H_4 (absent in the blank) and 0.1 M HClO_4 at a scan rate of 100 mV s^{-1} . Adapted with permission from ref 18. Copyright 2015 American Chemical Society.

5. Conclusions and Outlook

The way in which electrochemical processes can be studied is changing. Rather than having to rely on the analysis of a cyclic voltammogram recorded at a macroscopic electrode to derive information about heterogeneous electrode activity, with all the issues and ambiguities this entails, one can now rapidly obtain high resolution spatially-resolved information that can be played back as *movies*, to observe the evolution of fluxes in space, time and potential across an electrode surface. Immense advances result from the analysis of such datasets, especially if one also knows the surface structure from complementary microscopy or micro-spectroscopy measurements from the same area (*correlative electrochemical multi-microscopy*). The imaging techniques described in this article are of wide applicability to contemporary problems in electrochemistry and electrochemical technology, and will be powerful in studies of electrocatalysis, understanding battery electrodes and designing electrochemical sensors. We should also point out that the SECCM technique, and closely related methods, can also be used to pattern surfaces with new composite materials [40, 41] and create nano-devices [42], whose activity can be investigated with the same probe.

The strategies outlined for improving the speed, spatial resolution, functionality and/or sensitivity of SECCM can be extended to other SEPMs due to the versatility of the instrumentation and universality of the LabVIEW (National Instruments, U.S.A.) interface operating with an FPGA card [1]. Indeed, in a recent study, we showed that scanning ion conductance microscopy (SICM) can be employed to simultaneously map interfacial reactivity and surface topography in both high-speed and voltammetric modes [43]. These techniques are available on the Warwick Electrochemical – Scanned Probe Microscopy platform that provides access to a wide variety of SEPM techniques and easy means of switching between them (www.warwick.ac.uk/electrochemistry/wec-spm).

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