Editorial: **Electrochemical techniques: smart approaches for timely problems**

The potentiostat – the single tool that is unique to electrochemists, used for the automated, precise control of the electrochemical driving force for an electrode reaction, and enabling the extent of the interfacial charge transfer reaction to be monitored, was developed in Leicester, UK, 82 years ago, and published during the Second World War [1]. Just thirty years later, potentiostats bore "little resemblance to the original device", [2], owing to the advancement of solid-state operational amplifiers. This empowered electrochemists with a multitude of opportunities to innovate, capitalising on their high-speed, low current specifications, together with single, rather than dual rail power requirements. This opened-out the creation of electrochemical equipment capable of accessing the nanosecond time domain, forging miniaturized, integrated detection systems, and with potentiostatic circuitry of reduced energy footprints, the longevity of power sources when electrochemical equipment is translated from laboratory to the field.

These days, what is simpler than a potentiostat? Just a few components (or even a single integrated circuit chip and associated firmware) and one can start implementing sophisticated electrochemical techniques. One can then wonder if there is still something to invent beyond simply technical improvements in electrochemical techniques. In practice, it is exactly the opposite! As the applications of electrochemistry widens, this drives requirements for novel approaches, where instrumental developments cannot be separated from analytical and theoretical ones. The interaction between an electrode and a substrate resorts by definition from quantum mechanics and complex bonds between reactive species are implicated, but the solvent and electrolyte are also known to play a major role. Spatial and temporal inhomogeneities also present increasing interplay on several orders of magnitude and their understanding has become key, for example, in producing efficient electrocatalysts. In the field of nanosciences, one faces very heterogenous 3D interfaces for which the reaction/diffusion dynamics laws are extremely complicated to established. Getting information to understand and optimize these fundamental processes is key for widening applications of electrochemistry, from analytical applications up to environmental remediation or in the energy field.

In this special issue of *Current Opinion in Electrochemistry*, the contained 14 reviews cover a very wide field of sophisticated electrochemical approaches. Here, "sophisticated" does not necessarily mean expensive components, but rather, the involvement of a new way of recovering information. These advances in electrochemical discovery – from physical and analytical chemistry to device engineering and sensors, demonstrate the versatility of, and innovation in, electrochemical measurements, and their relevance to modern trends in the subject and society.

The trend in physical electrochemistry has, for several decades now, been towards the coupling of electrochemical with spectroscopic or molecular imaging techniques, with increasing focus on the electrochemistry at small scales, up to the single entity or molecule. Starting with nanoelectrochemistry, Xiao-Shun Zhou reviews the electrochemical gating of electron transport across single-molecule junctions, where scanning tunneling microscopy systems are able to exquisitely control the mechanical break-up of those junctions. Both emerging molecular materials and quantum inference manipulation are considered. This trend in "watching chemistry in action" is followed by Katsuyoshi Ikeda's overview of the use of low-frequency, surface-enhanced Raman scattering to monitor surface phenomena under electrochemical or photoelectrochemical conditions, providing, non-destructively, mass and chemical information simultaneously, enabling a better understanding of heterogeneous reactions at the molecular level.

The need to understand the complex nature of active sites at an electrochemical interface is explored in Yao Yang's review of two complementary tools to investigate reaction dynamics across multiple spatiotemporal scales comprehensively: operando electrochemical liquid-cell scanning transmission electron microscopy and correlative synchrotron X-ray methods. Of course, problems associated with beam-induced damage in these exquisite techniques need greater consideration by the community, but their application to challenging problems is important: Benedikt Lasalle-Kaiser reviews the use of synchrotron-based techniques to understand electrocatalysis in water splitting.

This adaptation of spectroelectrochemical approaches to give insight into timely problems is covered in three further reviews. First, Richard Webster describes how electron paramagnetic resonance spectroscopy can unravel the reactions that take place during oxidative water purification. He illustrates how this powerful technique can help develop the understanding of the systems proposed for organic batteries and supercapacitors. Second, Sagnik Basuray outlines how spectroelectrochemisties involving nuclear magnetic resonance, dark field microscopy, Raman and ultraviolet/visible absorption, can enable insights into processes within microfluidic systems. Third, Junsoon Han reviews the coupling of electrochemistry with inductively coupled plasma atomic emission spectrometry, exploiting a technique with a parts-per-billion analyte resolution to monitor element-specific reaction mechanisms, with a focus on material degradation rates – a topic of importance to a broad range of subjects – from corrosion to solar cells, from biomedical implants to environmental monitoring.

The various "shades of grey" that distinguish between "electroanalytical chemistry", "electroanalysis" and "analytical electrochemistry" are confusing even to professional electrochemists. But "sensors" and "sensing systems" mean two different things. Nevertheless, innovations in the use of electrochemistry for analytical detection are typically based so that the information they provide can be taken-up by end users, who may discover solutions to their problem from those data. Two papers demonstrate this for ecological and medical professional end-users. First, Damien Arrigan explores the possibility of electrochemical sensing systems per- and polyfluorinated alkyl substances in groundwater. The World Health Organisation has proposed that the threshold limit for some of these toxic, "forever" chemicals to be 100 parts-per-trillion; accordingly, the detection challenge for electrochemists is significantly demanding. Likewise, the challenge to measure sodium ion concentration, particularly in the growing aging population, is of immense importance in the identification of the early onset of hyponatremia. James Davis reviews the procedural and technological barriers in developing minimally invasive, wearable electrochemical sensors for monitoring hyponatremia, and the innovations needed to engineer progress.

The creativity needed to side-step obstacles and rally progress in the development and uptake of electrochemical technologies features heavily in this special issue, even though the underlying concepts are simple. The work of Javier del Campo tackles the question of sensing without providing external power ("self-powered sensors"). While the idea remains on the battery concepts that are taught at the undergraduate level, when putting figures to make the system work, one realizes that clever implementation is needed. Likewise, Yiqi Zhou illustrates how the relatively esoteric field of bipolar electrochemistry can be employed in the study of a classical subject of electrochemical engineering, corrosion. The degree by which this important work may impact on regulatory standards will demonstrate, in time, how electrochemical research can impact on civil engineering projects.

No special issue concerning impactful electrochemical technologies can disregard the importance of energy and water treatment devices that employ electrochemical systems. We are delighted to showcase three papers in this field. Although there is no such thing as "electrochemical energy" *per se*, electrochemical devices are powering a chemical revolution as we progress across the current energy transition. Thomas Kadyk reviews the performance of these devices – fuel cells, batteries and electrolysers through their frequency-response diagnostics, and identifies the importance of accounting for non-linear information. The large majority of commercial fuel cells and electrolysers involve membranes to spatially separate oxidation and reduction reaction products. However, as electrochemical systems are miniaturized, novel types of membrane processes are needed. Here, Frank Marken argues the case for ionic diodes to take on this role, and, tantalizingly, offers applications for both water desalination and water harvesting. Emmanuel Mousset reviews the use of electrochemical technologies for resource recovery, such as water treatment, in the last paper of this issue. These involve a number of techniques: electro-conversion, electro-filtration, electrosorption, electrodeposition, electro-precipitation and electrocoagulation, for which, whilst the instrumentation is often more simple than a potentiostat (a galvanostat), it requires high-voltage operational amplifiers, so that the applied current can drive the Faradic reactions.

And so, in turning a full circle of innovation in physicochemical techniques for electrochemistry and its applications, we hope you will enjoy reading this novel issue of *Current Opinion in Electrochemistry* as much as we had, through its handling!

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References

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[2] J. A. von Fraunhofer, C. H. Banks, *Potentiostat and its Application*, Butterworths, London, 1972.

Bio Jay

Jay Wadhawan trained in electrochemistry in Oxford (with Professors Richard Compton, Frank Marken and Clive Hahn) and Paris (with Professors Christian Amatore, Emmanuel Maisonhaute and Bernd Schöllhorn). He was elected as the University of Hull's first Professor in Knowledge, Innovation and Engagement, in 2020. His research interests range from molecular to analytical and industrial engineering aspects of electrochemistry.

Bio Emmanuel

Emmanuel Maisonhaute realized his PhD at Ecole Normale Supérieure in 2000 where he performed ultrafast electrochemistry under the guidance of Christian Amatore. He then went to Oxford as a post-doctoral student in the group of Richard Compton for one year before returning to Paris as associate professor. He was then appointed professor at Sorbonne Université in 2008. He has developed several instrumental setups to decipher complex mechanisms in electrochemistry. Among them are an ultrafast potentiostat, a coupled system to monitor transient species produced by radiolysis and more recently several Raman approaches to explore electrochemical reactivity or low cost instrumentation for emerging countries or teaching purposes.