

Report

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**Scanning electrochemical
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ABSTRACT

Scanning electrochemical microscopy has been employed to spatially map the electrocatalytic activity of model proton exchange membrane fuel cell (PEMFC) catalyst films towards the hydrogen oxidation reaction (the PEMFC anode reaction). The model catalyst films mimicked the composition, structure and three-phase boundary conditions present in PEMFCs. The electrochemical characterisation was correlated with a detailed physical characterisation, achieved via dynamic light scattering, transmission electron microscopy and field-emission scanning electron microscopy. The platinum and carbon nanoparticle catalyst film constituents were found to be reasonably mono-dispersed, although the latter exhibited a strong tendency to agglomerate into porous bead-type structures when spun-cast. The number of carbon nanoparticles with little or no platinum was much more than would be expected based on the platinum-carbon mass ratio. Furthermore, the platinum-rich carbon particles tended to agglomerate and the clusters formed tended to be non-uniformly distributed. This morphology was reflected in a high degree of heterogeneity in the film activity towards the hydrogen oxidation reaction.

Keywords: Scanning electrochemical microscopy, SECM, fuel cell catalyst films, hydrogen oxidation, platinum nanoparticles.

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1 INTRODUCTION

Extended use of proton exchange membrane fuel cells (PEMFCs) requires a combination of increased fuel cell efficiency and reduced cost. Improvements in system management are being made but a key component is to reduce the catalyst loading per unit power output. Whilst new catalyst materials are being sought¹, processing still has an impact on catalyst performance for the carbon-supported platinum nanoparticle (NP) catalysts used in most PEMFCs. A more complete understanding of the structure-activity link in catalyst films is needed to facilitate improved processing techniques and increase catalyst performance.

Meaningful testing of catalyst efficiency currently requires evaluation in an operational fuel cell in response to current demand. However, there are many factors that affect the overall performance of a fuel cell and decoupling the performance of the catalyst from factors associated with water management, transport through the diffusion and agglomerate layers, the extent of three-phase (fuel, catalyst, electrolyte) boundaries and transport through the membrane can be difficult. Furthermore, evaluation of catalyst performance in a fuel cell is costly and time consuming. Thus, there is merit in establishing a preliminary experimental approach that allows ready ex-situ discrimination of catalytic activity with respect to catalyst loading and processing route and can rank the response to varying catalyst composition as well as different forms of the carbon substrate.

Scanning electrochemical microscopy²⁻⁴ (SECM) provides such an approach, albeit confined as yet to near ambient temperature applications (though extension to high temperature environments is a current research goal). SECM stands out as a technique able to spatially investigate the activity (mass transport, electron-transfer kinetics) of liquid/liquid, liquid/gas and solid/liquid interfaces. In the context of fuel cell research, most SECM studies have focused on very idealised samples, exploring the potential of SECM for catalyst screening using combinatorial approaches to the development of new catalyst (Pt-X) materials for both the anode (hydrogen oxidation)⁵⁻¹² and cathode reactions (oxygen reduction)¹²⁻¹⁸ in a PEMFC. Relatively little work has been done in mapping the activity of “real” catalyst films using SECM.

Herein we adopt the approach of Hiller *et al*^{6,7} to investigate the electrocatalytic activity heterogeneity towards the hydrogen oxidation reaction (HOR) and apply it to a model system that mimics the composition, structure and three-phase boundary conditions present in the catalyst layer in an actual fuel cell. Two (Pt-on-C NP) catalyst loadings were studied, 10 wt % and 60 wt %, which correspond to typical lower and upper limits for practical loadings⁵. In addition, a higher loading, and slightly different composition, catalyst film was studied comprised of 80 wt % loading of Pt:Ru catalyst particles in a multiwall carbon nanotube (MWCN) matrix. We complement the electrochemical characterisation with detailed physical characterisation using transmission electron microscopy (TEM), field-emission electron microscopy (FE-SEM), dynamic light scattering (DLS) and optical microscopy in order to obtain a physical understanding of the catalyst film morphology and to address the structure-activity link in the films.

2 EXPERIMENTAL DETAILS

2.1 MATERIAL

All chemicals and solvents used were of the highest commercially available purity and were used as received. Catalyst powders (Dart Sensors Ltd) consisted of Pt NPs supported by C Black NPs (Vulcan XC72R) in the ratios of 1-9 and 6-4 Pt-C. In addition, a Pt:Ru catalyst supported on multi-wall carbon nanotubes in a 8-2 ratio PtRu-MWCN was also studied. As a reference, a 100% C-Black powder (Fuel Cell Store) was also included. Unless specified, ratios refer to mass:mass.

2.2 FORMATION OF CATALYST LAYERS

Catalyst films were fabricated via spin coating using a Speciality Coating Systems, G3-8 spin coater. Details are described elsewhere¹⁹ and only a succinct summary is included here.

Relatively uniform and flat films can be produced using spin coating as long as a dispersed spreading solution is used and a good adherence to the substrate is achieved. The solubility of the catalyst powders in most common solvents is inherently low so a quasi-stable suspension has to be used to prepare the spreading solvents. Propan-2-ol was used as the solvent as it was found to have a propensity to prevent particulate coagulation. Once made, the solution was ultrasonicated for at least 30 minutes prior to use. This step disperses the catalyst in the solvent and drastically improves suspension uniformity. To facilitate good film coverage a high concentration of solute is required. A constant concentration of 8 mg mL⁻¹ (catalyst powder / propan-2-ol) was used for all films. This is close to the maximum amount of C-Black material that can be uniformly dispersed. Each film consisted of 4 spin cast layers sequentially deposited onto each other. Each layer was spin cast from a droplet of solution (*circa* 90 μ L) placed onto the substrate and rotated at 2000 rpm for 60 seconds with an initial acceleration time of less than 0.1 s.

It was found that substrate hydrophobicity affected film uniformity: less clumping occurred in more hydrophobic films¹⁹. Thus, highly orientated pyrolytic graphite (HOPG) was used as the substrate for SECM measurements. The HOPG was of type ZYB and was supplied (NT-MDT Ltd) in the form of 1 cm $\times$ 1 cm $\times$ 1.2 mm pieces. Prior to spin coating the basal plane (top layer) of the HOPG was cleaved using 3M Scotch tape²⁰. As well as providing a clean, flat and hydrophobic surface the HOPG acted as a conductive carbon underside for the catalyst film, akin to the carbon cloth commonly used as a backing layer in PEMFCs.

For the FE-SEM measurements, films were spin-coated onto polished single crystal (CZ) highly doped (n-type, P dopant, resistivity = 0.010 $\pm$ 0.001 Ω cm) silicon (Siltronix). Prior to spin-coating, the silicon wafers (4 inch diameter, 525 $\pm$ 25 μ m thick) were cleaved into *circa* 1 cm $\times$ 1 cm pieces with a diamond tip pen and cleaned (ultrasonicated for 5 minutes each in acetone, propan-2-ol and cyclohexane) and then blown dry with filtered compressed air. They were then rendered hydrophobic by immersion for 60 minutes in a 5% v/v solution of 1,1,1,3,3,3-hexamethyldisilazane (98% Acros Organics) in acetone, rinsed with copious amounts of acetone and then

ultrasonicated for 5 minutes each in cyclohexane, propan-2-ol and acetone, and finally blown dry with filtered compressed air.

As judged by optical microscopy¹⁹, there did not appear to be any appreciable differences in the films deposited on HOPG and silanised Si.

2.3 PHYSICAL CHARACTERISATION

A small amount of film material accumulation occurs, as a by-product of the spin coating procedure, at the edge of the substrate. Therefore, all physical characterisation was measured at, or near, the centre of the films.

Dynamic light scattering (DLS, also known as Photon Correlation Spectroscopy) measurements of a suspension of the catalyst powder were carried out with a PD Expert (Precision Detectors) workstation. DLS is a commonly used technique for the characterisation of sub-micron particle size in colloidal suspensions, providing a statistical average of particle size taken from many thousand measurements. Dilute (10^{-3} mg mL⁻¹) and freshly ultrasonicated (> 60 mins) propan-2-ol solutions of the catalyst powders were measured. Ten measurements were recorded and the results are the average of these.

Optical microscopy was carried out with a Medline Scientific Ltd Ferox PL inverted microscope equipped with a 3MP digital camera and placed on an optical table.

Field-emission electron microscopy images were taken with a Zeiss Supra 40 microscope operating at 10 kV. Most images were taken with the high efficiency in-lens detector at working distances of 3 mm - 4 mm. A small drop of silver-loaded conducting paint (RS) was used to make an electrical connection between the surface of the substrate and the underlying metal chuck.

Transmission electron microscopy images were taken on a Jeol 2000 FX microscope operating at 200 kV. Carbon-supported copper grids (400 mesh, Agar scientific) were used. For experimental reasons, drop-casting was more appropriate than spin casting to fabricate the films. For this, two drops of 10^{-3} mg mL⁻¹ Pt-C 6-4 propan-2-ol solution were carefully placed on them and left to evaporate over a hotplate set at 50°C. The carbon film provides a mechanical support but is sufficiently thin to be transparent to the electron beam.

2.4 ELECTROCHEMICAL MEASUREMENTS

All electrochemical measurements were made in aqueous solutions made from deionised water (15 MΩcm). 1 mM Ferrocenemethanol (FcMeOH, 97%, Acros Organics) and 10 mM sulphuric acid (Fisher Scientific) were used as redox mediators with 50 mM potassium sulphate (Fisher Scientific) as the supporting electrolyte. Unless stated otherwise the electrolyte solution comprised of FcMeOH, sulphuric acid and potassium sulphate. For the voltammetry under a 1 atm hydrogen gas atmosphere the FcMeOH was omitted. A relatively high concentration of supporting electrolyte was always present to suppress migration currents, thus making diffusion the predominant mode of mass transport. All voltammetry sweeps were recorded at a scan rate of 50 mV s⁻¹.

For the hydrogen oxidation voltammetry experiments, hydrogen gas was produced with a hydrogen generator (HOGEN 40, Proton Energy Systems) and bubbled through the electrolytic solution at a rate of 100 mL min^{-1} for at least one hour prior to any electrochemical measurements to ensure deaeration and saturation with hydrogen. Bubbling of hydrogen gas through the solution was maintained at this rate during the electrochemical experiments.

The working electrodes for voltammetry measurements consisted of 2 mm diameter Pt and 4 mm diameter glassy C disk electrodes (MF-2012 and MF-2013 respectively, Bioanalytical Systems) as well as a $10 \text{ }\mu\text{m}$ diameter Pt disk ultramicroelectrode (UME, CH Instruments) which was used for all SECM experiments. The UME was encased in borosilicate glass in a conical shape to produce a disk-in-plane geometry with an RG ratio of 8 (where $\text{RG} = r_g/a$, where a and r_g are the UME and probe tip radius respectively).

All working electrodes were polished with $0.05 \text{ }\mu\text{m}$ alumina slurry (Agar Scientific) prior to use. The UME was pre-treated by potential cycling between water oxidation and hydrogen evolution in 0.5 M sulphuric acid, followed by thorough rinsing in deionised water. The surface of the UME was inspected for remaining alumina and/or scratches under an optical microscope prior to any measurements.

A Ag/AgCl (3M KCl) electrode ($E = 0.196 \text{ V vs SHE}$, CH Instruments) was used as the reference electrode for all experiments and all potentials herein are quoted with reference to it. A $1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ mm}$ Pt foil and a 0.5 mm thick Pt wire were used as the auxiliary electrodes for the bulk voltammetry and SECM experiments respectively.

The SECM (CHI 900B SECM, CH Instruments) was computer controlled and consisted of a bipotentiostat to generate and record the electrochemical signals and piezo inchworms (Burleigh Instruments Inc) to control the x-y-z displacement. The SECM was placed on a vibration isolation workstation (Newport) and employed a PTFE cell mounted on a tilt-levelling plate to reduce sample tilt. A schematic of the SECM is shown in Figure 1.

SECM mapping was carried out in feedback mode^{2,21} where a faradaic current is measured at the UME in response to an applied potential at the tip. The scan rates for the SECM mapping ranged from $25 \text{ }\mu\text{m s}^{-1}$ to $75 \text{ }\mu\text{m s}^{-1}$. For the SECM scans, the tip-sample separation was set, at the origin, at $5 \pm 2 \text{ }\mu\text{m}$ (the uncertainty due to inchworm backlash), determined via approach curves, *vide infra*. The approach curve speed was $10\text{--}25 \text{ }\mu\text{m s}^{-1}$.

All measurements were made at $22 \pm 2^\circ\text{C}$.

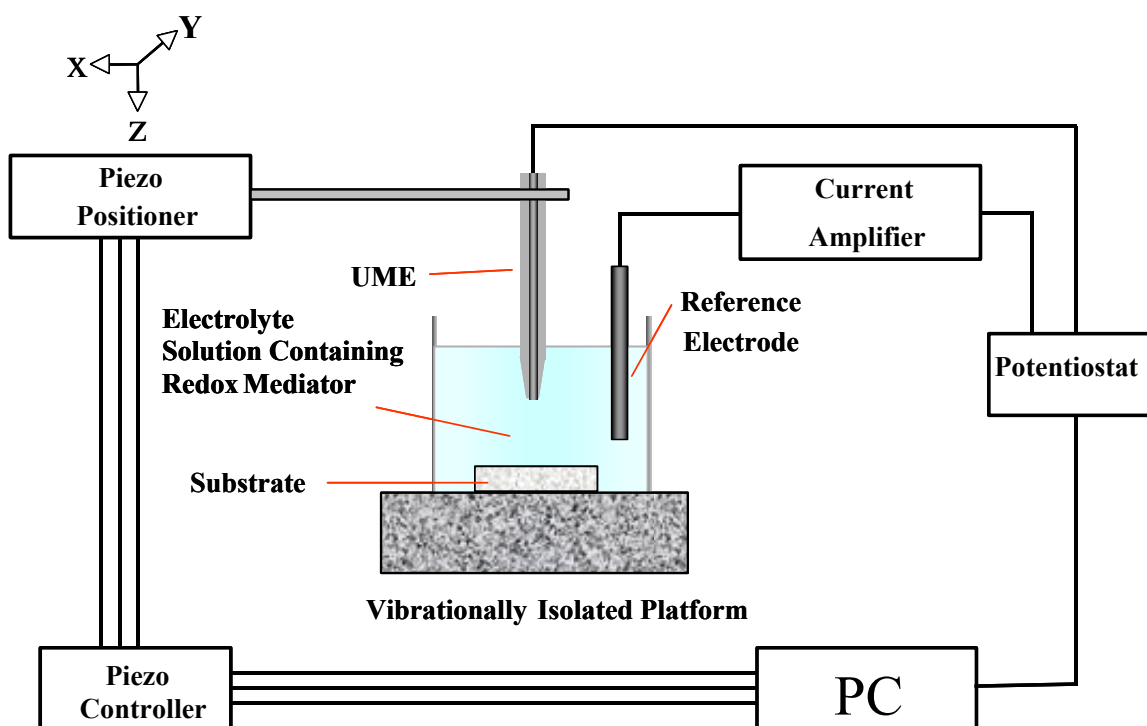


Figure 1. Scanning electrochemical microscopy schematic. For simplicity, a two-electrode configuration is shown.

3 RESULTS

3.1 PARTICLE SIZE DISTRIBUTION

Dynamic light scattering measurements were made for a dilute solution of Pt-C 6-4 catalyst powder. Since the NPs are in a dilute liquid suspension, there is a lower tendency for them to aggregate compared to the solid phase. Ten DLS measurements were taken. A representative example of one the measurements is shown in Figure 2. The particle size spread was fitted well by a Gaussian distribution with an average size of 21 nm with a standard deviation of 5 nm. Overall, the average particle size was 20.2 nm. The results suggest that the particle sizes are quite monodisperse.

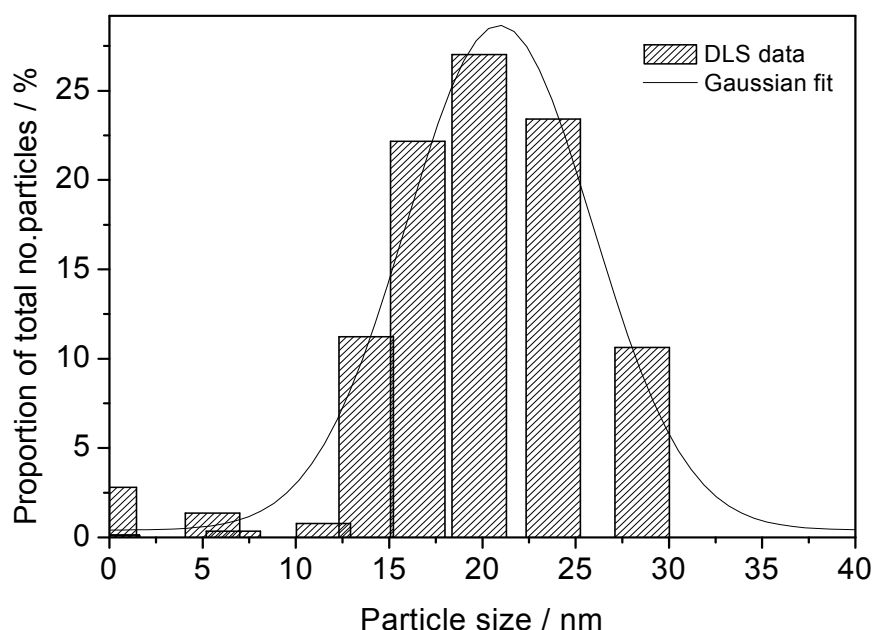


Figure 2. Particle size distribution of a dilute solution of a Pt-C 6-4 w/w catalyst as determined by dynamic light scattering measurements. The data are fitted to a Gaussian distribution with a mean particle size of 21 nm and a standard deviation of 5 nm.

TEM was used to elucidate the fine structural details of the NPs. Due to differences in atomic mass, C should be more transparent to the TEM electron beam than Pt, in effect appearing as lighter regions, and hence provides a route for distinguishing C NPs from Pt NPs.

Figure 3 shows TEM images of a dilute Pt-C 6-4 drop cast film. Figure 3a shows a typical C-Pt cluster. Although individual C NPs are not discernable, contours corresponding to individual C NPs can be seen and are roughly 20 nm - 30 nm in diameter, similar to the average sizes determined by DLS. The image, as with all TEM images, is a 2-D representation (*i.e.* depth information is missing) and hence Pt-on-C coverage is, in effect, being exaggerated. In other words the Pt (dark) regions are not necessarily on the surface of the cluster. Thus, the presence of significant light regions is an indication of a non-uniform Pt-on-C coverage. Figure 3b is a high magnification image of an area with high Pt content. Individual Pt NPs are not readily resolvable, but a rough estimate of their size suggests about 5 nm in diameter.

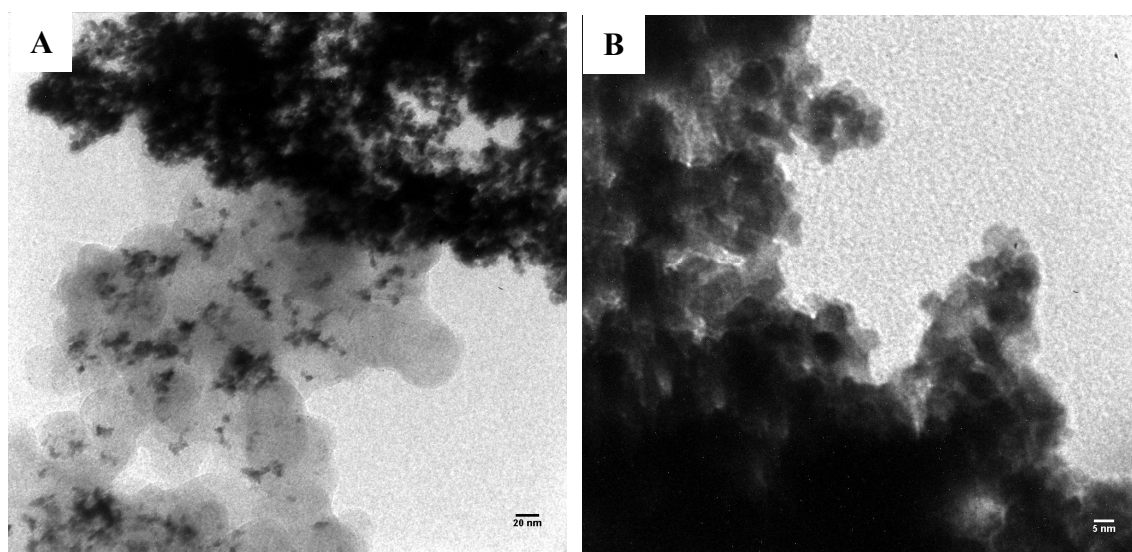


Figure 3. Transmission electron microscopy images of a Pt-C 6-4 w/w drop cast film. The scale bars are 20 nm (A) and 5 nm (B).

FE-SEM was also used to characterise particle size. However, FE-SEM images of the Pt-C films always showed particle aggregation. Very dilute (*circa* 10^{-3} mg mL⁻¹) Pt-C 6-4 spin cast films were prepared (acceleration time < 0.1s, 2000 rpm) on cleaned silanised Si in an effort to try and image individual particles. However, as seen in Figure 4, even at low concentrations, the NPs tend to agglomerate. Figure 4a shows an agglomerate of about 220 nm diameter. Figure 4b shows a large cluster with a bead-type morphology. In both images individual globular particles of about 17 nm - 60 nm diameter (thus likely to be C) are discernible. Although size discrimination is only approximate, it would appear consistent with the TEM and DLS measurements.

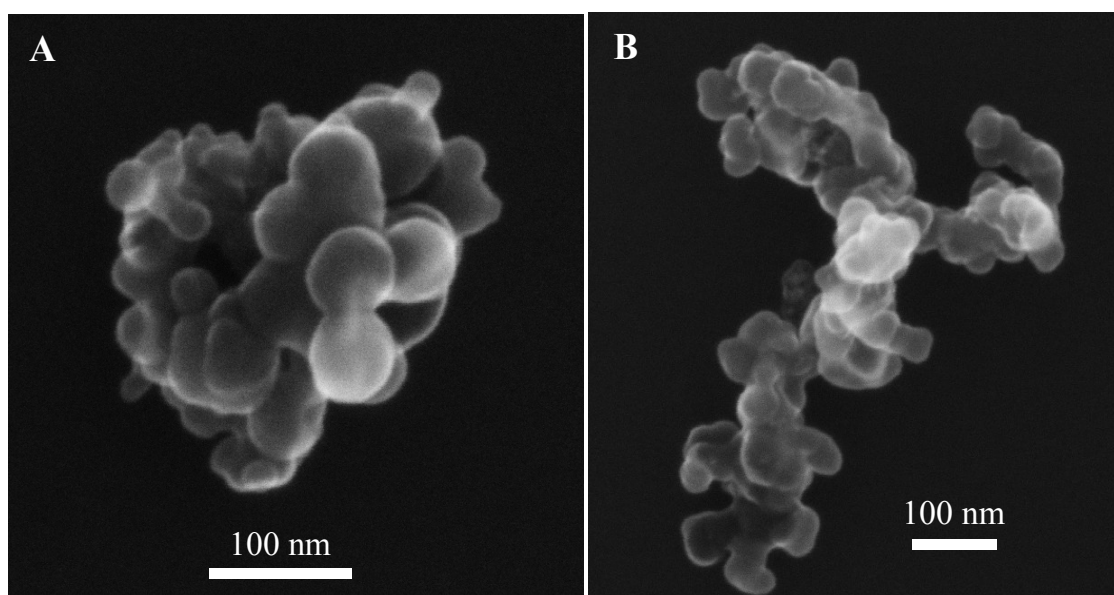


Figure 4. High-resolution field emission-electron microscopy images of a dilute Pt-C 6-4 spin cast film.

3.2 CATALYST FILM MORPHOLOGY

The concentration of spreading solution (*i.e.* amount of material), solution solvent, rotation rate, acceleration time, substrate hydrophobicity and number of layers were maintained constant in the fabrication of all catalyst films.

3.2.1 Optical Microscopy

Figure 5 shows optical micrographs of the films. The dark regions correspond to the catalyst material and the lighter regions to the underlying HOPG substrate. It is evident that as the proportion of Pt increases, surface coverage decreases. This is due to a greater amount of the solution being made up of higher density Pt with respect to C. It is interesting to note that despite 4 sequential layers being deposited in each case, significant patchiness occurs in the 6-4 Pt-C and 8-2 PtRu-MWCM films.

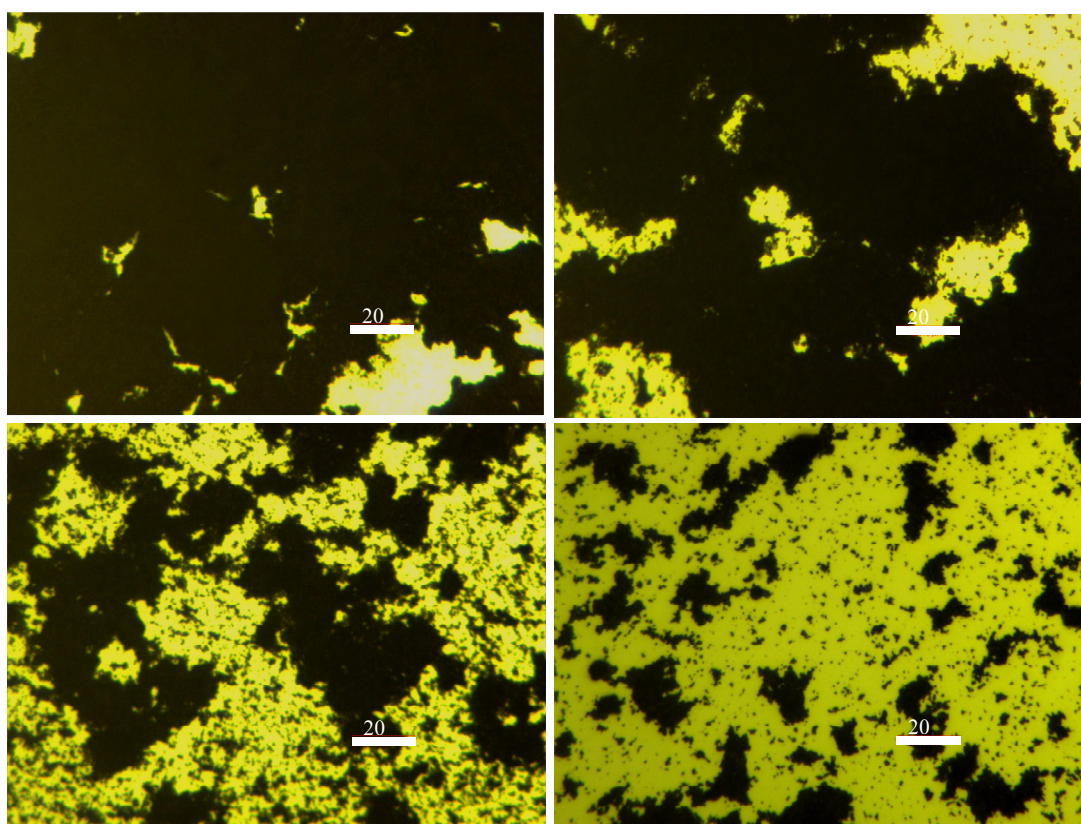


Figure 5. Optical microscopy images of, clockwise starting from the top left, 100% C, 1-9 Pt-C, 8-2 PtRu-MWCN, 6-4 Pt-C, spin cast (8 mg mL^{-1} , 2000 rpm) spin cast films on HOPG substrates. The scale bar in all images is $20 \text{ }\mu\text{m}$.

3.2.2 Field-Emission Electron Microscopy

The morphology of the films was studied greater detail by FE-SEM. Low magnification images of the films are shown in Figure 6. The magnification is similar to that in the optical micrographs, although the level of detail that can be resolved is much greater. This magnification is important because it is comparable to the resolution achieved by SECM mapping.

The 100% carbon film (Figure 6, top left) appears to show almost complete surface coverage and multiple layers can be discerned (appearing as varying degrees of contrast). The silicon substrate is distinguishable as black areas, as can be seen in the 1-9 Pt-C film (Figure 6, top right) where sub-monolayer coverage is evident. A few bright specks can also be seen in this film.

It is expected for Pt and C to show different levels of contrast and thus brighter areas are likely to correspond to Pt. In order to confirm this, energy dispersive x-ray (EDX) spectroscopy measurements were carried out on the 6-4 Pt-C film. However, although EDX confirmed the presence of C and Pt in the film, resolution was not sufficient to characterise individual areas.

The 6-4 Pt-C image (Figure 6, bottom left) shows incomplete film coverage. Bright specs and 5-15 μm clusters are evident, envisaged by default to be associated with Pt-rich regions, thus indicating a heterogeneous distribution of Pt-rich C agglomerates within the film (as was apparent in the TEM images, Figure 3).

The 8-2 PtRu-MWCM film (Figure 6, bottom right) is very patchy, with only scarce coverage of the substrate by *circa* 1-20 μm clusters and a high proportion of (non uniformly) bright areas. As seen in the optical micrographs, surface coverage decreased with increasing Pt content. Also the amount of bright areas increased with higher Pt loading, adding credence to the assumption that they correspond to Pt rich areas.

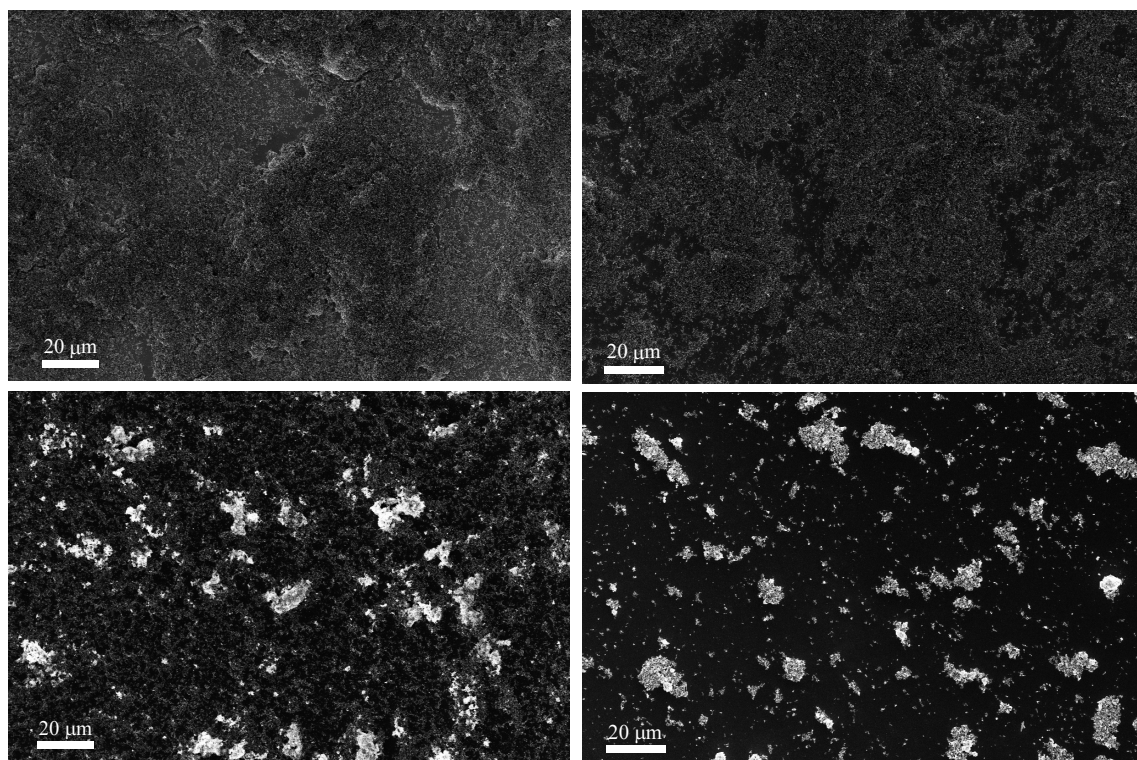


Figure 6. Low magnification ($\times 10\text{K}$) field emission-electron microscopy images of, clockwise starting from the top left, 100% C, 1-9 Pt-C, 8-2 PtRu-MWCN, 6-4 Pt-C spin cast (8 mg mL^{-1} , 2000 rpm) films on silanised silicon substrates.

Slightly higher magnification FE-SEM images, within the areas shown in Figure 6, are shown in Figure 7. The 100% C (Figure 7, top left) and the 1-9 Pt-C (Figure 7, top right) films exhibit a similar porous, granular, bead-type morphology with the latter showing a less complete coverage. The 6-4 Pt-C (Figure 7, bottom left) image is taken at lower magnification to frame a typical bright (Pt rich) cluster. Though the whole cluster is bright, differences in brightness (and thus presumably in Pt content) can be observed within the granular agglomerate. The bead-type morphology seen in the C rich films is evident in the darker regions of the film. The image taken of the 8-2 PtRu-MWCM film (Figure 7, bottom right) shows a higher magnification image of one of the clusters shown in Figure 6. Bright (catalyst rich) agglomerates within the cluster can be seen. These are not evenly distributed among the darker regions, where carbon nanotubes can be discerned as well as a significant amount of what is probably carbon debris (an expected by-product of the MWCN fabrication process).

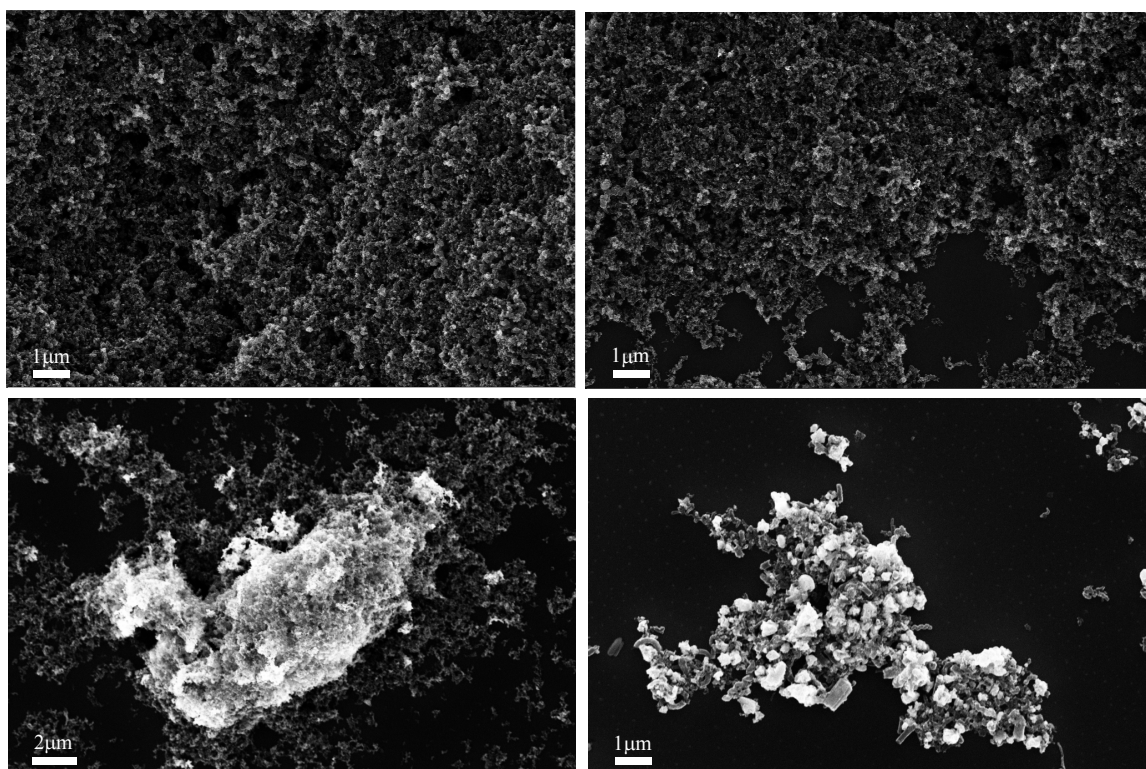


Figure 7. Low magnification field emission-electron microscopy images of, clockwise starting from the top left, 100% C, 1-9 Pt-C, 8-2 PtRu-MWCM, 6-4 Pt-C spin cast (8 mg mL^{-1} , 2000 rpm) films on silanised silicon substrates. The magnification is $\times 25\text{K}$ for all images except for the 6-4 Pt-C film, which is $\times 15\text{K}$.

Figure 8 provides a high magnification snapshot of the morphology of the films. The 100% C image ($\times 200\text{K}$, Figure 8, top left) shows a porous structure with most C NPs found in bead-like clusters, akin to the morphology found in the high resolution FE-SEM (Figure 4). Most of the C NPs appear to be around 18 nm - 80 nm in diameter, consistent with the DLS, TEM and high-resolution FE-SEM measurements. The Pt-C 1-9 image (Figure 8, top right) is of higher magnification ($\times 500\text{K}$) and shows a C NP cluster where a few bright specks are discernable. The 6-4 Pt-C image (Figure 8, bottom left) is of comparable magnification ($\times 250\text{K}$) to the 100%C and 8-2 PtRu-MWCM

images and shows a porous structure with the C NPs arranged in bead-type clusters, similar to the arrangement found in the 100% C films. However, in addition to the C NPs, a heterogeneous distribution of small bright specks on the C NPs can be discerned, as well as a bright cluster towards the top right hand side of the image. These are probably be due to the presence of Pt NPs though caution must be exercised as bright areas can also be seen in the 100% C film. As expected, at this magnification ($\times 200K$, Figure 8, bottom right) the morphology of the 8-2 PtRu-MWCN film is very different to the films based on C Black NPs. The MWCNs are evident and are of *circa* 100 nm in diameter. Amorphous carbon debris and bright (catalyst) clusters can also be seen.

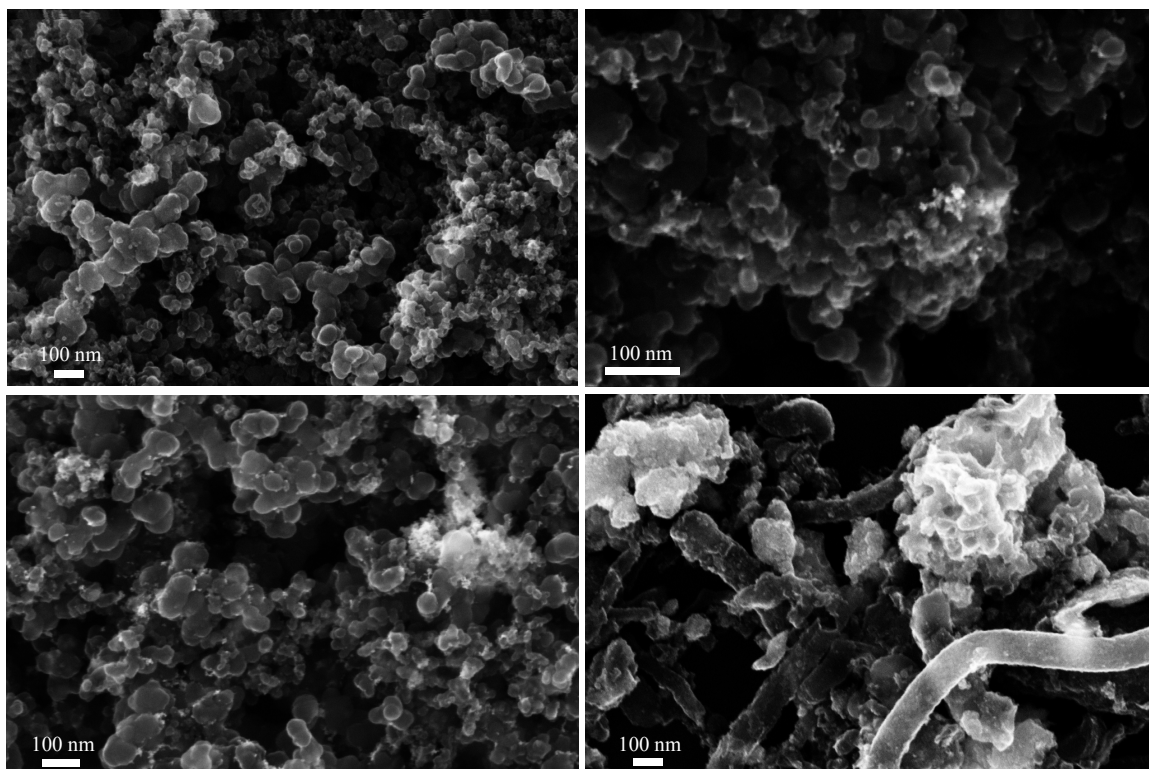


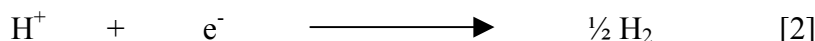
Figure 8. High magnification field emission-electron microscopy images of, clockwise starting from the top left, 100% C ($\times 200K$), 1-9 Pt-C ($\times 500K$), 6-4 Pt-C ($\times 250K$), 8-2 PtRu-MWCN ($\times 200K$) spin cast (8 mg mL^{-1} , 2000 rpm) films on silanised silicon substrates.

3.3 ELECTROCHEMICAL CHARACTERISATION

In carrying out SECM maps it is necessary to undertake preliminary electrochemical measurements to ensure that the tip and substrate conditions for the selected redox systems will provide the required discrimination. Here, we use a mixed redox system consisting of a non-catalytic redox couple ($\text{FcMeOH}/\text{FcMeOH}^+$) and a catalytic redox couple (H^+/H_2). The former is designed to interrogate the topography of the films; the latter is designed to interrogate the electrocatalytical activity of the films towards the hydrogen oxidation reaction (scheme 1), which is the anodic reaction in a PEMFC.



The UME is used to *in-situ* generate molecular hydrogen, from reduction of protons (scheme 2) under diffusion limiting conditions, in close proximity to the film surface.



To distinguish regions in the spin-cast film rich in Pt it is essential that the kinetics of proton regeneration on Pt are markedly greater than that on the more abundant C. The use of Pt as a fuel cell catalyst inherently implies that but it is useful to demonstrate this by appropriate electrochemical measurement. Accordingly, anodic voltammetry measurements were made on glassy C and Pt disk electrodes in an acidic solution under 1 atmosphere of hydrogen, Figure 9. A large difference in anodic current density can be seen between the C and Pt electrodes. At the Pt electrode there is an early onset of a diffusion-limited regime with a large plateau (from -0.28 V to $+1.27$ V) corresponding to the HOR, with a current density significantly greater than that found for the C electrode. At the C electrode the kinetics for the HOR are slow and a diffusion limited regime is not properly established. As the potential becomes more anodic the HOR current on C increases and is about an order of magnitude lower than that on Pt at $+1.0$ V. Moreover, close to open circuit, the difference in HOR current is approaching three orders of magnitude. This suggests that ready discrimination of carbon and Pt rich regions in the spin-cast films should be possible

Anodic voltammetry was performed on the same C and Pt electrodes in a solution of FcMeOH and K_2SO_4 (Figure 9b). In contrast to the catalytic HOR, the reaction rate of FcMeOH oxidation in the diffusion-limited region was similar on C and Pt. At more anodic potentials water oxidation becomes predominant, and greater current is recorded at the Pt electrode.

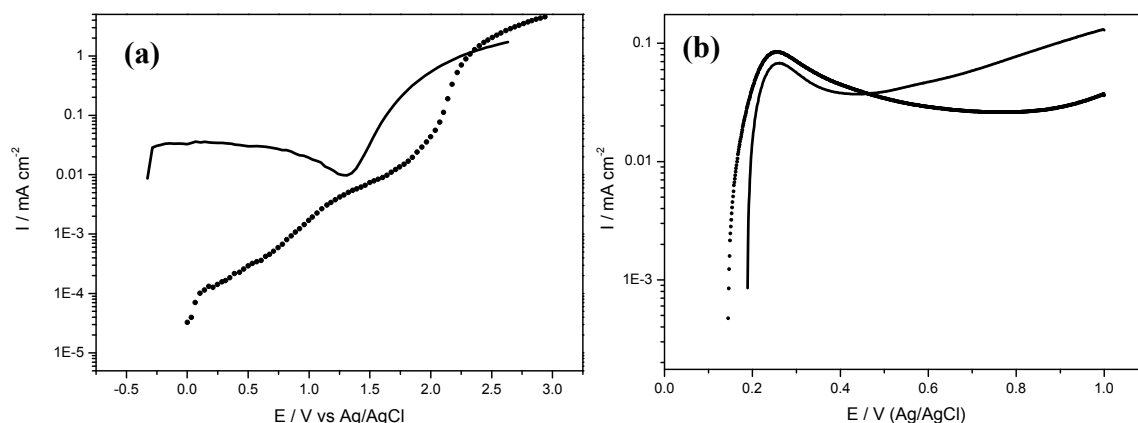


Figure 9. Anodic linear sweep voltammetry at C (dotted line) and Pt (solid line) electrodes in (a) an acidic solution (10 mM sulphuric acid, 50 mM potassium sulphate) saturated with hydrogen gas; (b) a 1 mM ferrocenemethanol and 50 mM potassium sulphate solution. Scan rate is 50 mV s^{-1} .

In order to determine the appropriate potentials to bias the tip for the SECM maps, voltammetry at the UME was undertaken, Figure 10.

The cathodic response (Figure 10a) was used to determine the diffusion-limited potentials for the *in-situ* hydrogen generation at the tip: between potentials of -0.6 and

–1.07 V a mass transport-limited current for proton reduction of about –90 nA can be observed and hence the probe potential was set within that region (a value of –0.8 V was selected). At more negative potentials water reduction dominates. For these diffusion-limited conditions hydrogen gas bubbles are not formed, *i.e.* the solubility limit for dissolved molecular hydrogen (*circa* 50 mM⁶) has not been exceeded. To account for the cathodic current contribution, if any, due to FcMeOH, cathodic scans were measured both in the mixed redox system (continuous line trace in Figure 10a) and solely in acidic media (dotted line trace in Figure 10a). Clearly, reduction of FcMeOH is not significant compared with that of proton reduction within the cathodic potentials studied and can be neglected.

Similarly, the anodic response (Figure 10b) was used to determine the diffusion-limited potentials for the tip oxidation of FcMeOH, (scheme 3). A mass transport-limited current of *circa* 1.4 nA for the oxidation of FcMeOH can be seen between potentials of +0.3 V to +0.5 V. The tip was set at +0.4 V.

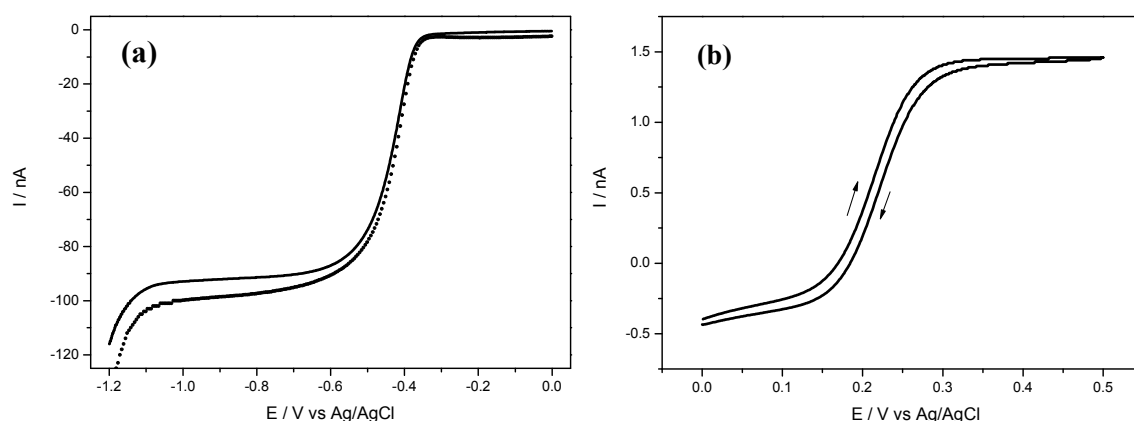


Figure 10. Voltammetry at a 5 μm Pt ultramicroelectrode. (a) Cathodic response in a solution of 10mM sulphuric acid and 50 mM potassium sulphate with (line trace) and without (dotted line trace) 1 mM ferrocenemethanol. (b) anodic response in a solution of 1 mM ferrocenemethanol, 10 mM sulphuric acid and 50 mM potassium sulphate. Scan rate for both scans is 50 m Vs⁻¹.

3.3.1 Scanning Electrochemical Microscopy

Prior to the commencement of each SECM scan, approach curves were measured and used to set the tip-substrate separation at the origin of the scan.

Note that, unlike other scan probe microscopies, SECM does not have a feedback loop mechanism that can be used to fix a constant tip-sample separation while scanning. Thus, scanning was done at constant height, *i.e.* tip-sample separation varied in response to film topography.

Approach curves consist of vertically translating the UME tip towards the surface, while applying a suitable potential corresponding to the diffusion limited reaction of a

redox mediator in solution, and recording the tip current. Here, the $\text{FcMeOH}/\text{FcMeOH}^+$ redox couple was used.

As the UME oxidises FcMeOH (scheme 3) at a diffusion-limited rate, tip-sample separation decreases. When the tip is in close proximity to the film, a high local concentration of FcMeOH^+ molecules between the tip and the film will start to be generated. The increase in local FcMeOH^+ concentration over the film surface will drive the reduction of FcMeOH^+ , which regenerates FcMeOH , and thus increases the current measured at the UME (i_{tip}) with respect to that measured in the bulk (i_{bulk}). Tip current will increase with decreasing tip-sample separation, and this is known as positive feedback.

Well-known expressions have been developed that predict the degree of feedback with respect to the rate of electron transfer kinetics at the substrate, *inter alia*^{21,22}. An example of one of the experimental approach curves measured, alongside a theoretical curve²¹, is shown in Figure 11. Excellent agreement between theory and experiment is obtained when pure positive feedback (*i.e.* fast and non-limiting electron-transfer reaction kinetics) is assumed, as can be seen in Figure 11. Thus, the recording of i_{tip} , as the UME is approaching the film, can be used to set the tip-sample separation.

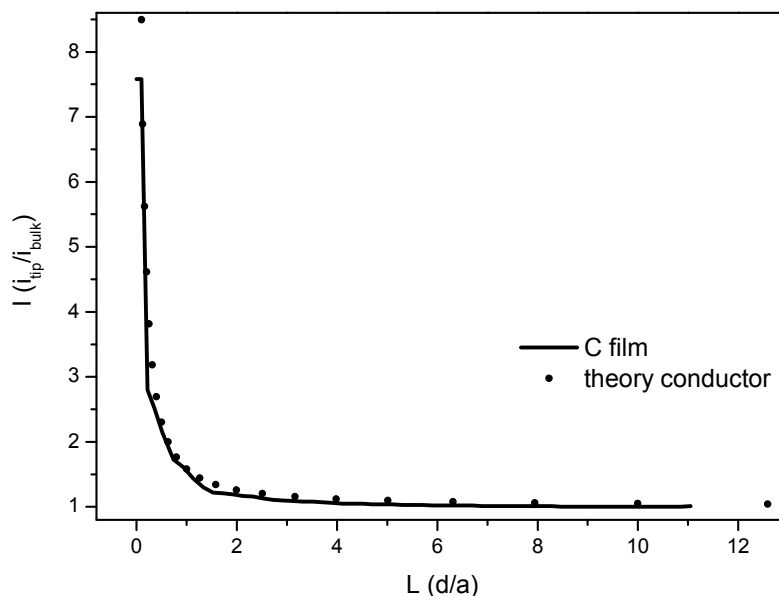


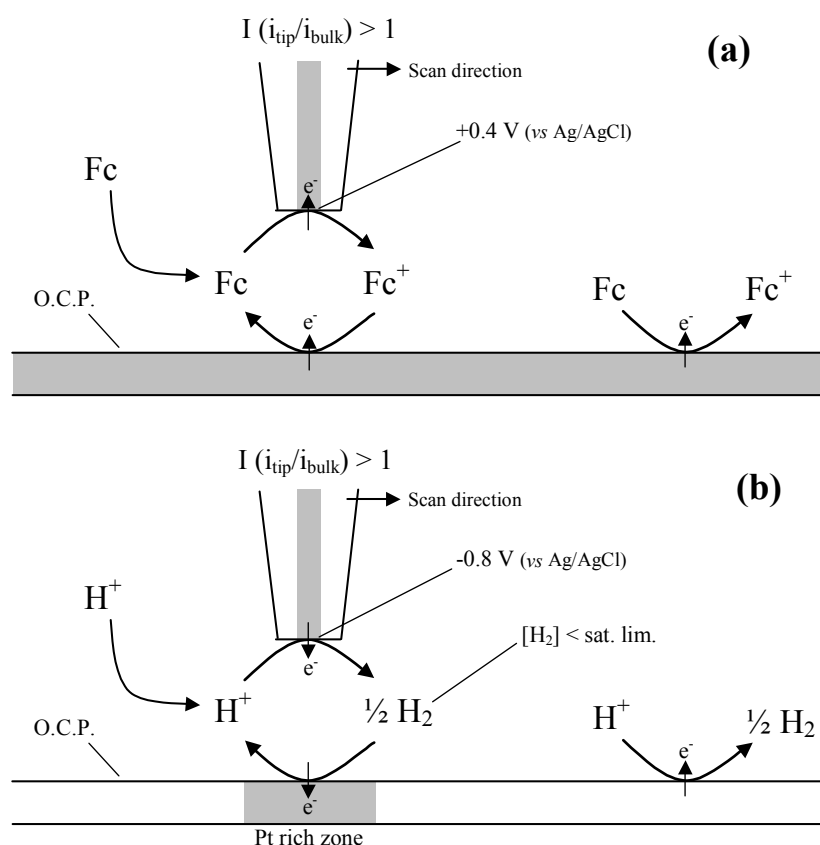
Figure 11. Approach curve of a 5 μm Pt ultramicroelectrode, whilst applying a potential sufficient to oxidise ferrocenemethanol at a diffusion-limited rate, towards a 6-4 Pt-C film. Tip current (i_{tip}) has been normalised with respect to bulk current (i_{bulk}) and distance (d) has been normalised with respect to the ultramicroelectrode radius (a). The line trace corresponds to the experimental curve and the dotted trace to simple theory for a pure conductor.

Once the tip-sample distance was set ($5 \pm 2 \mu\text{m}$), SECM scans were performed using the $\text{FcMeOH}/\text{FcMeOH}^+$ and H^+/H_2 redox systems. The procedure consisted of applying a suitable potential to the UME (either sufficient to oxidise FcMeOH at a diffusion limited rate, or sufficient to reduce protons at a diffusion limited rate) and raster scanning the UME over the film.

The use of the $\text{FcMeOH}/\text{FcMeOH}^+$ redox couple gave a measure of film topography as the degree of positive feedback measured is directly related to tip-sample separation, Figure 12a.

In contrast to FcMeOH oxidation, the kinetics of the catalytic HOR are markedly different on C and Pt surfaces (Figure 9a). Thus, when using the H^+/H_2 redox couple for SECM scanning, the resulting maps reflect film topography *and* activity. Positive feedback will be measured only when the presence of Pt is significant on the sample surface (Figure 12b). When C predominates, the kinetics of the HOR at the film surface are very slow. Hence, regeneration of protons from the substrate is not significant. Furthermore, the small tip-substrate gap significantly restricts the diffusion of reactants (H^+) to the UME, and products (H_2) away from the UME. As a consequence, i_{tip} will be smaller than i_{bulk} (Figure 12c). This situation of hindered diffusion is known as negative feedback. Here, i_{tip} will decrease with decreasing tip-sample separation. Therefore, although both activity and topographical effects are convoluted in the current signal, the nature of the feedback provides information on the sample activity (*i.e.* positive feedback only occurs if enough HOR occurs at the film to be picked up by the UME).

The combination of both redox systems provides, in principle, a route to deconvoluting the effects of topography and activity.



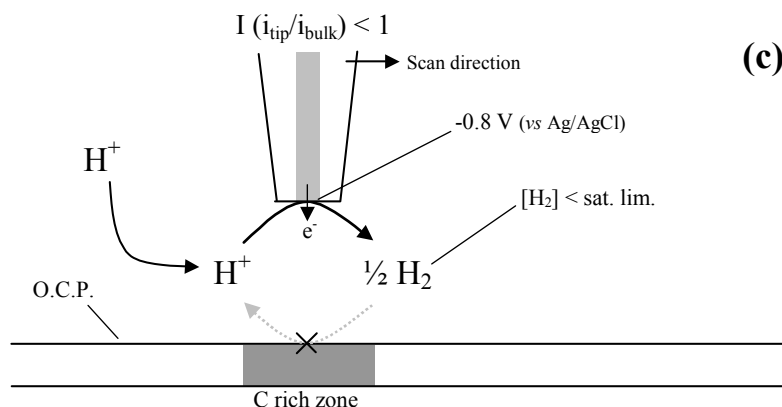


Figure 12. Scanning electrochemical microscopy experimental schematic. (a): Ultramicroelectrode (UME) tip is oxidizing ferrocenemethanol at a diffusion-limited rate and the degree of positive feedback is due to differences in sample topography. (b): UME tip is reducing protons at a diffusion-limited rate over a Pt rich area of the film and the degree of positive feedback is due to Pt content and differences in sample topography. (c): UME tip is reducing protons at a diffusion-limited rate over a C rich area of the film and the degree of negative feedback is due to differences in sample topography. O.C.P. stands for open circuit potential.

SECM maps of the films are shown in Figures 13 - 16. The colour charts correspond to normalised current values (I), where i_{tip} has been normalised with respect to i_{bulk} .

Unfortunately, a significant backlash detected belatedly in the UME position-control inchworms posed difficulties in re-scanning the same area with both mediators. Thus, the maps of the 100% C, 1-9 Pt-C and 8-2 PtRu-MWCN films are of different areas; two of the 6-4 Pt-C film maps are roughly of the same area.

SECM maps ($200\ \mu\text{m} \times 200\ \mu\text{m}$) of a 100% C film on HOPG are shown in Figure 13. FcMeOH oxidation at the UME is shown in Figure 7a. The degree of positive feedback is indicative of the topographical features of the film. The film appears relatively flat with the notable exception of a high feature towards the bottom right corner. The map produced via proton reduction at the UME is shown in Figure 13b. As expected, no positive feedback is present and changes in measured current are due to varying degrees of hindered diffusion (in essence reflecting the topography of the film). This check is useful: any positive feedback detected in the Pt-C films can be assigned with confidence to the presence of active Pt. The film appears to have a relatively flat base plane (albeit possibly affected by a small experimentally induced tilt) on to which a few features protrude.

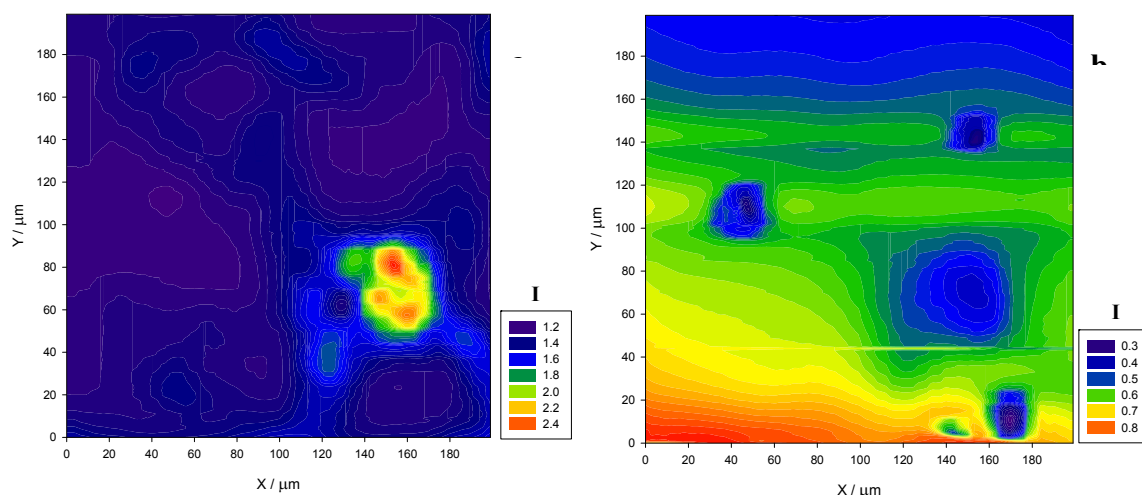


Figure 13. Scanning electrochemical microscopy maps (of different areas) of a spin cast (8 mg mL^{-1} , 2000 rpm, 4 layers) 100% C film deposited on a HOPG substrate. (a) Ferrocenemethanol oxidation at the ultramicroelectrode. (b) Proton reduction at the ultramicroelectrode. Colour scale corresponds to normalised current (with respect to bulk current). Current ratios <1 indicate negative feedback and those >1 indicate positive feedback.

Figure 14 shows SECM maps, obtained via FcMeOH oxidation (Figure 14a) and proton reduction (Figure 8b), of a 1-9 Pt-C film. The former shows that, as detected by SECM, the 1-9 Pt-C film is fairly flat (differences in current ratio, I , are only $\pm 20\%$). The proton reduction map is interesting. Most of the film is inactive towards the HOR, with only a small area of activity present. The areas scanned are quite large, $400 \mu\text{m} \times 400 \mu\text{m}$, making the SECM characterisation reasonably representative of the whole film.

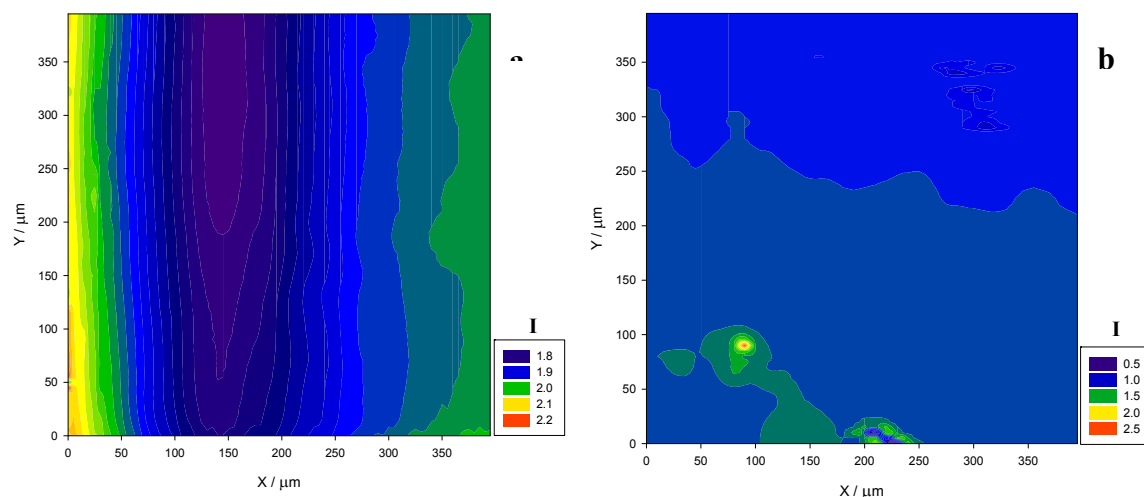


Figure 14. Scanning electrochemical microscopy maps (of different areas) of a spin cast (8 mg mL^{-1} , 2000 rpm, 4 layers) 1-9 Pt-C film deposited on a HOPG substrate. Left: ferrocenemethanol oxidation at the ultramicroelectrode. Right: proton reduction at the ultramicroelectrode. Colour scale corresponds to normalised current (with respect to bulk current). Current ratios <1 indicate negative feedback and those >1 indicate positive feedback.

Figure 15 shows SECM maps of a 6-4 Pt-C film. Figure 15a was obtained while oxidising FcMeOH at the tip, whereas Figures 15b, 15c and 15d were obtained while reducing protons at the UME. Figure 15a shows that the film appeared more or less flat to the UME, with some small features apparent towards the top of the image. Therefore, it is expected that film topography should not exert a dominating influence on the activity maps. This expectation is borne out in Figure 15b, for which the area scanned is mostly within that of Figure 15a. Here the measured features do not coincide, in number or location, with the SECM measured topography shown in Figure 15a. Therefore, changes in i_{tip} in Figure 15b are largely determined by film activity. It is reasonable to assume that the same is most likely the case in general for the 6-4 Pt-C films, further examples of which are shown in Figures 15c and 15d. Figure 15c (200 $\mu\text{m} \times 200 \mu\text{m}$) gives the best measure of overall activity but it is apparent for all scans that a high degree of activity heterogeneity towards the HOR exists. A horizontal blurring artefact can be seen in Figure 15c, probably due to fast UME scanning (in the x direction). A lower scan rate was used in generating the data of Figures 15b and 15d, these higher magnification images providing a higher level of detail in the activity non-uniformity.

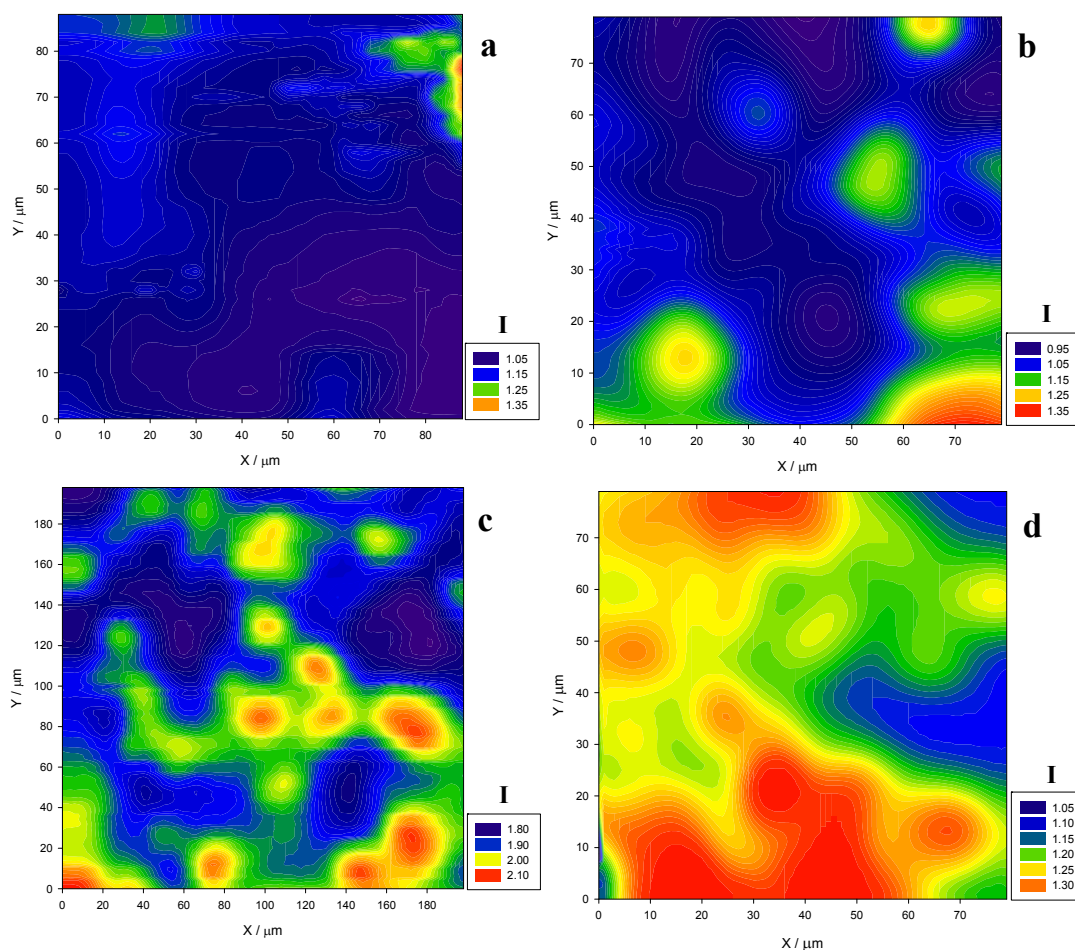


Figure 15. Scanning electrochemical microscopy activity maps of a spin cast (8 mg mL⁻¹, 2000 rpm, 4 layers) 6-4 Pt-C film deposited on a HOPG substrate. (a): ferrocenemethanol oxidation at the ultramicroelectrode; (b), (c), (d): proton reduction at the ultramicroelectrode. Scans (a) and (b) are roughly of the same area. Colour scale corresponds to normalised (with respect to bulk current) current. Scale increments are different for image (d). Current ratios <1 indicate negative feedback and those >1 indicate positive feedback.

Figure 16 shows a relatively large SECM map of a 8-2 PtRu-MWCN film measured while reducing protons at the tip. Unfortunately, a map using the $\text{FcMeOH}/\text{FcMeOH}^+$ redox couple was not measured successfully. Interestingly, despite scarce film coverage (Figure 6) all the imaged area ($400\ \mu\text{m} \times 400\ \mu\text{m}$) shows activity towards the HOR. Moreover, the measured activity is more or less uniform (difference in I are solely $\pm 5\%$) thorough the film. The small differences in measured current are probably mostly due to an experimental tilt.

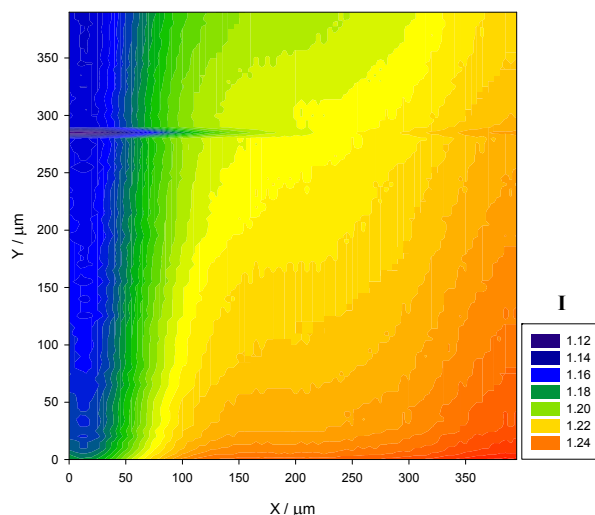


Figure 16. Scanning electrochemical microscopy activity map of a spin cast ($8\ \text{mg mL}^{-1}$, 2000 rpm, 4 layers) 8-2 PtRu-MWCN film deposited on HOPG substrate. A potential is applied for proton reduction to occur at a diffusion limiting rate at the ultramicroelectrode. Colour scale corresponds to normalised current (with respect to bulk current). Current ratios <1 indicate negative feedback and those >1 indicate positive feedback.

4 DISCUSSION

Insight into the size and shape of the NP film constituents is useful in understanding the morphology of the catalyst films. A relatively small C NP size dispersity, and a high C-C affinity preferentially arranges the C NPs into bead-type structures. These are porous and provide a high surface area electrical conduit, ideal as a support for catalyst NPs.

Knowledge of NP sizes also allows mass ratios to be converted into NP number ratios. Assuming spherical NP volumes* (diameters 5 nm and 20 nm for the Pt and C NPs respectively), the calculated number ratios are thus 0.75 Pt NPs per C NP (1-9 Pt-C) and 10.2 Pt NPs per C NP (6-4 Pt-C). A density for Pt of $21.45\ \text{g cm}^{-3}$ and for C of $2.27\ \text{g cm}^{-3}$ was assumed for the calculation. Consequently, with high Pt loading and optimum processing there should be very few C NPs with no attached Pt NPs. In practice, there were significant numbers of C NPs with low or no Pt coverage, as shown

* Based on the TEM and FE-SEM measurements and thermodynamic considerations, it is reasonable to assume a spherical geometry. Although a small amount of surface diffusion is expected, the platinum-carbide bond is relatively weak and hence the affinity for compound formation is low.

in Figures 4, 6 and 7. At low loading more individual C NPs will be expected but the area fraction would be very much larger than would be inferred from the Pt to C ratio.

In addition, the catalyst-rich C NPs appear to agglomerate (Figure 6). These catalyst-rich C clusters vary in shape (Figure 6), are inhomogeneous themselves (Figure 7), and are unevenly distributed throughout the films (Figure 6) resulting in a poor uniformity of catalyst coverage.

SECM was useful in translating structural information into spatially resolved electrocatalytic activity. The SECM scan areas (from $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$ to $80\text{ }\mu\text{m} \times 80\text{ }\mu\text{m}$) are comparable in size with the lower magnification FE-SEM images. These showed that the coverage of the 100% C film was almost complete, and multiple layers within the film were present. As a consequence, the film did not appear flat and topographical features were detected by SECM. The coverage of the 1-9 Pt-C film was incomplete and a scattered distribution of small Pt rich areas was present. SECM characterisation showed that the film appeared relatively flat. Activity, however, was only detected in small areas in the film, presumably only when a high enough concentration of surface Pt occurred to be detected by SECM, inferring a very uneven distribution of Pt within the film.

The coverage of the 6-4 Pt-C film was also incomplete. Moreover, the distribution of Pt-rich C NPs was heterogeneous, with high Pt content $5 - 15\text{ }\mu\text{m}$ clusters scattered throughout the film. From an SECM perspective the film appeared as effectively flat. Consequently, film activity dominated the SECM signal over film topography in the H^+/H_2 maps. These showed that although most of the film was active towards the HOR, a high degree of activity heterogeneity was present. Clusters of high activity of about $15 - 30\text{ }\mu\text{m}$ were observed, and these can be related to the high Pt content clusters seen in the FE-SEM images.

The significant amount of C debris present in the PtRu-MWCN films does not allow the mass ratio to be converted to particle number ratio. However, it follows from the argument above that at 80% mass loading a good catalyst coverage throughout the film is to be expected, albeit 80% mass loading is above the practical loading used in commercial PEMFCs⁵. Though catalyst is present in the film clusters, these are not uniformly bright (Figure 6) and are, in fact, quite inhomogeneous (Figure 7). Despite this, the activity of this film towards the HOR appeared uniform as detected by SECM.

It is important to note with respect to SECM resolution that, as well as taking into account the size of the UME, tip-sample distance at which scanning is measured is a crucial consideration and determined by sample roughness. The UME is scanned at a distance from the film surface and hence lateral resolution is affected by blurring due to lateral diffusion of detectable reaction products⁴. Indeed, if active sites are in close proximity, diffusional overlap might occur, in effect presenting a continuous front of reactants to the UME. This is evident in the 8-2 PtRu-MWCN film where film coverage is sparse, but measured film activity is uniform throughout the (large, $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$) mapped area as a consequence of the high catalyst loading in the film. This also explains why the topography of the 1-9 Pt-C film is measured as flat in SECM although film coverage is submonolayer and why the 6-4 Pt-C film is almost completely active despite less than uniform film coverage.

Activity heterogeneity is undesirable in PEMFCs catalyst layers as a combination of inactive areas and hot-spots would occur, indicative of an inefficient use of the expensive platinum and possibly accelerating local membrane failure. Although significant heterogeneity was found in our model catalyst films, this does not imply that other processing routes cannot produce more uniformly distributed catalyst films. However, even if ideally distributed films were to be made, NP sintering driven by fuel cell potential, particularly at open circuit, is a well-known problem in PEMFC catalyst layers.

Extension of this research to account more properly for the topography is in place, and SECM measurements at modest (*circa* 60°C) elevated temperatures are planned. In addition, the development of nanoelectrodes to resolve the activity in individual clusters, where electrode and tip-sample separation dimensions are orders of magnitude smaller than in conventional SECM, are current research goals.

5 CONCLUSIONS

Model catalyst films that mimic the composition, structure and three phase boundary (reactant, catalyst, electrolyte) conditions present in typical proton exchange membrane fuel cell catalyst films were fabricated via spin-coating of carbon and platinum nanoparticles onto highly orientated pyrolytic graphite substrates.

The number of carbon nanoparticles with little or no platinum was much more than would be expected based on the platinum-carbon mass ratio.

The platinum-rich carbon nanoparticles agglomerate. These platinum-rich carbon clusters distribute non-uniformly throughout the catalyst films.

The consequence was a significant degree of heterogeneity of electrocatalytical activity towards the hydrogen oxidation reaction over the film surface.

The work here highlights a preliminary route towards the development of a screening tool for “real” catalyst films and factors affecting performance prior to their implementation in a fuel cell.

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7 REFERENCES

1. V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science*, **315**, 493-497, (2007).
2. A.J. Bard and M. V. Mirkin (eds), *Scanning Electrochemical Microscopy*, Marcel Dekker, New York, 2001

3. P. Unwin (ed), *Instrumentation and Electroanalytical Chemistry*, Vol. 3 of Encyclopaedia of Electrochemistry, A.J. Bard and M. Stratmann, eds, Wiley-VCH, Weinheim, 2003.
4. A. Turnbull, Electrochemical Scanning Probe Microscopy - An Overview, *NPL Report DEPC MPE 011*, 2005.
5. A.R. Kucernak, P. B. Chowdhury, C.P. Wilde, G.H. Kelsall, Y.Y. Zhu and D.E. Williams, *Electrochim. Acta*, **45**, 4483-4491, (2000).
6. B. C. Shah, A. C. Hillier, *J. Electrochem. Soc.*, **147**, 8, 3043-3048, (2000).
7. S. Jayaraman, A. C. Hillier, *Langmuir*, **17**, 7857-7864, (2001).
8. T. Kallio, C. Slevin, Sundholm, G., P. Holmlund, K. Kontturi, *Electrochem. Commun.*, **5**, 561-565, (2003).
9. S. Jayaraman, A. C. Hillier, *J. Phys. Chem. B*, **107**, 5221-5230, (2003).
10. S. Jayaraman, A. C. Hillier, *J. Comb. Chem.*, **6**, 27-31, (2004).
11. M. Black, J. Cooper, P. McGinn, *Meas. Sci. Technol.*, **16**, 174-182, (2005).
12. G. Lu, J. S. Cooper, P. J. McGinn, *J. Power Sources*, **161**, 106-114, (2006).
13. J. L. Fernandez, A. J. Bard, *Anal. Chem.*, **75**, 2967-2974, (2005).
14. J. L. Fernandez, D. A. Walsh, A. J. Bard, *J. Am. Chem. Soc.*, **127**, 357-365, (2005).
15. D. A. Walsh, J. L. Fernandez, A. J. Bard, *J. Electrochem. Soc.*, **153**, 6, E99-E103, (2006).
16. K. Eckhard, X. Chen, F. Turcu, W. Schuhmann, *Phys. Chem. Chem. Phys.*, **8**, 5359-5365, (2006).
17. K. Eckhard, W. Schuhmann, *Electrochim. Acta*, **53**, 1164-1169, (2007).
18. G. Lu, J. S. Cooper, P. J. McGinn, *Electrochim. Acta*, **52**, 5172-5181, (2007).
19. P. Nicholson, *On the fabrication of model proton exchange membrane fuel cell catalyst films*, NPL report MN 3 (2008).
20. R. R. Moore, C. E. Banks, R. G. Compton, *Anal. Chem.*, **76**, 2677-2682, (2004).
21. J. Kwak, A. J. Bard, *Anal. Chem.*, **61**, 1221-1227, (1989).
22. A. J. Bard, M. V. Mirkin, P. R. Unwin, D. O. Wipf, *J. Phys. Chem.*, **96**, 1861-1868, (1992).