Science and technology of electrochemistry at nano-interfaces: concluding remarks

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ABSTRACT

The Faraday Discussion on electrochemistry at nano-interfaces presented a platform for an incredibly diverse array of advances in electrochemical nanoscience and nanotechnology. In this summary, I have identified the factors which drive the development of the science and which ultimately support many impressive technological advances described. Prime among these are the emergence of new physical behaviors when device dimensions approach characteristic physical scaling lengths, the steadily increasing importance of surfaces as device dimensions shrink, and the capacity to fabricate and utilize structures which are commensurate in size with molecules, especially biomolecules and biomolecular complexes. In this Faraday Discussion we were treated to outstanding examples of each of these nanoscience drivers to produce new, and in many cases unexpected, electrochemical phenomena that would not be observed at larger scales. The main thrust of these collective activities has been to realize the promise implicit in several transformational experiments that were carried out in the last decades of the 20th century. Our task is not complete, and we can look forward to many additional developments springing from the same intellectual wellhead.

INTRODUCTION

I would like to begin by thanking the organizers, Frank Marken and Yitao Long, for the opportunity to present these concluding remarks at the end of what has been a remarkable two days of scientific presentations and discussions. Furthermore, these discussions have taken place against the backdrop of a beautiful city, Bath – or Bath Spa if you're trying to arrange for the correct train from the US – a wonderful university setting, and what I am told is "typical" 80° F/ 27° C cloudless blue skies and low humidity, see *Figure 1*. Together with the organizing committee – which also included Shelley Minteer, Zhongqun Tian, Patrick Unwin, and Lane Baker – they brought together an outstanding collection of investigators performing research at the boundaries of our science.

Initially, one has to admit that the subject we understand as electrochemistry is dominated by the transfer of electrons across a liquid–solid interface (at least in most cases), which is inherently a nanoscale (or more properly, an Å-scale) event. So describing the connections between electrochemical phenomena and nanoscale structures and properties should be a bit like shooting fish in a barrel. However, digging a little deeper shows that how we approach the problem can benefit from different perspectives, perspectives that can usefully be subdivided into nanoscience and nanotechnology. The question is, are they really different? I think they are, and I believe the papers delivered during this Faraday Discussion illustrate the differences quite effectively.

To begin, it is useful to think about the concept of the scaling length, as it applies to various physical interactions that are important in electron transfer. *Table 1* shows some of these – pertaining to electronic transport, optical interactions, and fluid transport – that determine electrochemical behavior along with the physical lengths that characterize them. The importance of scaling lengths for our purposes derives from their utility in guiding our preparation of electrochemically active nanostructures. For example, if we are interested in using the interaction of electromagnetic radiation with electrochemical phenomena, then constructing devices with characteristic dimensions of the order of, or smaller than, the wavelength of the radiation used will be important. Similar comparisons can be made for the importance of the scattering lengths and Fermi wavelength on electronic transport as well as the charge screening, or Debye, length and hydrodynamic radius in determining fluid transport at the nanoscale.

Why are these scaling lengths so important to our discussions here? To answer this question, I will start with a list of characteristics that distinguish nanoscience from nanotechnology. In short, they include (at least) the following:

- New phenomena.
- Surface-to-volume ratio.
- Enhanced transport.
- Commensurate in size with (large) molecules.

New nanoscale phenomena are illustrated amply by the evolution in electronic devices. For example, in 1980 the state-of-the-art was represented by discrete packages that could be assembled on a motherboard, such as the quad NAND gate based on TTL logic. Fast forward three decades, and single electron transistors, based on exquisite field-based control of electron tunneling, now define the state-of-the-art.[1] So, in 30 years technology spanned the gap between current-based control of electrical signals across bipolar junctions in three terminal devices to the control of fundamentally quantum mechanical events occurring at nanometer–scale interfaces. Our own group has exploited the distinct characteristics of electronic transport in electrochemically prepared atomic-scale junctions; where instead of resistance being determined by stochastic scattering events, electron transport is ballistic, and the apparent resistance is determined solely by physical constants.[2,3]

Our second point of distinction arises from the linear increase in surface-to-volume ratio with decreasing dimensions. We are all familiar with small droplets of rain sticking to a car windshield, while larger drops drain away – a physical manifestation of the crossover between the magnitudes of gravitational and interfacial forces at roughly the millimeter size regime. At the nanoscale, a number of electrochemically useful phenomena are governed by the surface-to-volume ratio and a beautiful example of this comes from the laboratory of one of our delegates, Richard Crooks.[4] They developed an ingenious method to create a space charge region in a microfluid channel by oxidizing a small fraction of the anions contained in brackish water, thereby creating large electric fields which exclude ion-containing fluid components from one branch of the device. The resulting physical separation of the de-salted water from heavy brine components is an intriguing direction in desalination technology, one which depends intimately on the surface-to-volume ratio for the creation of strong integral electric fields to direct the transport of ions.

The third characteristic, the use of diffusion as an efficient mass transport mechanism, results directly from the diffusion equation, $\tau \sim \langle x2 \rangle$. As a result, diffusive transport of a particle or molecule from the center of a $\sim$100 nm nanoscale feature to a reactive site on the periphery requires a time only $\sim$10 μs. Consequently, coupling advective delivery of redox active substances through a longitudinal feature to the region of a nanoscale electrode can rely on diffusive transport to bring the species in contact with the electrode surface at high-efficiency.[5,6] The Péclet number, Pe, which is the dimensionless group describing this process is typically small, Pe $\ll$ 1, for 1-D nanostructures, indicating reaction efficiencies approaching unity. Thus, whereas on the macroscale, the effect of diffusion is to establish the familiar diffusive boundary layer at a macroscopic electrode, at the nanoscale diffusion can function effectively to mediate transport in support of faradaic electron transfer reactions.

Finally, we have reached a point in the development of nanofabrication capabilities where it is realistic to design and construct artificial nanostructures with sizes commensurate with the dimensions of biological macromolecules and macromolecular assemblies.[7–10] This is important inasmuch as it is now possible to think about the construction of hybrid assemblies that control the directionality of electron transfer processes in much the same way that Mother Nature uses the three-dimensional assembly of complex macromolecular aggregates to control the coupling of energy sources, such as light-to-proton concentration gradients, which alter cellular processes. The coupling of intrinsically functional biological macromolecules, such as proteins in their many forms, with artificial nanostructures capable of controlling electron transfer raises the possibility of exciting new applications in therapeutic agent delivery, controlled nanocatalysis, light harvesting, and even artificial life that would not be possible without functional hybrid architectures incorporating both living and non-living structural units.

Taken together, these characteristics serve as a set of guidelines to understand how the principles of nanoscale construction and assembly can produce structures that access properties and behaviors not known in larger scale architectures. None of this is meant to demean the important advantages that accrue simply from making functional structures smaller. It is implicit in the consideration of nanotechnology that decreasing size has important salutary effects on device performance in speed, power consumption, materials costs, bandwidth, and thermal management. However, over and above these real and important advantages to performing electrochemical manipulations at the nanoscale, there is new previously inaccessible science to be performed as well.

NANOSTRUCTURE PREPARATION AND VISUALIZATION

It is perhaps trite to point out that the ability to prepare and characterize nanostructures is a necessary, but not sufficient, condition to their effective utilization in realizing novel electrochemical behavior, *viz. Figure 2*. While the nanostructure fabrication problem is not unique to electrochemical problems, several conferees presented innovative new methods to fashion electrochemically competent nanostructures that integrated structural features with the electrochemical performance. Having said this, it remains a challenge to fabricate nanoscale devices, because the feature sizes are small, thus presenting problems with shadowing, particle diffraction, and other processes which can degrade resolution. One clever approach to circumventing the size constraints is to flip the geometry and use deposition along a vertical axis to define lateral feature sizes. Mount's group has been in the vanguard of deploying this strategy to realize nanoband electrodes, which are constructed by exposing the edges of vertical stacks of multilayer stacks of materials. In their recent work described here (DOI: 10.1039/c8fd00063h) they employed lithographically defined patterns of square nanoband electrodes to template the growth of hierarchically organized gels. The resulting biofouling-resistant hydrogels were shown to be capable biosensors, but one could also imagine extensions of this approach which would support transport in the opposite sense making it possible to use this strategy for delivery of valuable cargoes, *e.g.* in therapeutic delivery.

Whereas Mount focused on the construction of novel architectures, Zhao and Crooks separately outlined new routes to interesting electrochemically defined materials. Zhao's group developed an approach for the preparation of highly active catalysts for CO_2 reduction through selective dealloying of rapidly solidified Mg–Ag alloys to produce highly nanoporous Ag catalysts (DOI: 10.1039/c8fd00056e). The resulting nanostructures were composed of organized bands of material, termed ligaments, which mediate catalytic activity. The interesting and exciting features of this approach surround the vast phase space of materials characteristics that could be explored in the starting alloy and their relationship to the resulting electrocatalytic properties obtained after etching, as evidenced by the higher activity of the 21 nm banded structure over the 85 nm structure. In contrast and showing that creativity can be achieved by different routes, Crooks described the use of high-frequency square wave voltammetry to template the growth of single Pt nanocrystals on a recessed carbon fiber electrode (DOI: 10.1039/c8fd00018b). They were able to access different well-defined nanocrystalline topographies by simply changing the features of the medium and square wave excitation. Furthermore, this strategy produced single nanocrystals exhibiting a variety of high index crystal faces, as determined by *in situ* electron diffraction and transmission electron microscopy (TEM). Clearly, the single nanocrystals obtained by this novel growth methodology are important, because their structure can be characterized in detail one at a time and the resulting structural properties related to the follow-on determination of catalytic activity – a particularly valuable, but infrequently observed, connection of structure to function in studies of catalysis.

A strong contingent of delegates addressed various aspects of characterizing nanoelectrochemical structures once fabricated. Some of these efforts (Kranz, Moore, and Bentley/Unwin) represented sophisticated extensions of imaging and chemical characterization approaches, while Kanoufi and Hillman described optical and neutron reflectivity measurements. Kranz and her coworkers are interested in the fascinating problem of electron transfer at immiscible solvent interfaces. The nanoscale versions of these experiments have typically been carried out with the liquid–liquid interface constrained by a physical nanopore,[11,12] but this then begs the question of the geometric structure of the nanopore and how this can be used to direct ion transfer at immiscible interfaces. In a tour-de-force characterization experiment (DOI: 10.1039/c8fd00019k), these authors combined four separate tools – focused ion beam imaging (FIB), ultra high resolution atomic force microscopy (AFM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDX) – with scanning electron microscopy (SEM) based tomographic imaging to produce images that simultaneously produced depth resolved topographic and chemical information, thereby providing an exquisitely nuanced picture of the environment in which liquid–liquid interfaces can direct ion transfer phenomena. In a similar vein, Moore and coworkers applied their ultrahigh speed contact-mode AFM to obtain near video-rate AFM images addressing metastable pitting, grain boundary (GB) dissolution and short crack formation during stress corrosion cracking (DOI: 10.1039/c8fd00017d). In another contribution that aligns with this intellectual direction, Bentley and Unwin described an extension of the scanning electrochemical probe microscopy technique that is closely associated with the Unwin laboratory (DOI: 10.1039/c8fd00028j). To extend their now well-known dual barrel nanopipette technology, they used a single-channel nanopipette to implement an imaging probe based on a simple single meniscus, thereby realizing an alternative version of scanning electrochemical cell microscopy (SECCM). The exciting feature of this development is that topographical and voltammetric data are acquired synchronously at spatial resolution approaching 50 nm. With the high bandwidth capabilities of the instrumental suite developed in the Unwin laboratory, it is now possible to map the topographic features of an entity along with its electrochemical activity. The authors posit that these developments will enable them to directly view electroactive nanomaterials and relate topographic features to structure, thus revealing structure–function relationships at active sites.

Kanoufi took the characterization of electrochemical interfaces in a different direction by extending the use of backside absorbing layer microscopy (BALM), an optical approach capable of addressing the metal–solution interface with high spatial resolution and sensitivity to the interfacial dielectric response (DOI: 10.1039/c8fd00037a). The technique is enabled by preparing an anti-reflecting thin film metal electrode structure. The antireflection characteristics of the structure are highly sensitive to the dielectric response – essentially the polarizability – in the near surface region, making it possible to observe nm-scale alterations in the structure of metallic nanoparticles undergoing redox-active collisions with the electrode surface. Because the technique is interferometric, it is highly sensitivity to spatial position and nanoparticle size, thus making it possible to assess the collisional reactivity of nanoparticles one-at-a-time. In so doing, these experiments complement the use of surface plasmon microscopy to explore nanoparticle-based electrochemical processes developed by Tao and others.[13–15] In another departure for more standard characterization approaches, Hillman described the combination of quartz crystal microbalance measurements with specular neutron reflectivity (NR) in order to simultaneously characterize the thickness and electrochemistry of metal deposition and dissolution (DOI: 10.1039/c8fd00084k). These measurements go beyond more commonly encountered characterization approaches by making it possible to assess internal structure below the metal–solution interface. While recognizing the substantial investment required to access neutron reflectivity measurements, it is clear that the recently-realized technical improvements to the NR measurement, such as event mode recording capability, have reduced the observation time 10-fold, thus bringing the approach closer to wider use.

In total, we were treated to a smorgasbord of cutting edge characterization experiments applied to difficult electrochemical problems. It was particularly noteworthy that technical advances in chemical measurement capabilities were reflected in improved characterization performance across multiple instrumental platforms. This type of evolutionary improvement is well poised to benefit electrochemists well into the future.

NANO-ENABLED PROPERTIES

Given the strong electronic polarizability of metals, it should come as no surprise that there are rich connections between electrochemical phenomena and the optical response of metals. Above, we recognized the use of surface plasmon-polaritons to probe interfacial electron transfer events, and several papers extended these very useful ideas into the realm of localized surface plasmons in metallic nanoparticles, single molecule conductors, and nanoscale bipolar electrochemistry – all of which are enabled by the distinct conductance behavior of molecules and nanoparticles in the small electronic scaling length regime.

There is currently a great deal of interest in the use of nonequilibrium electron distributions during the excitation of localized surface plasmon resonances (LSPR) to increase electron transfer rates across the metal nanoparticles–liquid interface.[16–18] The great challenge in these experiments lies in extracting the carrier from the particle prior to thermalization, a process which can occur as fast as the femtosecond timescale. Willets turned this problem on its head by essentially focusing on the waste heat generated from non-radiative decay of LSPR excitations (DOI: 10.1039/c8fd00057c). A nearby SECM probe was used to observe both a change in the current resulting from altered mass transfer rates at the higher local temperature, as well as a shift in the equilibrium potential for the redox process. These measurements open a new route to measuring the local temperature of metallic nanoparticles with specific advantages over Stokes/anti-Stokes intensity ratios from surface-enhanced Raman scattering, for which the temperature dependence of the enhancement factor frequently limits experimental accuracy. A different type of plasmonic nanostructure, resembling Au LSPR-supporting nanomushrooms, was used by Zhan to explore the role of oxygen species in the LSPR-initiated chemistry (DOI: 10.1039/c8fd00012c). They observed dramatic differences in the redox behavior of ferrocenemethanol with and without the presence of molecular oxygen, leading them to hypothesize the role of, as-yet-undetermined, oxygen species which can mediate electron transfer between the transient photoinduced hot electron population in the LSPR architectures and the redox-active species in solution. These results are potentially of great interest, not least because of the intense interest in the controlled use of reactive oxygen species.

Other ways in which the special conduction properties of small structures can be exploited are exhibited by molecular conductors and nanoscale bipolar electrodes. Vezzoli expanded upon the possibilities for probing molecular conduction properties at semiconductor–molecule junctions using GaAs, a direct gap semiconductor, to mediate photoconduction to a metal collector electrode (DOI: 10.1039/c8fd00016f). The resulting M-mol-S structures permitted a number of different molecular architectures to be substituted for the "mol" portion, and the resulting differences in conduction properties to be characterized at high precision. Interestingly the conduction properties can be tuned either by control of the semiconductor and doping density and polarity or by the molecular architecture. Fine control over the extent and nature of the space charge layer and thus tuning of the rectification and optoelectronic current were thus obtained. Furthermore, the molecules were amenable to electrochemical gating which subsequently altered alignment of the molecular orbitals with semiconductor band edge states, adding yet another element of control over the operation of the structures. Finally, the details of the electronic structure of these multielement junctions presents a rich area for future investigation, especially in the identification of so-called "gateway states" which can mediate long-range conduction. In an analogous set of experiments, Mirkin developed an exquisitely sensitive probe of the shift in behavior between the tunneling regime and nanoscale bipolar electronic electrode operation for single nanoparticle using SECM (DOI: 10.1039/c8fd00041g). They developed an approximate model for fitting current–voltage relationships, which allowed them to pinpoint the conditions under which the system changed from one mode of electron transfer to the other. There is currently intense interest in the capacity to direct-write structures and reactions using various kinds of electrochemical processes with a scanned probe tip, so the detailed modeling and careful assessment of the electric field environment as a detailed function of the position of the tipping the particle are likely to be very helpful in directing efforts to use these powerful non-lithographic fabrication modalities for the creation of localized chemical structures. In our own work, we have seen how the positioning of a conductive AFM tip relative to a nanoparticle bipolar electrode can dramatically affect nanofilament formation and dissolution kinetics,[19] so we will be watching this work from Mirkin's lab with intense interest.

SURFACE-TO-VOLUME RATIO AND SINGLE ENTITIES

It is now well understood that observing the behavior of single entities (particles, molecules, complexes, *etc.*) and/or single events requires a combination of two features: the sensitivity needed to generate and observe a signal from the single entity of interest combined with a strategy to reduce the contribution of the background to the measured signal. In fluorescence measurements, for example, constraining the volume observed to the sub-femtoliter range is sufficient to isolate optical signals from single molecules and elevate them above the noise floor of the background.[20] Two papers by McKelvey (DOI: 10.1039/c8fd00014j) and Ewing (DOI: 10.1039/c8fd00020d) presented results which highlight the combined effect of reducing the volume (thereby intrinsically increasing the surface-to-volume ratio), thus enhancing the effect of, and the signal from, single events. McKelvey reported on an interesting new variation of the nanoparticle–electrode collision experiment in which two microscale planar electrodes were held in registry a specific distance (600–2000 nm) from one another, and oxidation events at the anode released ions which were then collected at the nearby cathode. The experimental geometry was designed to provide a window onto the complex temporal dynamics that accompany Ag nanoparticle dissolution and to track the fate of the released Ag^+. In dynamic experiments of the type undertaken by McKelvey, the chemical composition of the small volume changes in time with nanoparticle dissolution which, in turn, affects the electrical and chemical properties governing both further nanoparticle collision dynamics as well as collection of the oxidation products. In doing so it highlights a generic problem of work at the nanoscale which often involves femtoliter, attoliter, or even zeptoliter volume containers, in which even a modest change in chemical activity can dramatically alter the positions of chemical equilibria and potentials applicable to electron transfer processes of interest, E_{eq}. In a similar vein, Ewing exploited the surface-to-volume ratio associated with single catecholamine containing vesicles, using a combination a vesicle impact electrochemical cytometry and centrifugation to fractionate the population of catecholamine-containing vesicles obtained from PC12 cells. These experiments are essentially electrochemical titrations, in that they quantify the catecholamine content by counting electron transfer events. The surface-to-volume ratio is naturally constrained by the nanometer sizes of the vesicles studied, and fractionating the vesicles allowed these investigators to assign a relatively constant catecholamine concentration independent of vesicle size. One of the goals of single entity or single event work is to gather individual characteristics across a sufficiently large population, such that one can begin to understand the meaning and development of statistical indicators, while at the same time not losing track of rare events or entities on the overall average behavior of the assembly. The work to characterize these nanoscale catecholamine vesicles and their released characteristics is a nearly canonical example of realizing this ideal.

BIOCOMMENSURATE NANOSTRUCTURES

The fourth in our list of nanoscience drivers involves construction of artificial nanostructures with size commensurate to the dimensions of biological macromolecules and macromolecular assemblies. This description naturally describes a number of the resistive pulse architectures that were described by Jiang (DOI: 10.1039/c8fd00025e), Pelta (DOI: 10.1039/c8fd00030a), Balme (DOI: 10.1039/c8fd00008e), Siwy and Baker (DOI: 10.1039/c8fd00071a), and Wang (DOI: 10. 1039/c8fd00059j). All of these contributions focused on phenomena emanating from the special properties of transport in one-dimensional nanostructures, especially when they were chemically derivatized to accentuate the mediated-transport characteristics of the structures. Pelta makes the case for augmenting the powerful armamentarium of naturally occurring membrane proteins with artificially-constructed biomimetic architectures that allow non-naturally occurring chemical functionalities to be incorporated into the membrane, thereby accessing non-natural modalities of transport control. While the construction and characterization of the short cyclodextrin based nanotubes described by this group point the way to further synthetic elaboration, this contribution also importantly served as a focal point for a discussion of the relative merits of naturally occurring protein based nanopores *vs.* their synthetic counterparts. Although I am not here to declare winners and losers, I believe all recognize the value in identifying the positive and negative attributes of each approach, and I think we can look forward to seeing this debate continue in the literature and in future Faraday Discussions. Balme presented surprising results on the transport of ionic species through uncharged conical nanopores. The surprise was the observation of rectified currents and constant conductance at low salt concentration. The former has been thought to require charged, geometrically asymmetric surfaces, while the latter observation has most frequently been assigned to a surface charge hopping mechanism, which would clearly be excluded in these uncharged nanopores.[21] Instead, the authors identified the surprising observations in the absence of surface charge with the presence of a structured water layer which served to organize surface-slip, which dominated transport in these nanopores. Siwy and Baker reported on a fascinating class of ionogels that exhibit scale-dependent morphology and dynamics, being solid at the macroscale, while maintaining fluidity and high conductance in nanoscale architectures. After developing two independent measurement strategies designed to characterize the conductance of these materials both in the presence and absence of external liquid phase electrolytes, the authors characterized the nanopore-confined ionogels over a range of conditions, demonstrating their applicability to energy storage applications. As a final example Wang reported on electrochemical studies carried out on actual biological nanostructures (which are, of course, biocommensurate by definition). In this hypothesis-driven set of experiments, scanning ion conductance microscopy (SICM) was used to follow the morphological effects of α-synuclein aggregate binding to the distal processes of neuroblastoma cells. SICM showed clear evidence of progressive cell membrane disruption, ultimately resulting in complete cleavage of the process from the cell body. This kind of sophisticated application of SICM is important in the present instance, not only for the light it sheds on this particular route to neurodegeneration, but also because it serves as a proof-of-principle for the use of SICM to define disease etiology.

The last example of a biocommensurate nanostructure being used in a resistive pulse experiment was reported by Ying and Long (DOI: 10.1039/c8fd00023a). It has long been the paradigm that information in these experiments is carried by pulse magnitude, Δi, and duration, Δt, during blockage events associated with passage of the target.[22] However, these authors elected to study the detailed dynamics of current processes during the blockage event. By setting out to obtain dynamic information from the complex current trace, as analyzed by the Hilbert–Huang transform, they were able to study the detailed motional dynamics resulting from translocation of single molecules through the confined nanopore. These highly innovative experiments and data treatment developments push our science in interesting new directions. Recent studies from a number of different perspectives have highlighted intrinsic molecular contributions to noise and how these may be exploited to derive chemical information. This is true, for example, in chemical sensing where interactions of an analyte population with a surface or nanoscale feature result signals that at first appear to be stochastic, but in fact contain frequency domain information that reflects the underlying chemical dynamics defined by the interaction of the analyte with the structure. Previous applications of this idea have focused on gas sensors,[23,24] the effects of adsorption and desorption on electrochemical signals in nanoscale systems,[25] sensing in ion channels,[26,27] non-ergodic behavior, and chemical noise effects in molecular adsorption at atomic-scale junctions.[2,3] The experiments reported by Ying and her collaborators highlight a forward-looking aspect of electrochemical science – one with both deep fundamental importance as well as far-reaching potential impact on critical applications in chemical sensing.

FUNDAMENTALS

As exciting as these developments are, they stand on a long history of fundamental development in electrochemical science. Thus, our use of nanoscience to create new electrochemical modes of measurement and processing must remain firmly rooted in this understanding of the fundamentals. Papers presented by Koper (DOI: 10.1039/c8fd00062j), Schuhmann (DOI: 10.1039/c8fd00029h), and Aoki (DOI: 10.1039/c7fd00212b) constitute shining examples of this dictum. Reminding us that our ability to do something as seemingly simple as preparing a pure crystalline face of Pt is thwarted by the native complexity and nanostructuring of the surface that occurs spontaneously but especially accompanies the imposition of an external potential on the surface. Starting with something as simple as an oxidative potential program, they correlate the gross roughening of the surface to incorporation of a high density of (110) step edges, which in turn display a characteristic behavior in the hydrogen region of the voltammogram. These observations are important not only for the insights the yield into the fundamental chemistry of Pt surface reconstruction, but also because the ultimate utility in electrocatalysis can be linked to the detailed nanostructuring of these surfaces. Similar to the emphasis on characterization Crooks made in developing single particle catalysts, structure determines function – electrocatalytic activity in this case – and must be carefully addressed. The paper by Schuhmann addressed the important but refractory problem of defining the intrinsic catalytic activity of a single nanoparticle from measurements which naturally integrate behavior of many particles over large area structures. In doing so, they hoped to deconvolute the effects of catalysts site blocking, variable mass loading, inhomogeneous conductivity, and variable porosity to extract the intrinsic electrocatalytic activity of a nanoparticle. Their scheme highlighted the use of careful quantitative normalization strategies, in particular using diffusion-limited currents as normalization factors, in order to assign fractional contributions to the observed catalytic activity. By combining imaging data to assess structure and loading with carefully calibrated electrochemical measurements, they were able to unravel the effects of nonuniform spatial distribution at high loadings and, in the case of nanoparticles displaying sufficiently distinct catalytic rates from the underlying electrode, quantitative measures of catalytic activity were obtained. Finally, Aoki described the complex multivariate structurally diverse issues that connect molecular and electronic structure in the electrical double layer with dissipative electronic response in the frequency domain. These effects arise whenever we use steady state voltammograms acquired at nanoscale electrodes. In particular, they assessed the effect of double layer structure on the apparent impedance and its impact on time-dependent voltammetry. By developing detailed models of the effect of charge transfer on solvent and ion structure in the double layer, they were able to tease out the effect of solvent–dipole orientation as being of equal, or even greater, importance to ion spatial distribution. Thus, frequency domain behavior accompanying electron transfer necessarily involves cooperative phenomena, meaning that we must exercise great care in applying simple models to their interpretation.

END AT THE BEGINNING

After several days of intense scientific exchanges surrounding the excellent presentations, posters, and papers that were part of this Faraday Discussion, the delegates might be excused for feeling in a self-congratulatory mood. In this context, it is important to end our summary by going back to the beginning and the excellent introductory lecture given by Henry White. White chose to set the stage for the conference by giving an historical overview highlighting the technical and scientific advances that set the stage for nanoscale electrochemistry. Some of these involved advances in technical capabilities, such as the scanning tunneling microscope and the many scanned probe microscopy techniques that sprang from that seminal advance, the Nobel Prize winning development of patch-clamp structures, and the ability to fabricate what were then known as ultramicroelectrodes in formats that facilitated their incorporation in voltammetric measurements. Other scientific advances were revolutionary at their inception, such as thin-layer cells, redox cycling, and the rotating ring-disk dual electrode structure. It was interesting, if not humbling, to realize that the initial conceptions leading to many of these advances are now decades old. So while we congratulate ourselves on riding the tip of the rocket in electrochemical nanoscience, we should remember that we are fleshing out the possibilities inherent in truly transformational experiments and theory developed by our predecessors.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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FIGURES

Figure 1. Local flavor – note the cloudless evening sky in Bath!

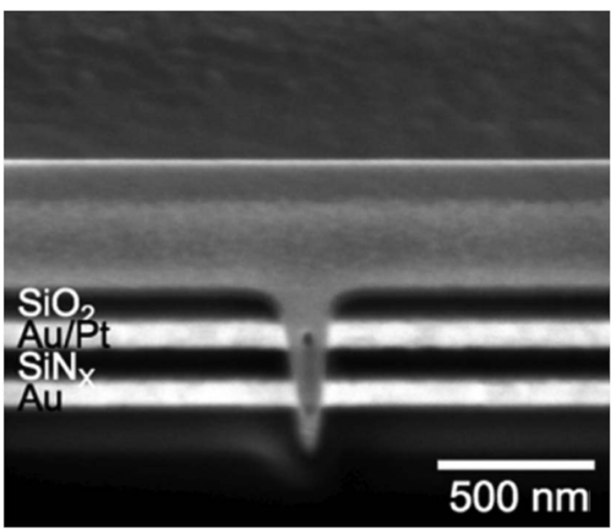

Figure 2. Cross-sectional SEM image of a focused-ion beam milled nanopore presenting two annular ring electrodes suitable for single molecule spectroelectrochemistry.

Table 1 Scaling lengths relevant to nanoscale electrochemistry

Phenomenon	Electronic transport	Optical interactions	Fluidics
Interactions	Fermi wavelength (λ_F)	Wavelength of light in the medium	Charge screening (Debye length)
	Scattering length *(l)*		Hydrodynamic radius
Length scale	λ_F ~ 0.1 nm	$\frac{\lambda}{n}$ ~ 100–300 nm	λ_D ~ 0.3–30 nm (aqueous)
	l ~ 10–100 nm		r_H ~ 2–20 nm for macromolecules