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Highlights from the Faraday Discussion on Single Entity Electrochemistry, York, UK, August-September 2016

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Faraday Discussions, organised by the Royal Society of Chemistry (RSC), bring the concept of the flipped classroom to scientific conferences, promoting lively debate and discussion with the opportunity to hear complementary and contrasting views on topics spanning physical chemistry. The Faraday Discussion on the topic of single entity electrochemistry, in the picturesque setting of the University of York (31st August to 2nd September, 2016), presented an opportunity for researchers pushing at the lower limits of electrochemistry to engage in such lively discourse. The topic single entity was chosen to be as inclusive as possible, and proved to be so, with researchers probing single nanoparticles, nanopores, nanorods, vesicles and even single molecules, with a wide range of electrochemical techniques, both experimental and theoretical.

The flipped format begins conventionally with the submission of abstracts; however, this is where things begin to change. Upon acceptance, the presenter must submit a paper on the work that they will present. Papers are reviewed by the scientific panel for their suitability, but not for their scientific merit. Papers are then distributed to all attendees with sufficient time to read them and such that they may perform further experiments or calculations, or perhaps a reanalysis of the results presented. At the conference is where the fun really begins, where a 5 minute 'refresher' presentation by the author is followed by 'discussion' for ~40 minutes on each paper. In the discussion, attendees may ask questions about the paper, as in a traditional conference, but they are also encouraged to take part in a live peer review process. Comments, criticisms and counter-arguments, as well as further experiments on the theme are all welcome, to which the presenter has the right to reply. All the while, the RSC appointed 'stenographers' are feverishly working to note key-points from each question/reply which are emailed to those asking and responding. Final edited copies of these questions are published alongside the papers, preserved as a testament to the intellectual contributions of all of the participants.

To the uninitiated, reading the instructions for the discussion may prove rather daunting and a little confusing. However, for the four first-timer authors of this report, this Faraday Discussion must go down as one of the most intense and stimulating experiences of our scientific careers, providing a chance to observe and participate in the shaping of the future of our field. The discussion may sound combative and confrontational, but it is actually far from it. Multiple new collaborations were developed from complementary experiences and techniques, and collaborative manuscripts were drafted based on the competing analyses of data.

Introductory Lecture

The opening lecture of this Faraday Discussion was given by Prof. Nongjian Tao (Arizona State University, USA) and started off by bringing all of the attendees on the same level concerning the meaning of the term 'single entity'. Indeed, although many of us will encounter similar problems associated with small signals and stochastic behavior, the studied topics vary widely, with each of them asking for their own specialized tools. These tools can be roughly divided in those that study single entities one-by-one, such as scanning probe microscopy (be it through the use of a physical or an electrochemical probe) or those that study many entities simultaneously, such as many of the optical techniques. Specializing in the latter approach, particularly those based on surface plasmonic resonance (SPR) imaging, Prof. Tao spent the remainder of the talk demonstrating the impressive capabilities of this technique.

Apart from its high temporal resolution, a major advantage of SPR is that the measured signal depends on concentrations rather than electrochemical current. Thus, the sensitivity is independent of the probed surface area. Although single molecule detection is currently not feasible, probing the electrochemical reactivity of single nanoparticles has been shown to be well within reach (DOI:10.1021/acs.accounts.6b00348). While this is already very impressive, Professor Tao has taken this approach one step further by performing reactivity mapping through the measurement of impedance rather than electrochemical current. With this approach, it is possible to determine the effective charge of individual nanoparticles with a detection limit of only 0.2 electrons (DOI:10.1021/nl1026748).

Prof. Tao concluded the lecture by highlighting that while plasmonic (and other optical) techniques allow us to image electrochemical reactivity with high resolution, they also make us aware of some of the challenges we will face as we approach smaller length scales. As time and length scales are fundamentally related, a higher spatial resolution also requires for a higher temporal resolution. Here we will be limited by the gain-bandwidth product. In addition, while high resolution (electrochemical) mapping is no doubt a powerful analytical tool, it will not tell us everything, as we need information for a range of time (and length) scales. Thus, the final take home message from Prof. Tao was “do not let too much detail obscure the big picture”.

Session 1: From Single Cells to Single Molecules

Prof. Paul Bohn (University of Notre Dame, USA) kicked off the session by presenting on the fabrication of high density, ordered arrays of nanopores, embedded in vertically stacked metal–insulator–metal electrode structures, which he used for highly-efficient redox cycling (DOI: 10.1039/C6FD00062B). With the small volume of each nanopore (1.77 aL), the authors calculated that single molecule occupancy could be achieved at μM concentrations. Prof. Bohn conjectured that the use of an array and the high amplification factors generated by redox cycling should enable measurements of single molecules; however, this assertion was questioned during the discussion.

Prof. Andrew Ewing (University of Gothenburg, Sweden) took the podium next, presenting on vesicle impact electrochemical cytometry (DOI: 10.1039/C6FD00102E). He presented a model where a vesicle sits on an electrode and the electrical potential causes electroporation at the vesicle/electrode interface, with the pore size depending on the chemical nature of the vesicle. This model generated an intense discussion, as several attendees questioned his assumptions. Prof Ewing argued back that, based on experimental data and simulations, the pore should open at the vesicle/electrode interface.

The next speaker was Assoc. Prof. Lane Baker, (Indiana University, USA) who presented an interesting approach for performing functional measurements on living cells (DOI: 10.1039/C6FD00133E). The approach he described involved using a functionalised, double-barreled nanopipette as a scanning ion conductance microscopy probe. One barrel of the probe was functionalised with a membrane patch containing an ion channel, which was employed as a molecular sensor. The other barrel was left open and was used for distance control. During the discussion, it was argued that, as the probe was so small, most of the molecules released would not be detected.

Following a short tea break, the topic of discussion was changed from single cells to single molecules, with Prof. Simon Higgins (University of Liverpool, UK) presenting results obtained with electrochemical scanning tunnelling microscopy (STM) in metal|single molecule|metal junctions (DOI: 10.1039/C6FD00080K). He provided evidence that hopping conduction occurred across metal|molecule|metal junctions, even with short conjugated molecules. Prof Higgins highlighted the importance of the choice of media, explaining how it influences the conductance mechanism across a metal|molecule|metal junction more than the chemical nature of the molecule in the junction. The author was on questioned whether temperature-dependent measurements would help in further elucidating conduction mechanisms.

Prof. Jens Ulstrup (Technical University of Denmark, Denmark) then described the interfacial electrochemical behaviour and single-molecule structure of stacked G-quadruplexes, including a bound hemin, immobilized on single-crystal Au(111)-electrode surfaces, as studied using in situ STM imaging (DOI: 10.1039/C6FD00091F). Prof. Ulstrup was questioned on why the electrochemical properties of the hemin changed when it was physisorbed vs covalently linked, to which he argued that ordering on the surface may play a key role. Prof. Ulstrup also agreed that measurement of the adsorption isotherm of hemin on gold could be an informative experiment. Prof. Ulstrup concluded with a citation borrowed from Michael Faraday himself. One day, a civil servant asked him "what was the application of his research?", to which Faraday sarcastically replied "One day you can put a tax on it!".

Next, Assoc. Prof. Dongping Zhan (Xiamen University, China) presented his work on the catalytic response of a single redox enzyme on a nanoelectrode (DOI: 10.1039/C6FD00061D). The authors employed lipid-bilayer functionalised gold nanoelectrodes to monitor the electrocatalytic reduction of H_2O_2, catalysed by single molecules of horseradish peroxidase (HRP). The very high measured HRP turnover rate generated an intense discussion on the mechanism of electrochemical detection, which was only partially addressed by the speaker.

Prof. Serge Lemay (University of Twente, The Netherlands) concluded the session by describing the application of lithographically fabricated nanogap electrodes for single-molecule electrochemistry experiments (DOI: 10.1039/C6FD00075D). The author, following the discussion, agreed that using inner sphere redox couples could lead to important insights. Prof. Lemay also stated that he always observed molecular adsorption, regardless of the molecule (redox probe) used, and that he has never performed post-mortem analysis to characterise his nanogap electrodes. During the discussion, it was suggested that he could compare the electrochemical signals before and after in situ electrochemical surface roughening to tune the molecular adsorption. Prof. Henry White (The University of Utah, USA) commented that the effects seem to be more geometrical than chemical and that grain boundaries may play a very important role.

Session 2: Reactions at the Nanoscale

Session 2, chaired by Prof. David Fermin (University of Bristol, UK) focused on the nanoscale behavior of processes that are typically described on the macroscale and contained papers from Prof. Olaf Magnussen (Kiel University, Germany), Prof. Katharina Krischer (Technische Universität München, Germany), Thom Hersbach (Leiden University, The Netherlands), Prof. Henry White (The University of Utah, USA), Dr. Jan Clausmeyer (Ruhr-Universität Bochum, Germany), and Prof. Shengli Chen (Wuhan University, China).

First up was Prof. Olaf Magnussen, who presented his work on the electrochemical deposition of bismuth on Au single crystals (DOI: 10.1039/C6FD00086J). In situ video-STM was employed to provide atomically resolved data on the adsorption mechanism and dynamics of the bismuth structures. For Au(111), needle-like structures were observed, whereas on Au(100), a combination of nanowires and islands were formed. As STM experiments are performed under conditions where the tip and sample double layers overlap, the influence of the tip on the observations is always a point of discussion. Indeed, underneath the tip, the deposition rate was found to be slower due to hindered diffusion. Although it is possible that the tip could induce the nucleation of the nanowires, the morphology of the resulting structures do not seem to be influenced by the tip.

Gas phase CO oxidation is known to have an oscillatory behavior due to the existence of separated domains with high and low CO coverages. In her paper, Prof. Katharina Krischer discusses the role of these domains in the observed electrochemistry when the catalytic surface area is decreased to a size which is on the same order of magnitude of the domains (DOI: 10.1039/C6FD00115G). It turns out that in this regime, the intrinsic noise (which scales with $1/f^2$) increases significantly due to the nonlinear kinetics. Perhaps due to the complexity of the implications of these results, the discussion formed mainly around practical issues concerning the use of microelectrodes. Although everyone agreed that edge effects and contamination are difficult to circumvent in these experiments, it is not clear if these factors have any influence on the observed behavior.

As last speaker of the first set of papers, Thom Hersbach presented his work on the anisotropic cathodic corrosion of rhodium and gold (DOI: 10.1039/C6FD00078A). Careful electrochemical characterization combined with scanning electron microscopy allowed him to describe the structural preference of the formation of etch pits. The working hypothesis for this preference is based on the adsorption strength of the employed cation, which in this case was Na^+. As may be expected, the main part of the lively discussion focused on how to prove this hypothesis by studying the role of different cations, concentration dependencies, and using single crystal electrodes. Crucially, the proposed intermediates in cathodic corrosion (anionic clusters or metal anions) are probably unstable and thus short-lived which makes in situ detection extremely challenging.

How many gas molecules does one need to form a stable gas bubble? This was a key question in the paper by Prof. Henry White, studying the formation of individual gas bubbles at nanoelectrodes (DOI: 10.1039/C6FD00099A). Depending on the experimental parameters, a few thousand molecules are enough to form nanobubbles, implying that their internal pressure is in the hundreds of atmospheres range. One memorable moment during the discussion was where Prof. Olaf Magnussen brought up some of his own slides to illustrate the energetics of wetting angles.

Instead of bringing a scanning probe towards an electrochemically active surface, Dr. Clausmeyer deposited Ag nanoclusters directly on the probe to study their reactivity towards electrocatalytic oxygen reduction (DOI:10.1039/C6FD00101G). The silver clusters are deposited on a carbon nanoelectrode in one channel of a θ-pipette whereas the other channel is used to locally deliver oxygen molecules. This approach leads to a very neat way to mimic the gas diffusion-electrodes used extensively in industry. Interestingly, the smaller the electrode, the more the selectivity might shift towards the formation of peroxide as the final product, relating to increased diffusion rate of this intermediate away from the electrode surface. A practical issue associated with these experiments is that the Ag clusters also tend to form on the glass, in addition to the carbon nanoelectrode surface. This observation delighted Prof. Patrick Unwin (University of Warwick, UK) as the electron microscopy images shown by Dr. Clausmeyer confirm what he suspected was also occurring in his own experiments.

Where Prof. Krischer presented work on adsorbate domains that will not fit onto small electrodes, Prof. Shengli Chen took this a few order of magnitudes further. Prof. Chen presented a theoretical framework to describe the interactions between ions and electrode surfaces that are similarly sized (DOI: 10.1039/C6FD00087H). Describing a system at the boundary between finite size effects and a continuum approach, combined with practicalities such as edge effects, results in a theoretical description where concessions (concerning ion-electrode interactions) need to be made. It took some time before everyone in the audience was aware that this study was meant as pioneering work towards a final description. Once everyone was looking in the same direction, the only conclusion that could be drawn is that Prof. Chen's work will likely play an important role in the theoretical description of nanoscale electrochemistry. Perhaps it can even provide an insight into other 'unexpected behavior', such as that observed for 'large' nanopores.

Faraday Discussions, York, UK 2016-09-01

A Theoretical Consideration of Ion Size Effects on the Electric Double Layer and Voltammetry of Nanometersized Disk Electrodes

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Figure 1. Prof. Shengli Chen, Dr. Jan Clausmeyer and Prof. Henry White discussing their papers during Session 2.

Session 3: Electrochemistry of Single Nanoparticles

The third session, chaired by Profs. Justin Gooding (University of New South Wales, Australia) and Marc Koper (Leiden University, The Netherlands), focussed on detecting and interpreting the electrochemical and/or spectroscopic signal(s) arising from single nanoparticles (NPs) and featured papers from Prof. Keith Stevenson (Skolkovo Institute of Science and Technology, Russia), Assoc. Prof. Mario Alpulche (University of Nevada, USA), Jun.-Prof. Kristina Tschulik (Ruhr-University Bochum, Germany), Vitor Brasiliense (CNRS Universite Paris Diderot, France), Prof. Christine Kranz (Ulm University, Germany) and Chao Jing (East China University of Science and Technology, China).

The first paper was presented by Prof. Stevenson on assessing the mechanistic aspects of Pt NP aggregation in solutions typically used for detecting NP/electrode impacts by electrocatalytic amplification (DOI: 10.1039/C6FD00121A). Using a combination of electrochemical and non-electrochemical methods, it was concluded that in the absence of hydrazine, intermolecular H-bonding in the citrate capping layer imparts exceptional colloidal stability to large Pt NPs (50 nm) in relatively high ionic strength buffer solution (ca. 50 mM). Furthermore, the gaseous and surface bound products arising from the catalytic decomposition of hydrazine (on Pt) are thought to destabilize the citrate layer, causing colloidal instability under comparatively low ionic strength conditions (ca. 20 mM). Following a comment from Prof. Henry White on deconvoluting the effects of NP size from electrocatalytic activity in NP impact analysis, Prof. Stevenson reiterated the importance of colloidal stability in these type of measurements, while Prof. Patrick Unwin emphasised the importance of undertaking complementary microscopic techniques in tandem with NP impact analysis in order to understand the relationship between NP structure and activity (a common theme in these discussions).

Assoc. Prof. Alpulche presented the second paper on the stochastic interaction between colloidal dye sensitized anatase NPs and a Pt ultramicroelectrode in the dark and under illumination (DOI: 10.1039/C6FD00100A). In the dark, NP impacts were detected as anodic steps (attributed to the oxidation of the loaded dye), while under illumination, NPs were detected as both anodic and cathodic steps (attributed to the reduction of the oxidized form of the dye generated after electron injection into TiO_2). Furthermore, the NP impact photocurrent response is thought to be dominated by large NP agglomerates (formed under illumination) rather than single NPs. During the discussion, Profs. Olaf Magnusson and David Fermin weren't convinced by the mechanisms proposed in the paper, and asked for further clarification, while Prof. Richard Crooks (University of Texas at Austin, USA) suggested that tracing impacts at an optically transparent electrode could provide fruitful information on colloidal stability, as well as the charge-transfer mechanism during NP impact.

The third paper was presented by Jun.-Prof. Tschulik on using NP impact analysis as an alternative to scanning transmission electron microscopy (STEM) for sizing and compositional analysis of individual AgAu alloy NPs (DOI: 10.1039/C6FD00112B). Through a combination of cyclic voltammetry on ensembles of NPs, as well as single NP volumetric (anodic stripping) analysis under chronoamperometric conditions, sizing and compositional analysis of 14 nm diameter $Ag_{0.73}Au_{0.27}$ NPs was shown to be possible through careful control the applied potential. Profs. Julie Macpherson (University of Warwick, UK), Justin Gooding and Patrick Unwin all agreed that although electrochemical NP impact analysis is a powerful analytical method, it does not provide information on the structural morphology or chemical identity of the metals present in the bimetallic NPs and therefore complementary STEM would still be necessary for complete NP characterization. Furthermore, Prof. Unwin pointed out that there are still many aspects of the anodic NP stripping response that are not fully understood, and further emphasised that although NP impact experiments are conceptually 'simple', in practice they are difficult, requiring the measurement of fast (sub-ms to ms) stochastic events which give rise to extremely small currents (pA to tens of pA).

Following a break for tea, the session continued with Vitor Brasiliense presenting the fourth paper on coupling NP impact analysis with dark-field imaging/spectroscopy for tracking the dissolution of single Ag NPs or NP agglomerates in thiocyanate solution (DOI: 10.1039/C6FD00098C). By coupling electrochemistry with spectroscopy, it was shown that the oxidation of Ag NPs is accompanied by a slow phase transformation, followed by dissolution and under some circumstances recrystallization of AgSCN from the local supersaturated solution. In addition, spectrometric interrogation of single entities during oxidation (electro-dissolution) allowed the qualitative discrimination between single NPs and NP agglomerates. Prof. Henry White was intrigued by the timescale of the dissolution events (several seconds), and correctly pointed out that this likely to be controllable with the anion present in solution (e.g., the events can be shorted to the millisecond timescale by switching from SCN^- to NO_3^-). The rest of the discussion focussed on highlighting the strengths and limitations of coupling spectroscopy and electrochemistry, with valuable contributions from Prof. Nongjian Tao on the practical limits of techniques of this type.

Prof. Kranz presented the fifth paper on the challenges associated with nanoelectrochemical and nanomechanical studies of individual anisotropic gold NPs (DOI: 10.1039/C6FD00128A). Atomic force – scanning electrochemical microscopy (AFM-SECM) was used to characterize soft PDMS substrates modified with gold nanostars in peak force tapping mode, which, in conjunction with electrochemical mapping, provides information on the adhesion, deformation properties and Young's modulus of the sample. The electrocatalytic activity of Au NPs towards hydrogen peroxide oxidation was correlated to size and shape, with the Au nanostars showing enhanced catalytic activity compared to spherical NPs of similar size. Prof. Frederic Kanoufi (CNRS Universite Paris Diderot, France) sparked a detailed discussion on deconvoluting the effects of activity and topography in AFM-SECM (and related scanning probe techniques), while Prof. Patrick Unwin and Prof. Kranz discussed the robustness (advantages/disadvantages) of AFM-SECM compared to scanning probe techniques based on nanopipettes.

Chao Jing presented the sixth and final paper of this session on the imaging of electrocatalytic processes on gold nanorods by coupling cyclic voltammetry to dark field microscopy (DOI: 10.1039/C6FD00069). Using hydrogen peroxide oxidation as the model electrocatalyic process, spectral changes (i.e., scattering intensity) at individual nanorods were correlated to catalytic activity, which was found vary substantially from nanorod to nanorod (attributed to structural heterogeneities). During the discussion, Prof. Justin Gooding pointed out that the observed heterogeneities in catalytic activity seemed to be spatially dependent and proposed that it could arise due to the positioning of the counter electrode with respect to the semiconducting ITO substrate (i.e., due to a potential gradient across the working electrode surface). Prof. Marc Koper further pointed out that the choice of counter electrode material is very important in studies on electrocatalysis (e.g., due to dissolution/redeposition of the counter electrode material), and emphasised the importance of designing the electrochemical cell setup to avoid such artefacts.

At the conclusion of this session, several delegates engaged in a discussion on the importance of single NP measurements (compared to 'ensemble studies'), as well as the current difficulties (fast timescale, small currents) and future directions of this field, with the ultimate goal being to correlate structure (size and morphology) and function (electrocatalytic activity) at the single NP level.

Session 4: Nanopores

The final session of a conference, following a conference dinner the night before, can often prove to be a low-energy affair; thankfully, the high energy format of a Faraday discussion led to a continuation of the engaging discussion and dialogue we had been treated to during the previous sessions. The topic of the session, 'nanopores and nanotubes', was explored in contrasting directions by the six contributors, who hailing for universities in 5 different countries, highlighted the internationality of these discussions.

The first half of the session began with two theoretical investigations. Prof. Wolfgang Schmickler (Ulm University, Germany) began by introducing us to his density functional theory calculations on the insertion of anion-cation pairs into a ~1 nm carbon nanotube (DOI: 10.1039/C6FD00076B). His modelling approach contrasted with the approach of Prof. Michael Eikerling (Simon Fraser University, Canada) who used finite element calculations to investigate somewhat larger (10 nm) Pt nanopores in aqueous solutions (DOI: 10.1039/C6FD00094K). In the discussion part of the session, the speakers proved that questions were not restricted to the audience, questioning each other on their respective works.

Dr. Sanli Faez (Utrecht University, The Netherlands) returned us to experimental investigations by presenting a new take on the Millikan oil drop experiment (DOI: 10.1103/PhysRev.2.109). Using state-of-the-art optical techniques he was able optically track the motion of single colloidal particles in a solution filled nanocapillary (DOI: 10.1039/C6FD00097E). Through a theoretical framework, including fluid flow and electric fields, he showed us how one can deduce the charge on a single particle from its track.

The second half of the session covered the use of nanopores for sensing. While Drs. Tim Albrecht (Imperial College, UK) and Robert Johnson (The University of Utah, USA) both presented on the detection of DNA, their pores and topics were quite different. Albrecht's presentation focussed on a new high-bandwidth amplification strategy (DOI: 10.1039/C6FD00109B), which piqued the interest of a number of members of the audience who could see how the 'open source' device might benefit their own work. Albrecht's work using pulled glass pipettes contrasted with the work of Johnson, who used the protein pore α-hemolysin to investigate the kinetics of base flipping in DNA (DOI: 10.1039/C6FD00058D). By varying the temperature in his experiments, he was able to probe activation energies of a single molecular motion, which was measured on a single molecule basis.

Dr. Mark Platt (Loughborough University, UK) concluded the scientific presentations by contrasting two ways in which a nanopore can be used to quantify a biomarker (DOI: 10.1039/C6FD00072J). In the first, he used an aptamer-modified pore to quantify the rectification (ratio of the currents at equal potentials, but opposite polarities), a measure which is sensitive to the surface charge of the pore (DOI: 10.1021/acs.accounts.6b00395). In his second method, the pore remained unmodified and instead a particle was modified with the aptamers. The passage time of a particle through the pore on application of an applied voltage proved to be a sensitive measure of surface charge, which was modified by biomarker binding.

As well as specific questions directed at their work, the speakers answered more general questions. A personal highlight was hearing an honest dialogue on the future of nanopore techniques. The presenters each discussed where they believe nanopore measurements might make scientific advances in the future; however, they were also frank about where they believe they would not. The format of the Faraday write-up means that these remarks remain stored for posterity.

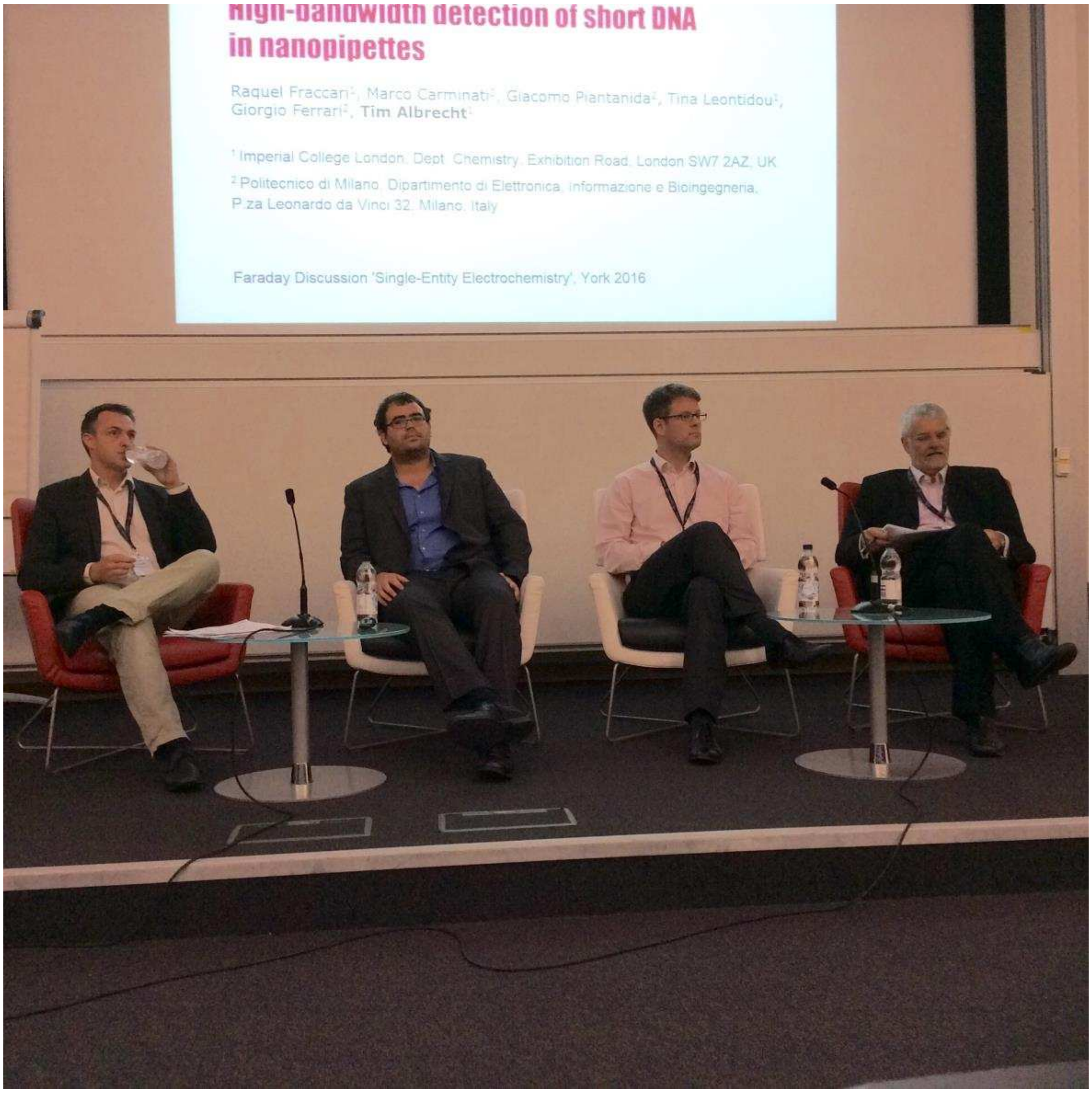

Figure 2. Drs. Mark Platt, Robert Johnson, Tim Albrecht and Prof. Phil Bartlett during the general discussion at the end of Session 4.

Conference Dinner and Social Events

The highly anticipated dinner event is another Faraday Discussion tradition, namely the Loving Cup Ceremony. During this event the attendees pass each other an 18th century silver cup, from which they sip port wine and toast to the long term employees of the Faraday Society, ‘‘in piam memoriam of G. S. Marlow and Angela and Tony Fish’’. Unfortunately, the Loving Cup was at a concurrent Faraday Discussion being held in Cambridge; nevertheless, we continued the much-loved tradition with our own glasses, which according to some of the Discussion veterans, was a much better alternative.

Figure 3. Profs. Justin Gooding, Nongjian Tao and Patrick Unwin leading the Loving Cup Ceremony.

During the dinner, Prof Phil Bartlett (University of Southampton, UK) awarded the Faraday Division poster prizes to Finn Reikowski (Kiel University, Germany) for his work on "Transmission surface diffraction for operando studies of heterogeneous interfaces" and to Vitor Brasiliense (CNRS Universite' Paris Diderot, France) for "In operando optical monitoring of single particles during oxygen species with modified carbon nanoelectrodes"

The Nanoscale Horizons poster prize was awarded to Na Kong (Deakin University, Australia) for her poster entitled "Real-time electrochemically monitoring formation of chemical bonds in solution". The organising committee also awarded an honourable mention to Hiroki Ida (Tohoku University, Japan) for his poster on "Continuous evaluation of microvilli movements on cell membrane using fast scanning ion conductance microscopy".

Concluding Remarks Lecture

The concluding remarks (DOI: 10.1039/XXXXXXXXXX) were delivered by Prof. Richard Crooks (University of Texas at Austin, USA). After thanking the organizing committee, he gave a light-hearted summary of the meeting by listing the most important 'things he learned' over the three-day period. Specifically, he relayed the practical difficulties in making reliable and reproducible measurements at the single entity level, relating to the necessarily small geometries (e.g., nanoelectrodes), volumes (e.g., nanogaps) and signals (e.g., sub-pA to pA currents) involved. Two points he emphasized in particular were: (i) the need to work with well-defined and impurity free systems and; (ii) theory and simulations are currently underutilized in this field. On the latter point, he acknowledged the difficulty in applying simple continuum theory to explain single entity phenomena, as they may collapse at the small size scales involved.

Crooks continued by putting together a ‘wish list’ of sorts, with his ‘dream’ objective being to use first-principles theory to predict the size, structure and composition of catalytically active nanomaterials, and then synthesize, characterize and test the resulting catalysts. Recapitulating his own work in the field, he pointed out that in reality the process described above is actually reversed, with phenomena first being observed from experiments carried out under a well-defined (and usually strict!) set of conditions, and then later explained using the appropriate theories through simulation. He went on to explain that the ultimate goal in electrocatalysis, and indeed any form of materials science should be to correlate structure to function, and realistically, this can only be achieved at the single particle (or more generally, single entity) level, as this is the only way to rule out the possibility that a small proportion of particles (among a heterogeneous population) are responsible for an observed phenomenon (e.g., catalytic activity).

One of the highlights of Crooks’ lecture was the electrochemical readaptation of the famous Steve Jobs’ quote “Stay hungry, stay foolish” which sounded like “There is nothing more boring than a reversible cyclic voltammogram”. This sentence was a strong encouragement to the electrochemical community to look for, and share, those results that cannot be explained by well-understood theoretical frameworks.

Figure 4. Prof. Patrick Unwin introducing Prof. Richard Crooks ahead of his Concluding remarks lecture.

Crooks concluded by looking forward to what he believes the future will hold for single entity electrochemistry, summarizing what will need attention in order to advance the field, including: (i) better control over experimental systems; (ii) advances in theory, as well as closer coupling of experiments and theory; (iii) better measurement systems, complemented by non-electrochemical methods where possible and; (iv) more attention given to the small details which are often neglected in experimental analysis. The concluding remarks were followed by well-deserved acknowledgements to the hosts and organizers, and then lunch, where the delegates had one last chance to discuss the talks and posters, before going their separate ways.

Overall, the 2016 Faraday Discussion on single entity electrochemistry was a great success, with great diversity in the papers and posters presented, borne out of the loose definition of the term ‘entity’ (e.g., nanoparticle, vesicle, molecule, etc.). Indeed, the success of the meeting was reflected in the vibrant and stimulating discussion sessions, which, due to the abundance of questions and remarks, were often concluded prematurely by the sessions’ chairs in order to stay on schedule. Looking forward to the future, further advances in instrumentation (both electrochemical and non-electrochemical) and theory will undoubtedly lead to advances in the understanding of electrochemistry at the single entity level, bringing us closer to establishing (and predicting) the relationship between nanomaterial structure and function (activity).