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Concluding remarks: next generation nanoelectrochemistry – next generation nanoelectrochemists

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Received 28th January 2022, Accepted 7th February 2022

DOI: 10.1039/d2fd00020b

The aim of this paper is to describe the scientific journey taken to arrive at present-day nanoelectrochemistry and consider how the area might develop in the future, particularly in light of papers presented at this *Faraday Discussion*. By adopting a generational approach, this brief contribution traces the story of the nanoelectrochemistry family within the broader electrochemistry field, with a focus on scientific capability and themes that were important to each generation. I shall consider research questions and the impact of technology that was developed or available in each period. Nanoelectrochemistry is still somewhat niche, but is attracting increasing numbers of researchers. It is set to become a major part of electrochemistry and interfacial science. It is studied by people with a fairly unique skillset, and I shall speculate on the skills and expertise that will be needed by nanoelectrochemists to address the challenges and opportunities that lie ahead. I conclude by asking: who will be the nanoelectrochemists of the future and what will they do?

Historical origins of nanoelectrochemistry

We start our journey in a time when there was huge interest in batteries, and this is not the present day! Volta's development of the pile, in 1799, reported to the Royal Society in 1800, was called an 'alarm bell for experimenters' by Humphry Davy¹ and led to a race by scientists across Europe to construct bigger and more powerful batteries for use in 'electrochemical incandescence', the isolation of elements and chemical analysis. In 1813, John George Children reported 'the greatest galvanic battery that has ever been constructed',² in the purpose-built laboratory in the grounds of his home, Ferox Hall, Tonbridge, Kent, England. The battery consisted of '20 pairs of copper and zinc plates, [and] each plate was 6 feet [*ca.* 1.83 m] in length, 2 feet 8 inches [*ca.* 0.81 m] in breadth'. It was filled with 4000 l of acid! On the first weekend of July of that year, a group of 38 eminent chemists and natural philosophers assembled at Ferox Hall to witness the great battery and perform a series of experiments. The resulting article by Children² was

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published under the heading: 'Scientific intelligence and notices of subjects connected with science'; but was the construction of ever larger batteries the most intelligent trend for electrochemical analysis at this time? William Hyde Wollaston (who was among the chemists at Ferox Hall and made suggestions to Children about sample size) did not think so. Davy's biographer, John Parris, recollected:^{3,4} 'shortly after he [Wollaston] had inspected the grand galvanic battery constructed by Mr Children... he accidentally met a brother chemist in the street, and seizing his button, (his constant habit when speaking on any subject of interest) he led him into a secluded corner; when taking from his waistcoat pocket a tailor's thimble, which contained a galvanic arrangement, and pouring into it the contents of a small vial, he instantly heated the platinum wire to white heat'. By miniaturising the experiment, and passing current through a Pt wire of just *ca.* 4 μm diameter, Wollaston was able to perform the same experiments using a pocket device for which others were using giant batteries.

Wollaston recognised the importance of *current density* in electrochemistry as early as 1801, reporting:⁵

'It has long been thought necessary to employ powerful machines and large Leyden jars, for the decomposition of water; but, when I considered that the decomposition must depend on duly proportioning the strength of the charge of electricity to the quantity of water, and that the quantity exposed to its action at the surface of communication [electrode] *depends on the extent of that surface*, I hoped that, by reducing the surface of communication, the decomposition of water might be effected by smaller machines, than have hitherto been used for that purpose; and, *in this hope, I have not been disappointed.*' (italics my emphasis).

To decrease the 'surface of communication', Wollaston set about constructing increasingly smaller electrodes and, in fact, fabricated microelectrodes (or, equivalently, ultramicroelectrodes)⁶ in the same way as they were introduced separately by Fleischmann and Wightman from the late 1970s onwards (more on microelectrodes later). He wrote:⁵

'Having procured a small wire of fine gold, and given it as fine a point as I could, I inserted it into a capillary glass tube; and, after heating the tube, so as to make it adhere to the point and cover it in every part, I gradually ground it down, till, with a pocket lens, I could discern that the point of the gold was exposed.'

We might even reasonably speculate that Wollaston made the first nanoscale electrode:⁵

'In order to try how far the strength of the electric spark might be reduced by proportional diminution of the extremity of the wire, I passed a solution of gold in *aqua regia* through a capillary tube, and, by heating the tube, expelled the acid. There remained a thin film of gold, lining the inner surface of the tube, which, by melting the tube, was converted into a very fine thread of gold, through the substance of the glass.'

Although Faraday referred to the significance of Wollaston's work in his electrochemistry research in the 1830s,⁷ it seems to have largely been forgotten. What is true is that Wollaston's work was distinct and well ahead of its time. Incredibly, some of the steps in the process described above resemble those used in the present-day fabrication of pipette-based gold nanopore devices, which are powerful for nanoscale analysis.⁸ Nanoelectrochemistry has long relied on the crafting of small scale electrodes and devices.



Our journey recommences over a century later, after the Second World War, which marked a turning point for science and society. I shall describe developments generationally, not in terms of the birth years of scientists, but rather the themes, influences and trends in each generation.

Boomer electrochemistry (1946–64)

The 1947 *Discussion of the Faraday Society on Electrode Processes* provides a good indication of the key topics at the start of this period. Almost 200 people gathered in Manchester, England⁹ to discuss papers under the headings general and theoretical, the deposition of hydrogen and metals, and anodic and other electrochemical processes. It was anticipated that advances in “physical chemistry in the next decade will lie in the application of the science of the techniques of electronic engineering, developed particularly during the war, and the field of electrode processes may be one which will yield readily to attack by the new weapons”.⁹ Many of the papers from the 1947 *Discussion* are grounded in firm mathematics and theory, and some of the comments are ‘robust’ (even on paper!). Among those contributing in person or by communication were scientists who have made major contributions to the field and on whose work we continue to rely today, including Randles, Butler, Hickling, Mott, Levich, Bockris, Fleischmann, Parsons, Heyrovsky and Lingane. Perusing the volume, one is struck by the fact that a number of key problems to be solved in electrochemistry are longstanding. In the present *Discussion* the need to better understand ion and concentration distributions near electrochemical interfaces arose in several papers, and this was the case 75 years ago; for example, a communication from W. F. Berg at the 1947 *Discussion* proposed that an interferometric method, used to study the ion distribution around a growing crystal, could be applied to “electrode chemistry, since there is much speculation and little detailed knowledge of the concentration distribution of ions”.¹⁰

This period also saw the birth of the Coulter Counter: there is a very nice description of this device, and many other historical developments in a ‘Perspective and Prospectus on Single-Entity Electrochemistry’ written by Lane Baker in 2018,¹¹ which is highly recommended. This period was naturally dominated by home-built instrumentation and electronics. While mainstream electrochemistry was to become (over)reliant on commercial instrumentation in later generations, the nanoelectrochemistry community is presently heavily engaged in instrumentation development, particularly in pushing the capability of low noise and high bandwidth current amplifiers for single entity analysis, as evident from the paper from Zhong *et al.* (DOI: 10.1039/D1FD00055A) in this *Discussion* on high throughput single entity analysis. Such developments will continue to be important in our field moving forward. In addition, the Boomer period was concerned about solutions and salt purity, particularly with a switch in focus away from polarography to the electrochemistry of solid electrodes, as described in Adams’ classic text.¹² There was considerable interest in understanding the electrical double layer, electrode kinetics and mass transport, including increasing attention towards hydrodynamic electrodes, all of which are timeless themes in electrochemistry. Consequently, the work by this generation has a long influence.



Generation X (1965–80)

This period saw a significant diversification in the scope and application of electrochemistry. At the core, there was a focus on kinetics and mechanisms, especially electron transfer coupled to homogeneous processes (*e.g.* the Savéant school, and others),¹³ which extended into subsequent generations. In this *Discussion*, Gundry *et al.* (DOI: 10.1039/D1FD00050K) showed that such processes are a useful testbed for the deep neural network classification of electrochemical processes. A further major advance in this period was the seminal work from Allen Hill's group on the electrochemistry of redox proteins, which ultimately led to the development of sensors in the 1980s that revolutionised blood glucose analysis and provided an inspiration for much other work on electrochemical sensors in subsequent generations.¹⁴

Chemically-modified electrodes,^{15,16} particularly polymer-modified electrodes,¹⁷ came to the fore in the 1970s and one gets a good sense of the status of this burgeoning field in the next generation from *Faraday Discussion 88* (1988) on *Charge Transfer in Polymeric Systems*. In the papers from Walcarius and co-workers on polyaniline nanowire arrays (DOI: 10.1039/D1FD00034A) and Bohn *et al.* on nanopore-based sensors (DOI: 10.1039/D1FD00048A), we see that it is now possible to control and characterise the architecture of complex electrode structures at the nanoscale. This ability to design functional electrodes with exquisite control will lead to a better understanding of mass transport at small scales, open up new sensing paradigms and lead to improved material performance.

This era marked the birth of neuro-electroanalysis through the pioneering work of Adams,¹⁸ together with Wightman¹⁹ and the scientists who came through these groups and those of their descendants, several of whom have contributed to this *Discussion*. Carbon materials of various types have proven to be the electrodes of choice for the electrochemical detection of neurotransmitters, and this *Discussion* highlighted the improved detection capabilities of carbon electrodes when the nanoscale architecture is engineered, controlled and characterised: (i) nanospikes electrodes that could also be batch fabricated with good reproducibility, which is an important development, as described by Venton and co-workers (DOI: 10.1039/D1FD00053E) and (ii) the use of different Ar plasma treatments of carbon-fiber electrodes to create nanostructured electrodes without affecting the surface chemistry, by Ross *et al.* (DOI: 10.1039/D1FD00049G). These fundamental advances in sensor design are important steps towards the rational design of nanostructured electrodes for *in vivo* and *in vitro* measurements.

The patch clamp technique was invented in this period by Neher and Sakmann, making use of micropipettes to measure ion currents in individual living cells, cell membrane patches and tissue sections.^{20,21} As we have seen in this *Discussion*, nanopipettes have become among the most important tools for various measurements in nanoelectrochemistry. Artificial bilayers are also useful model systems for understanding various physicochemical processes related to cell membranes and in this *Discussion*, Hirano-Iwata *et al.* (DOI: 10.1039/D1FD00045D) described the application of a lateral voltage to such devices. Bohn's paper (DOI: 10.1039/D1FD00048A) also took inspiration from biology in the design of a pH-sensitive nanopore membrane with potential-control of wetting/dewetting.



Spectroelectrochemistry assumed prominence, especially through leading developments in several areas by the Southampton Electrochemistry Group, where Fleischmann and colleagues first observed surface enhanced Raman scattering (SERS).²² In this *Discussion*, we saw the importance of *in situ* SERS for revealing molecular details at electrode/polyelectrolyte interfaces in the paper by Xiao *et al.* (DOI: 10.1039/D1FD00051A).

In this era, there were significant efforts to improve the signal to background (noise) and concentration detection limits in electrochemistry, which are key themes for nanoelectrochemistry today. Although pulse polarography was pioneered by Barker in the Boomer period,²³ Osteryoung's work on pulse voltammetry in the 1970s²⁴ rekindled interest in this field. Alternative approaches to improve the detection of electrochemical signals include the work of Bruckenstein and Miller on hydrodynamic modulation voltammetry with lock-in detection.²⁵ There is certainly scope for the greater use of such concepts in nanoelectrochemistry, for example, in self-referencing hopping-mode scanning electrochemical probe microscopy (SEPM) methods, where the signal at the probe is measured in bulk and near the surface at each pixel (position) in a scan.²⁶

Approaching the end of this period, there was the rediscovery of microelectrodes independently by Fleischmann and Wightman,^{27,28} and they were perhaps unaware that they were fabricating small scale electrodes in a essentially identical way to Wollaston almost two centuries earlier (see above). The impact of voltammetric microelectrodes in electrochemistry²⁹ cannot be underestimated; they have revolutionised the spatiotemporal scale of electrochemical measurements, opened up many possibilities for making electrochemical measurements in a diversity of unusual environments, expanded quantitative knowledge of diffusion and mass transport in electrochemical systems, and enabled subsequent developments in SEPM, providing the foundation for much of what we do in nanoelectrochemistry today.

Bard and Faulkner's *Electrochemical Methods*,³⁰ published in 1980, brings this period to a close. This textbook signalled a shift in emphasis in electrochemistry towards techniques and methodology, and brought the ways in which we study electrochemical processes to the front and centre. When reviewing the developments in methodology in this period, one can see why this book was so timely and has had a significant impact on generations of electrochemists. The updated 3rd edition of this classic text, with Henry White as a new coauthor, is imminent and is eagerly anticipated.

Millennial (1981–95)

We live in an age of imaging science, surrounded by impressive atomic-scale images of materials, surfaces and interfaces. The invention of scanned probe microscopy (SPM), originating with scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), was a watershed in surface and interfacial science and heralded new ways to visualise electrochemical interfaces *in situ* with unprecedented resolution. These methods continue to be hugely important in understanding dynamic electrode surfaces at the nanoscale, as evident in the paper of Mao on the visualisation of lithium electrodeposition under battery electrode conditions using *in situ* AFM in a glovebox (DOI: 10.1039/D1FD00051A).



This was the era of high-speed electrochemistry, with record-breaking scan rates employed in fast scan cyclic voltammetry. The digital revolution impacted electrochemistry with a transition from analog (chart recorders, oscilloscopes) to PC-based potentiostats and data acquisition systems. These developments, enabling in some ways, have not been without their drawbacks. Potentiostats available commercially were increasingly regarded as black boxes in some quarters and in subsequent generations, leading to a loss of knowledge and knowhow in the community. Likewise, while research on electrochemical sensors developed in this period, as with many large fields, it became something of a bandwagon, where sensor performance and metrics eroded fundamental science. More positively, digital simulation (home-coding) enabled increasingly complex and realistic electrochemical models to be developed. Efforts in this area were greatly aided by excellent texts from Feldberg³³ and Britz.³⁴ Code-development tended to be confined to individual labs and there are not many examples of code sharing at this time. The increasing use of COMSOL Multiphysics (especially) and other packages in subsequent generations has given many more groups access to numerical methods for analysing nanoelectrochemistry data (mass transport, kinetics) and also for the design of experiments (however, see also Generation Alpha below).

Generation Z (1996–2010)

Nanoelectrochemistry came into its own in this period, with various methods developed not only for the fabrication of nanoelectrodes and nanoscale devices, but also for their robust characterisation, visualisation and modelling. We see these key trends throughout the papers presented at this *Discussion*. Nanolithography strategies were used for the batch fabrication of multifunctional electrochemical imaging probes and nanogap cells for detecting and analysing single molecules. Where nanopores or nanopipettes were still crafted, they could be characterised with a high degree of confidence, especially using electron microscopy. Indeed, scanning electron microscopy, transmission electron microscopy, and variants thereof, arguably became as important as the electrochemical measurement. This was particularly true for nanomaterials electrochemistry, with the Brust and Schiffrin method³⁵ for the synthesis of gold nanoparticles proving seminal and leading to a nanomaterials electrochemistry revolution, driven in the present generation by the search for energy storage and electrocatalysis materials.

The rise of the nanomaterials field also brought about an identity crisis for electrochemical studies of such materials: how should the electrochemistry of



nanomaterials be studied most informatively and what types of studies constitute nanoelectrochemistry? As an illustration, studies published at about the same time on carbon nanotubes could consider, on the one hand, complex samples of commercial materials, with various contaminants, deposited on a carbon support electrode (many examples of such “carbon-on-carbon” electrodes); on the other hand, considerable effort was put into fabricating and characterising devices in which the electrode was only an individual single walled carbon nanotube on an otherwise inert support.³⁶ In the opening to the Introductory Lecture, Gooding *et al.* (DOI: 10.1039/D1FD00088H) defined nanoelectrochemistry as “where electrochemical properties and/or electrode materials are investigated in the nanoscale regime” aided by measurement tools that can address nanoscale features. Thus, the latter measurements of a carbon nanotube, an example of *single entity electrochemistry*, conform to an accurate descriptor of nanoelectrochemistry. Macroscopic electrochemical measurements of a complex and under-characterised sample of nanomaterial spread on an electrode, by contrast, do not fall within the definition of nanoelectrochemistry.

Generation Alpha (2011–)

This is the generation of single entity electrochemistry, which was defined at the 2016 *Faraday Discussion* (vol. 193) as ‘a new way of viewing electrochemical processes at the nanoscale, and provide a bottom-up approach for understanding electrochemical processes in complex systems’. The field of single entity electrochemistry, or the ‘electrochemistry of things’,¹¹ connects disparate problems that have common underpinning challenges, *e.g.* in measurement, instrumentation, data acquisition, analysis, modelling and so on. Single entity electrochemistry covers the study of: (i) individual nanoparticles, nanotubes and nanowires and (ii) nanopores and nanofluidics, which can be treated with a common language. But single entity electrochemistry also includes the study of complex surfaces and reactions at the nanoscale, where the idea is to break down surfaces into a set of more elementary structural or other features and try to understand the electrochemistry of the features. In the realm of molecular electroanalysis, single entity electrochemistry investigations vary from the detection of single molecules to single cells.

The new era of single entity electrochemistry, and nanoelectrochemistry more broadly, is connected strongly to imaging and visualization. Taking single particle electrochemistry as an example, studies can now be made with a range of different, but complementary, techniques, which provides a much more holistic view of structure–activity. SEPM³⁷ and optical imaging techniques³⁸ can be used to target individual nanoparticles, or groups of nanoparticles within an array or ensemble, and assess their activity and other properties. In this *Discussion*, Lemay and co-workers reported the innovative use of a CMOS-based nanocapacitor array device for local measurements of electrolyte impedance (DOI: 10.1039/D1FD00044F). The detection of the sedimentation of individual oil droplets in a water phase in real time, with sub-micron spatial resolution, illustrates the considerable potential of this approach. While nanoparticle impact studies do not usually involve imaging methods, if they are run for long times with high rate data acquisition, the resulting large datasets present similar challenges to those



of imaging experiments, with regard to the extraction of signals, and data handling, archiving, analysis and presentation.

The use of optical microscopy methods and SEPM, and combinations thereof, for nanoscale electrochemical measurements is developing apace and there will be significant advances in understanding from studies where both optical (including spectroscopy) and electrochemical signatures of single entities are tracked in real time. Within the SEPM field, there are interesting hybrid techniques with dual or multifunctional probes: AFM-SECM,^{39,40} SICM (scanning ion conductance microscopy)-SECM,⁴¹ SECCM (scanning electrochemical cell microscopy)-SECM,⁴² AFM-SICM⁴³ (FluidFM), *etc.* It is also possible to use these probes to exert considerable control over nanoscale systems, for example trapping, sampling and analysing single entities. These techniques, and others, are opening up exciting prospects for *operando* and correlative imaging at the nanoscale, which I shall address further below. As a consequence, huge datasets are being generated from multiple techniques applied in parallel or series that would not have been envisaged even a decade ago, and this presents a challenge to the experimentalist now and in the future.

Amber or red lights for Gen-Alpha are that COMSOL Multiphysics and similar programs should not simply be used as a black box. Furthermore, as nanoscale systems of interest become ever smaller, including nanoconfined systems, identified as a key topic in Gooding *et al.*'s Introductory Lecture (DOI: 10.1039/D1FD00088H), there will also be a need to transition from continuum models, including a reliance on the Gouy–Chapman–Stern model for the electrical double layer, to simulations that include atomistic detail.^{44,45}

There is a healthy trend towards innovation in home-built electronic instrumentation in nanoelectrochemistry (mirroring what happened in the Boomer period for electrochemistry generally; see above), including reports at this *Discussion*. Furthermore, the use of patch clamp amplifiers from electrophysiology and the emergence of companies that are developing instruments that push the capability of current amplifiers and other instrumentation is to be welcomed.

Many electrochemical materials papers contain beautiful images of nanomaterials, for example, from aberration-corrected (scanning) transmission electron microscopy, (S)TEM, and other atomic-resolution microscopes, but the quality of the electrochemical measurements does not always match. We have to ensure that structural microscopy does not overshadow the electrochemistry itself, or compensate for inadequate electrochemical measurements. As I have described, developments in single entity electrochemistry techniques mean that structure and electrochemical activity/property measurements can be on at least an equal footing. Liquid cell TEM offers excellent opportunities for *in situ* structure–activity measurements, particularly if the nanomaterial can be presented for electrochemistry in the TEM cell in a well-defined and reproducible way.⁴⁶ That (S) TEM can be used routinely to characterise nanoscale electrodes and devices after measurements is a positive advance for nanoelectrochemistry, but it should not detract from the need to design reproducible batch fabrication methods.

Emerging general themes and challenges

Some of the key themes arising at this meeting and from developments in the wider nanoelectrochemistry field are summarised in Table 1, grouped around



Table 1 Emerging themes, challenges and opportunities in nanoelectrochemistry

Data	Simulations	Instrumentation	Complexity	Education & environment	Materials
Open data/ open access	Linking FEM & atomistic simulations	Open instrument architectures	Nanoscale spectroscopy	Discipline hopping & multidisciplinary teams	Rational design
Curation & mining		“Intelligent” experiments & instrumentation	Detection of reaction intermediates	Consortia and networks	Multiscale aspects
Big data, but sometimes sparse or missing		High throughput and parallelisation	Peering inside the double layer	Curriculum	
Image analysis and processing		Active control of nanosystems & nanoscale reactions	Interacting entities	Integration of fundamentals & applications	
Presentation			Single atoms “Connections” between particles and particle/ support		

data, simulations, instrumentation, complexity, education and environment, and materials. This is not an exhaustive list, but rather is meant to be a starting point for discussion and debate. I expand on some of the topics in the sections that follow.

Data needs to be open access in a way that can be understood by other researchers, especially as datasets become ever bigger. This means that well-organised data curation and archiving is paramount. Some of the data in an experiment might be sparse, corrupted or missing and we can consider methods such as in-painting, *e.g.* as recently used in electrochemical imaging,⁴⁷ alongside the use of machine learning algorithms to deal with these situations. With these approaches, it should also be possible to speed up imaging and nano-electrochemistry measurements by collecting sparser data sets. The way in which large electrochemical datasets are presented is a major consideration. Movies are an attractive way to present large data and highlight key features,⁴⁸ in a spatio-temporal or other fashion, but interesting subtle (and rare) events within a large dataset need other methods of detection, display and presentation. We need to bring innovations in data mining to the nanoelectrochemistry field.

As mentioned earlier, nanoscale modelling largely relies on continuum models, but atomistic simulations, hand-in-hand with experiments, are really needed to understand what is happening at the nanoscale, particularly in the electrical double layer. Multiscale modelling, for example, through the integration of finite element method models and atomistic simulations also present great opportunities for understanding nanoscale electrochemical phenomena.

Under the instrumentation heading in Table 1, the idea behind open instrument architectures would be to make software and hardware designs more readily



available, so that researchers from different laboratories work collaboratively and share instrumental features and design as an instrument evolves. We have tried to achieve this with the Warwick electrochemical scanned probe microscopy platform,⁴⁹ especially through the efforts of the originator, Kim McKelvey (Victoria University of Wellington, New Zealand), along with Martin Edwards (Arkansas, USA), Minkyung Kang (now at Deakin, Australia), and James Edmondson, Enrico Daviddi and Dimitrios Valavanis (Warwick) amongst others, who have helped other groups set up this platform. A revolution in intelligent experiments and instrumentation for nanoscale electrochemistry can be envisaged. A number of nanoscale techniques are excellent candidates for the implementation of AI protocols, aiding the high throughput and parallelisation of experiments, and the active control of nanoscale processes (*e.g.* feedback between synthesis and analysis).

Now to some aspects for innovation in the future. A major challenge is to be able to implement powerful spectroscopies at the nanoscale and preferably *in operando*. There has been significant progress in SERS and tip enhanced Raman spectroscopy,⁵⁰ but what about the challenge of small-scale mass spectrometry in electrochemistry? This would be incredibly enabling in the study of structure–activity in complex (*e.g.* multiple product) reactions. The other topics I highlight under the Complexity heading in Table 1 should be self-evident and are among some of the most interesting challenges for the community looking ahead. I shall explore some of them below.

Considering the scientific and wider environment in which we ‘do’ nanoelectrochemistry, we need mechanisms that encourage greater discipline hopping and the formation of multidisciplinary teams, both within individual groups and, more importantly, in larger networks and collaborations. Alongside, the curriculum and education is important, as discussed further below. And under the Education and environment heading, I return to the relationship between fundamentals and applications at the nanoscale: they go hand-in-hand, and are of mutual benefit, rather than there being a linear trajectory from fundamentals to applications.

The intelligent synthesis of functional materials and their use in various devices will have a dominant role in the scientific landscape this century, particularly for energy applications. The nanoelectrochemistry community has an amazing opportunity to lead in this area by providing the information that will unlock the rational design of functional materials and provide the underpinning science that will allow the prediction of nanomaterial behaviour in devices across lengthscales and timescales.

Multiple interacting entities at the nanoscale

As our investigations transition from single particles to ensembles and aggregates, we shall increasingly need complementary views from a range of techniques and perspectives to ensure an holistic understanding. I made this point in my concluding remarks in the *Discussion* with two pictures of a group of nanoelectrochemists having dinner together, but from different angles and at different times, to demonstrate that one picture alone leads to one interpretation, but two pictures provide a different conclusion! Moreover, interacting entities, and the nature of those interactions, can result in something much more beautiful and



important than from single entities, as I illustrated with the example of The Beatles! These analogies were to draw attention to the importance of understanding interacting entities in electrochemistry, for example, in a very nice paper at the 140th *Faraday Discussion* (2008) from Behm's group⁵¹ on the oxygen reduction reaction (ORR) at a model electrocatalyst comprising active platinum nanodiscs on a glassy-carbon support, where the spacing between the discs and electrolyte flow rate were shown to have a significant impact on the yield of H₂O₂, rationalised through the use of a reaction model. We now have the capability to perform similar types of measurements, but with platinum clusters, which have mobility on the electrode surface as a consequence of the ORR and the resulting heterogeneous fluxes and mass transport at the nanoscale.⁵² In examining the transformation of reagent to product in electrocatalytic processes at ensembles of particles, we need to address the following questions: to what extent is the net transformation at a single entity or distributed across entities *via* inter-particle transport? In other words, what is the inter-entity diffusion of reaction intermediates? What is the reaction/interaction of reaction intermediates with the support? How do we go about trying to study these kind of processes?

Importance of the nano-entity electrode support

An aspect of considerable importance in the electrochemistry of nanomaterials (as a key example of single entity electrochemistry) is to understand the effect of the interaction between the support (current collector) and the entity being studied. The support–entity interaction can be tuned chemically, as illustrated in the paper from Ruixia Wang *et al.* (DOI: 10.1039/D1FD00054C) on collisions of functionalised nanoparticles at a functionalised nanoelectrode, where the interaction (and current) was controlled by host–guest chemistry, and the nature of the interaction was revealed through the electrochemical measurement. Recent work from Wei Wang's group has highlighted the importance of the eliminating effects of heterogeneous electrical contacts in order to measure the true activity of single nano-entities.⁵³ These studies serve to highlight the general importance of accounting for particle–electrode interactions in studies of particulate electrodes at all lengthscales, and is an aspect of single entity electrochemistry that needs further consideration.

The support used for the study of 2D materials is a particularly important consideration. In fact, the electrochemical and electrocatalytic activity of graphene heterostructures can be tuned *via* the support on which the graphene is placed.⁵⁴ In this *Discussion*, Tolbert and Hill described an innovative “carrier generation-tip collection SECCM” method for generating carriers locally in a 2D semiconductor and collecting them at an array of confined sites *via* a redox reaction at the SECCM meniscus (DOI: 10.1039/D1FD00052G). This extends electrochemical methodology to the visualization of key processes in solid state materials and is a particularly exciting development of SECCM.

“Well-defined” particles

In the paper from Yao *et al.* (DOI: 10.1039/D1FD00047K), control over the structure of PtCu nanoparticles was demonstrated. In the Introductory Lecture, Gooding *et al.* (DOI: 10.1039/D1FD00088H) suggested that effort should be put



into the synthesis of well-defined nanoparticles that could be studied as an array to reveal structure–activity relationships. However, it must be recognised that even if nanoparticles are closely identical structurally, they can have very different activities, as demonstrated by Baker's group, who used SECCM to assess the electrocatalytic activity of gold nanoparticles with well-defined surface facets, showing that the activity of nominally identical nanocubes (under SEM) had very different activity.⁵⁵ This can be explained generally by subtle distributions in the atomic arrangements and surface capping agents (if used) from one nanoparticle to another, which affects the surface free energy.⁵⁶ This is an important message for the community and makes single entity (particle) measurements imperative: “well-defined” nanoparticles may not be as well-defined as we might think they are.

Developments in SECCM

SECCM is finding an ever diverse range of applications and there are new innovations from an increasing number of groups. At the *Discussion*, SECCM was the subject of three papers and four posters. I have already mentioned Tolbert and Hill's experiment above, also described in Poster 17. The paper from Ren's group introduced several methods for assessing and compensating for the iR drop in SECCM, which will be useful for electrocatalytic and electrochemical measurements under some conditions (DOI: 10.1039/D1FD00046B). To advance the analysis of SECCM data, Anderson and Edwards also presented simple and robust analytical equations for the current response, which will be very beneficial to SECCM users (Poster 5). SECCM is a powerful method for targeting individual particles within an ensemble, and there were examples of two such studies from Chen (Poster 9) and Choi (Poster 11), who also demonstrated environmental control of SECCM. Our group at Warwick has been collaborating closely with Kanoufi's group in Paris to integrate SECCM and interference reflection microscopy (IRM); in the paper from Valavanis *et al.*, it was shown that this capability allowed the status of the SECCM meniscus to be tracked *in situ* during voltammetric measurements and it was also possible to peer inside the meniscus to detect and visualise phase formation processes (DOI: 10.1039/D1FD00063B).

Nanopipettes

Nanopipettes are established tools in an increasingly wide range of nanoelectrochemistry measurements.⁵⁷ These devices can be employed in single channel, dual channel and multichannel formats, providing a range of delivery and detection possibilities, as witnessed in this *Discussion*. Dual channel nanopipettes with an electrolyte filled channel, back contacted with a quasi-reference counter electrode and a solid-carbon electrode as the second channel were introduced by Takahashi *et al.* for combined SECM-SICM,⁴¹ and such probes have been used for quantitative molecular delivery (electrolyte channel)–detection (carbon electrode) external to cells.⁵⁸ An exciting development reported at the *Discussion* from He's group is that such probes can be used for intracellular injection and detection (DOI: 10.1039/D1FD00057H). The detection sensitivity afforded by nanopipettes was exemplified by Chen *et al.* who pushed the time limit of single channel functionalised nanopipette measurements to detect



protein–protein interactions at the single molecule level (DOI: 10.1039/D1FD00042J). These advances, coupled with other attributes of nanopipettes, from nanoparticle delivery and sizing with exquisite control⁵⁹ to nanoscale mixing, synthesis and analysis,⁶⁰ make nanopipettes an outstanding platform for nanoelectrochemistry.

Peering inside the electrical double layer

The surface force apparatus (SFA) is a powerful means of examining electrostatic forces between two surfaces in electrolyte solution.^{61,62} The developments reported in this *Discussion* by Kurihara's group (DOI: 10.1039/D1FD00060H) open up exciting prospects for performing electrochemical measurements in the confined space offered by the SFA, and generated considerable interest, as evidenced from the questions and comments on this work. Such measurements, alongside local surface charge measurements and new molecular dynamics models, point towards an improved understanding of the electrical double layer.

Single atoms in electrochemical processes

Single atom (electro)catalysis is a “hot” but established topic, concerned with macroscopic studies averaged over billions of atom catalysts dispersed in, or on, a support material. An important emerging topic in single entity nanoelectrochemistry, not touched upon in the *Discussion*, is the role of single atoms in electrochemical processes and the study of electrochemistry at *individual* single atoms. Ustarroz and co-workers identified the operation of non-classical routes to electrocrystallisation, involving the aggregation of small clusters to make larger particles,^{63,64} and recent work from Macpherson's group has shown the involvement of single atoms in such processes.⁶⁵ These studies were enabled by the use of (identical-location) aberration-corrected TEM, where the electrode is a TEM grid. The use of SECCM to make electrodepositions on a TEM grid further makes possible the analysis of many different electrodeposition experiments in a combinatorial fashion.⁶⁶

Inspirational work from Bard's group has proposed that a *single atom* can be deposited on a nanoelectrode and used for electrocatalysis.⁶⁷ This work is entirely electrochemical and uses classical models to infer the atom (or cluster) size from limiting current measurements of a redox reaction. Such work will be greatly advanced when complementary microscopy methods can be applied to prove unequivocally that single (individual) atom electrodes can be made.

Looking ahead: local to global

A wide range of single entity electrochemistry measurements are possible and many such experiments are now relatively straightforward. More challenging are studies in which the electrochemical activity and surface structure at the nanoscale are correlated, although this is increasingly possible through the use of a wide range of multi-microscopy strategies, with electrochemical imaging at the centre.⁶⁸ Detailed analyses of the resulting datasets, in tandem with modelling, is revealing structure–activity relationships with considerable detail, especially when complementary modelling is applied. This direction is crucial for both



fundamental advances and the rational design of next generation electrodes and electrochemical devices.

Scanning the horizon, I believe that nanoscale electrochemistry will increasingly be connected to measurements at longer timescales and larger lengthscales so that electrochemical systems, and kinetic limitations, can ultimately be understood holistically at any scale (local to global). Thus, the future of nanoelectrochemistry is not simply better measurements of single entities or groups of entities, but will be concerned with enabling science that ultimately helps to connect diverse aspects of electrochemistry.

As nanoelectrochemistry develops, the analysis and visualisation of increasingly larger datasets will become critical. This transition will be facilitated by experiments that are intelligent and autonomous. Nanoelectrochemistry experiments are not only excellent candidates to be automated, but are ideally suited to become adaptive and autonomous, which is a very promising direction for materials discovery generally.⁶⁹ So, I expect that the human nanoelectrochemist of the future will spend much less of their time in the laboratory doing experiments and more time as a data scientist, analyst, engineer and archivist/steward, and communicating their work to a diversity of audiences. And, of course, interacting with their robot labmates (and other robot analysts)!

Curriculum and education

Electrochemistry has traditionally been chemistry-centric, and most students entering the field have have a chemistry background. Yet, many of the challenges and opportunities presented by nanoelectrochemistry, now and in the future, might be better suited to scientists from other disciplines and multidisciplinary teams. We saw that in the Boomer period, advances in electronics heralded new opportunities for electrochemistry, and throughout its history, major developments in electrochemistry have resulted from the cross-fertilisation of different fields: chemistry, electronics, physics, engineering, life sciences, computer science and mathematics. To thrive, nanoelectrochemistry needs a diverse student body, attracted from a diverse range of scientific, educational and cultural backgrounds and who can learn from each other.

So, we need mechanisms and programmes that are truly multidisciplinary. This was achieved by the Warwick University, EPSRC-funded MOAC Doctoral Training Centre (2003–15), led by Alison Rodger, which sought to catalyse research and training across the physical/life sciences interface. By running as a 3 year PhD, preceded by a one-year multidisciplinary MSc, involving taught courses and projects from across the science, engineering and medical faculties, this programme was able to attract a similarly scientifically diverse student body, and particularly students with a strong mathematics background. Individual modules taught by academics from different departments also led to positive new interactions at the research level. Research in the Warwick Electrochemistry & Interfaces Group benefitted enormously, particularly from the contributions of students with degrees in mathematics and computer science, for example, Kim McKelvey and Martin Edwards (both of whom are well known in the nanoelectrochemistry community), along with Kate Meadows, David Perry, Ashley Page, Hayley Powell, and Jenny Webb, among many other talented PhD students who are authors on papers from this period.



We have drawn on some of the elements of MOAC in the EU-funded SENTINEL (Single Entity Nanoelectrochemistry) Innovative Training Network (ITN), led by Paolo Actis (University of Leeds). Although some of the aims, including extensive globally disperse secondments for the participating PhD students, have been severely impacted by the COVID-19 pandemic, it has been successful in building a cohort of early career researchers from different backgrounds who share knowhow and work together to tackle frontier problems in nanoelectrochemistry.

An innovative curriculum needs good teaching materials, an aspect of which is tutorial-style articles. Over the past year, there have been some superb articles that are highly educational, from a discussion of shot noise⁷⁰ and stochasticity in nanoscale and single entity electrochemistry⁷¹ to an overview of the working of the potentiostat.⁷² These efforts are to be applauded and augur well for the future.

Conclusion

Historically, electrochemistry was dominated by individuals, as in the story of big science from 1813 and work from the Boomer generation, which I introduced by name-checking scientists from 75 years ago whose work we still use and link to individuals. For next generation (nano)electrochemistry, the emphasis will surely be on teams, centres and schools. Next generation problems in electrochemistry are too large and diverse to be tackled by individuals alone and will require increasing cooperation within large teams (which already happens extensively) and between teams based in different countries and continents that work together and help each other (a developing trend). By coming together, these teams will be able to address the challenges and opportunities presented by big data and complex instrumentation that will characterise next generation electrochemistry and nanoelectrochemistry.

Although there are many facets to nanoelectrochemistry, as illustrated by this *Discussion*, I believe that a major aspect of next generation electrochemistry will to *understand local* and connect this understanding to *global*. This will be facilitated by treating “electrochemical systems” through a “systems electrochemistry” approach, in which nanoelectrochemistry is a key enabling component, and is not treated in isolation. As described here, next generation electrochemistry will present a continuum of opportunities in fundamental science and applications.

Conflicts of interest

The author is co-inventor of granted patent PCT/GB2011/051518 “Pipets containing Electrolyte and Electrodes”, which describes dual-channel SECCM.

Acknowledgements

The author dedicates this work to the memory of his late father, the historian Robert ‘Bob’ Unwin, who would have greatly enjoyed the theme of this article, especially the historical context of, and forward-look at, electrochemistry. In his later years, Bob was engaged in research on Humphry Davy and associated natural philosophers, upon which this article draws. The author thanks the Royal Society for a Wolfson Research Merit Award and the EPSRC for funding nano-electrochemistry-related research (EP/F500378/1, EP/H023909/1, EP/V047981/1,



EP/L015307/1). The author is grateful to many generations of researchers in the Warwick Electrochemistry & Interfaces Group who have been inspirational and contributed to our nanoelectrochemistry research. Finally, the author thanks Dr Daniel Martín-Yerga for the TOC graphic for this article.

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