Institution: University of Warwick

Unit of Assessment: B8 – Chemistry

Title of case study: Warwick Electrochemical-Scanned Probe Microscopy (WEC-SPM) platform

Period when the underpinning research was undertaken: 2010 – 2017

Details of staff conducting the underpinning research from the submitting unit:

Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Patrick Unwin	Professor	1991– present

Period when the claimed impact occurred: 2013 – 2020

Is this case study continued from a case study submitted in 2014? N

1. Summary of the impact (indicative maximum 100 words)

The creation of a world-leading platform of multifunctional nanoscale electrochemical probe imaging techniques (WEC-SPM) by Professor Pat Unwin's Group at the University of Warwick (UoW) has produced a variety of impacts in 5 distinct areas:
A. UoW inventions have been commercialised and are sold globally by 3 international companies, with sales totalling over [text removed for publication]: (i) [text removed for publication]; (ii) [text removed for publication]; and (iii) [text removed for publication].
B. [text removed for publication] partnership using WEC-SPM to support the development and launch of [text removed for publication] advanced tooth treatment (2014 launch), with annual sales [text removed for publication], and a new product in dentinal hypersensitivity (2020 launch).
C. WEC-SPM has been used to support future product development and enhanced know-how in agrichemicals (Syngenta) and corrosion science ([text removed for publication] and Tata Steel UK).
D. Major global companies and organisations have partnered with international research groups, using UoW nanoscale electrochemical imaging techniques, to discover improved battery materials and assess materials performance (corrosion).
E. Electrochemical images have provided inspiration for artworks presented at festivals, galleries, buildings and on social media.

2. Underpinning research (indicative maximum 500 words)

Unwin's group has an exceptional record of world-leading developments of scanning electrochemical probe microscopy for quantitative interfacial imaging. UoW research over the past decade has redefined the state of the art for electrochemical imaging through innovations and inventions that: (i) facilitate synchronous surface topography-activity imaging; (ii) allow true nanoscale multifunctional imaging with simple probes; (iii) speed up electrochemical imaging and data acquisition, so that movies comprising hundreds of image frames are obtained (rather than single images as had been the norm).

The major UoW research underpinning the impact has been the **invention** and **naming** of:
(a) **Intermittent contact-scanning electrochemical microscopy** (**ic-SECM**) **[3.1]**, a technique where a conventional SECM electrode imaging probe gently taps a surface to acquire simultaneous topography and activity data **[3.1, 3.2]**. This greatly advances conventional SECM by providing: (i) a non-electrochemical signal to determine (set) the tip-substrate distance and map the topography; (ii) an additional AC signal, as well as the DC electrochemical signal, which together can be used to resolve complex interfacial activity problems **[3.2]**.
(b) **Scanning electrochemical cell microscopy** (**SECCM**) **[3.3]**, an innovative nanoscale scanning droplet electrochemical (half) cell, which is scanned **[3.3]**, or hopped **[3.4]**, over a surface to acquire synchronous activity-topography data and/or to modify the surface and measure ion

fluxes **[3.5]**. SECCM comes in both a dual-channel **[3.3]** and single-channel **[3.6]** probe format, with the latter proving to be particularly powerful for creating voltammetric movies quickly and at high (30 nm) spatial resolution. SECCM data are most powerfully combined with complementary co-located microscopy and micro-spectroscopy data, in an electrochemical multi-microscopy strategy that provides holistic views of surface activity, and reveals active sites, and other interfacial properties, unambiguously, quantitatively and in unprecedented detail.

These techniques are brought together with new scanning ion conductance microscopy (SICM) techniques and combined SICM-SECM on the versatile **Warwick Electrochemical-Scanned Probe Microscopy** (**WEC-SPM**) platform, the software for which is freely available to the academic community, and which has been taken up by more than 30 groups globally. The UoW inventions are revolutionising the way in which electrochemists and surface chemists (academic and industrial) can investigate interfaces and interfacial processes, with **major** and **diverse applications** spanning (among others): (i) the electrochemical properties of materials and electrodes used as electrocatalysts, and in fuel cells, batteries and sensors; (ii) corrosion processes; (iii) surface processes and the performance of surface active agents in products used in advanced tooth treatments, agrichemicals and pharmaceuticals.

Warwick's electrochemical probe microscopy techniques have been developed as a team effort, with funding to Unwin (as PI) through: (i) an ERC Advanced Grant **[G1]**, and from EPSRC **[G2]**. Major initial contributions were made by several PhD students, notably Kim McKelvey and Martin Edwards, funded by EPSRC Warwick CDTs **[G3]** and Neil Ebejer, funded by a Warwick-EPSRC Collaborative Training Account project, co-funded by the National Physical Laboratory **[G4]**.

3. References to the research (indicative maximum of six references) **Warwick = Bold**

All research papers were published in peer-reviewed journals

[3.1] McKelvey, Kim M., Edwards, Martin A. and **Unwin, Patrick R.** (2010) *Intermittent contact-scanning electrochemical microscopy (IC-SECM): a new approach for tip positioning and simultaneous imaging of interfacial topography and activity.* Analytical Chemistry, Vol.82 (No.15). pp. 6334-6337. doi:10.1021/ac101099e

[3.2] McKelvey, Kim M., Snowden, Michael E., Peruffo, Massimo and **Unwin, Patrick R.** (2011) *Quantitative visualization of molecular transport through porous membranes : enhanced resolution and contrast using intermittent contact-scanning electrochemical microscopy.* Analytical Chemistry, Vol.83 (No.17). pp. 6447-6454. doi:10.1021/ac201489c

[3.3] Ebejer, Neil, Schnippering, Mathias, Colburn, Alex W., Edwards, Martin A. and **Unwin, Patrick R.** (2010) *Localized high resolution electrochemistry and multifunctional imaging : scanning electrochemical cell microscopy.* Analytical Chemistry, Vol.82 (No.22). pp. 9141-9145. doi:10.1021/ac102191u

[3.4] Chen, Chang-Hui, Jacobse, Leon, **McKelvey, Kim M.**, Lai, Stanley C. S., Koper, Marc T. M. and **Unwin, Patrick R.** (2015) *Voltammetric scanning electrochemical cell microscopy: dynamic imaging of hydrazine electro-oxidation on platinum electrodes.* Analytical Chemistry, Vol.87 (No.11). pp. 5782-5789. doi:10.1021/acs.analchem.5b00988

[3.5] Kinnear, Sophie L., McKelvey, Kim M., Snowden, Michael E., Peruffo, Massimo, Colburn, Alex W. and **Unwin, Patrick R.** (2013) *Dual-barrel conductance micropipet as a new approach to the study of ionic crystal dissolution kinetics.* Langmuir, Vol.29 (No.50). pp. 15565-15572. doi:10.1021/la403630u

[3.6] Bentley, Cameron L., Kang, Minkyung and **Unwin, Patrick R.** (2017) *Nanoscale structure dynamics within electrocatalytic materials.* Journal of the American Chemical Society, Vol.139 (No.46). pp. 16813-16821. doi:10.1021/jacs.7b09355

Grants

[G1] Unwin, Patrick (PI), ERC, Quantitative Multidimensional Imaging of Interfacial Fluxes *(QUANTIF)*, Sep 2010-Aug 2015, EUR 2,129,141.

[G2] Unwin, Patrick (PI), EPSRC, Uncovering the Electroactivity of Novel sp2 Carbon Materials through Quantitative High Resolution Visualisation (EP/H023909/1), Aug 2010-Aug 2014, GBP537,107.

[G3] Unwin, Patrick (supervisor), Rodger, Alison (PI), EPSRC Doctoral Training Centre (EP/E501346/1) Oct 2005-Sep 2011, GBP1,002,913, and LSI DTC (EP/F500041/1), GBP1,117,411, Oct 2007-Sep 2012.
[G4] Unwin, Patrick, EPSRC Collaborative Training Account studentship (part of EPSRC GR/T11371/01) with National Physical Laboratory, Sep 2008-Sep 2012 (GBP26,000).

4. Details of the impact (indicative maximum 750 words)

A. Commercialisation of instrumental techniques. The ic-SECM and SECCM components of the Warwick Electrochemical-Scanned Probe Microscopy (WEC-SPM) platform have been commercialised as follows:

(i) Patents (US/Europe); [text removed for publication]
(ii) [text removed for publication]
(iii) [text removed for publication]
(iv) [text removed for publication]

B. [text removed for publication] partnership on new active ingredients for dental products. [text removed for publication]

C. WEC-SPM integral to new product development and advanced commercial know-how. Many speciality chemical products target surfaces and surface processes and the commercial sector is increasingly recognising the value of electrochemical imaging, and the unique insights the WEC-SPM platform can provide on surface processes. (i) With Syngenta scientists, WEC-SPM has been used to gain new perspectives on the delivery of active ingredients to plant root hair cells and to probe interfacial kinetics of emulsion polymerisation. "*The learning from these [has supported] specific product and process work ranging from optimization of controlled release encapsulated products to identification of catalyst poisons...*" and *"the latter...is in support of the introduction of a new fungicide active ingredient with sales projected to be in the hundreds of millions of dollars.*" **[5.5]**. The relationship with Unwin's group "*has facilitated an increase in capability…to continually improve the quality of our internal work*", including the recruitment of 3 researchers from the Unwin group in the REF2021 period **[5.5]**. (ii) SECCM is providing industry with major new perspectives on corrosion processes and products. [text removed for publication] **[5.6]**. (iii) Tata Steel UK, the largest UK steel maker *"has R&D lab facilities on the University of Warwick campus (since 2015) and the collaboration between the Unwin Group and WMG is strategically important.*" **[5.7]**. The Technical Director at Tata Steel states that "*the unique experimental platform at Warwick has enabled us to assess our substrates and determine the technical specification requirements for evolving market sectors [thereby] supporting new product development towards differentiated products...*" **[5.7]**.

D. Further examples of industry using Warwick imaging technology for materials discovery and to understand materials performance.
WEC-SPM techniques are also having a significant impact through scientists internationally who have set up SECCM and are working in partnership with industry. Following are examples of the impact generated by 3 groups and acknowledging Unwin's pioneering of SECCM. [text removed for publication].

E. Artistic value of electrochemical images
The aesthetic value of electrochemical images was explored by Coventry artist, Mary Courtney, who spent 10 months of 2016 with Unwin's group (Leverhulme Artist in Residence), mining electrochemical images and scientific images of samples and apparatus for various artworks and activities **[5.9a]**, and "drawing on the nanoscale using high resolution electrochemical probe microscopes" **[5.9b]**. Mary Courtney noted: "*This vast untapped mine of images of matter and reactions at the micro and even tinier nanoscale, is what Professor Patrick Unwin and myself are keen to explore – we want to pick out the most beguiling or beautiful images that would otherwise never be seen, and we want to bring these out to share with the public.*" **[5.9c]**. Artworks were presented in many venues, including: the Earlsdon Festival, Coventry (May 2016), which attracts

an estimated 10,000 people; in a Courtney-Unwin public lecture "The Art of the Micronosphere" at the Herbert Gallery, Coventry (2017), attended by an estimated 100 people **[5.9d]**; on big screens in the entrance of the Oculus teaching building at the University of Warwick, at its launch in 2016 and for several months thereafter **[5.9e]**, with 1000s people passing through per day; and the video installation, "Planet Biscuit: Into the Micronosphere" **[5.9f]**. Dozens of images and artworks produced by Mary Courtney during the residency were circulated widely on social media (e.g. Warwick Chemistry Twitter, with circa. 4,000 followers, with each artwork tweeted throughout the period of the residency).

5. Sources to corroborate the impact (indicative maximum of 10 references)

[5.1] Statement from [text removed for publication]
[5.2] Statement from [text removed for publication]
[5.3] Statement from [text removed for publication]
[5.4] Statement from [text removed for publication] and [text removed for publication] toothpaste reviews on Amazon UK and US sites.
[5.5] Statement from Syngenta
[5.6] Statement from [text removed for publication]
[5.7] Statement from Tata Steel UK
[5.8] Statements from three international research groups partnering with industry using Warwick imaging technology; [text removed for publication]
[5.9] Local artist Mary Courtney collaboration with Unwin; (a) Mary Courtney's website; (b) Leverhulme Trust artist in residence grant; 2015-AIR-051; (c) Verse Reaction: art in Chemistry webpage; (d) Art of the Micronosphere public lecture webpage and YouTube video; (e) Oculus building project webpage (f) Planet Biscuit: Into the Micronosphere Youtube video