

# Challenges and opportunities of modern electrochemistry—a personal reflection

The area of electrochemistry is seeing rapid growth that can benefit other areas of science

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**Abstract** The first version of this article was published in January issue of the Canadian Chemical News in 2000. This issue featured Electrochemistry and coincided with the 200th anniversary of the famous Volta pile experiment. It also coincided with the 50th anniversary of the International Society of Electrochemistry. In that article I reflected on the past and I pondered on the future of electrochemistry. It was written for general community of Canadian chemists. The present version has been updated. However most of my original thoughts have been retained. I have also retained the original language of an article written to a non-specialized readership.

**Keywords** Electrochemistry · Molecular interpretation · Electrochemical science · Electrodes · Voltammetry

Electrochemistry, a mature and distinguished science, has undergone a tremendous transformation during the last four decades. The scope of electrochemistry is to study phenomena related to the measurement of potential, current or conductivity. In the past, electrochemists measured average properties of macroscopic samples and were able to provide only phenomenological descriptions of the potential or current-driven processes, using the formalisms of classical thermodynamics and kinetics. Molecular interpretation of these processes involved modelling and statistical mechanics. The status of traditional electrochemistry was well reflected in the first name of ISE. Created in 1949 in Brussels, Belgium, the society was initially called “Committee International de la Thermodynamique et Cinétique Electrochimique” (CITCE). It was only in 1970 that CITCE changed its name to ISE. This date also marks the beginning of the transformation of electrochemistry into a modern and interdisciplinary science that integrates the measurements of current or potential with modern spectroscopic, diffraction and imaging techniques. Electrochemical science is now able to provide molecular level descriptions of charge or potential-driven phenomena.

A few developments have revolutionized electrochemistry: (1) sample miniaturization, (2) availability of modern spectroscopic techniques, (3) development of scanning probe microscopies, such as the scanning tunneling microscopy (STM) and the atomic force microscopy, and (4) progress in scientific instrumentation that allowed

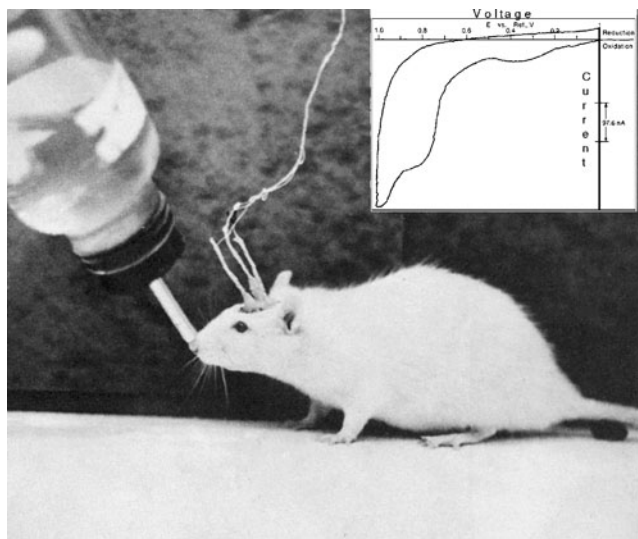
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nanosecond time gating and measurements of currents in the picoampere range.

The smallest electrodes used in earlier studies had dimensions in the range of a millimeter. New interests in the application of electrochemical methods for *in vivo* analysis of drugs and neurotransmitters stimulated development of ultra-small electrodes (ultramicroelectrodes) with dimensions in the range of micrometers. Such small electrodes may be inserted into the brain of a living animal without damage to the brain tissue as shown in Fig. 1 [1]. Voltammetric techniques may then be used to monitor the concentration of neurotransmitters in the extracellular fluid space following stimulated synaptic release. This *in vivo* voltammetry provides unique information concerning the kinetics of drug administration or shows changes in brain chemistry related to physiological process such as drinking or feeding. *In vivo* measurement in the central nervous system is a new and exciting direction of modern electrochemistry [2].

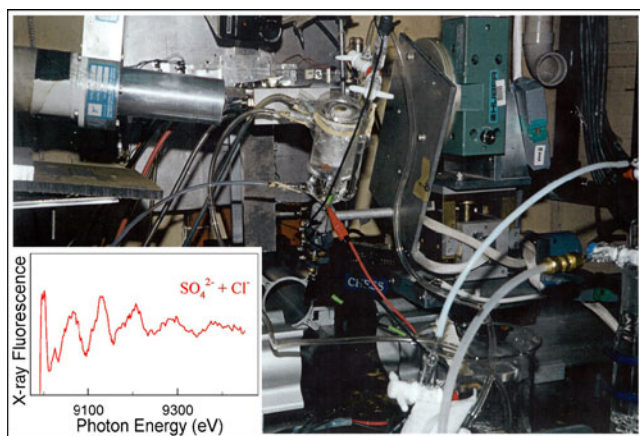
Ultramicroelectrodes also find applications in the study of secretion of molecules such as histamines or neurotransmitters from a single biological cell *in vitro*. In that case, a micron-size electrode is positioned at a distance of 1  $\mu\text{m}$  from a  $\sim 15\text{-}\mu\text{m}$  large single cell immobilised in a culture plate. In addition, auxiliary and reference electrodes are inserted in the culture disk. Fast voltammetry is then used for identification and quantification of molecules secreted from the cell [3]. Atomole quantities of molecules can be measured routinely, and a detection of only 4,700 molecules has also been reported [4]. The electrochemical measurements also provide unique information concerning the secretion kinetics and mechanisms [5].



**Fig. 1** Unstrained rat with permanently implanted electrodes. Inset typical voltammogram in rat brain tissue. Modified figures taken from ref [1]

The invention of ultramicroelectrodes had a significant impact on the field of electrode kinetics. The electrode-solution interface behaves as a capacitor. The electrolyte solution has a property of a resistor. The product of the electrode capacitance and the solution resistance has the dimension of a time unit (second). In fact, it is the time constant that determines the speed with which a potential perturbation may be imposed onto the cell. The studies of electrode kinetics are therefore limited to processes that are characterised by half times larger than the time constant of the cell. In the past, the time constant of the cell was in the range of 100  $\mu\text{s}$  or more. Consequently, electrode kinetics was restricted to investigations of processes that were much slower than that studied in other areas of chemical kinetics. With the use of ultramicroelectrodes, the time constant could be reduced to 100 ns, and the rates of electrode reactions could now be investigated up to the diffusion jump limit [6]. More recently, nanoelectrodes have been introduced to study ultrafast electrode processes. Nanoelectrodes are essentially metal STM tips coated with an insulating polymer layer so that only a nanometer size fraction of the sharp end of the tip is exposed to the solution. Instead of measuring the tunnelling current, this tip is used as an electrode. The time constant of the nanoelectrode may be as small as 1 ns [7]. This opens a possibility to study solvent relaxation phenomena at electrode surfaces.

Electrode reactions are heterogeneous processes and their rates and mechanisms depend on the structure and composition of the electrode-solution interface. The interfacial phenomena at the electrified solid-liquid interface are the objects of study in surface electrochemistry. The presence of the solvent restricts the number of techniques that may be employed to study electrode surfaces. For years, this interface was investigated chiefly with the use of traditional electrochemical methods that measured only macroscopic quantities such as charge or surface concentrations, and the solid surface was treated as a hard wall. In the last three decades, new spectroscopic techniques have been developed and applied to study the interfacial phenomena at the molecular level [8]. Thus, infrared reflection spectroscopy may be employed today to study coordination of ions and molecules to electrode surfaces. Synchrotron-based X-ray diffraction and X-ray absorption techniques are used to determine long-range and short-range order at the interface. Electroreflectance spectroscopy, second harmonic generation and sum-frequency generation spectroscopies are applied to probe electronic structure of the electrode surface and the molecular dynamics of interfacial phenomena [8, 9]. To minimise absorption of photons by the solvent, these spectroscopic techniques require a specially designed thin-layer cell, in which the electrode is pressed against an IR, X-ray or

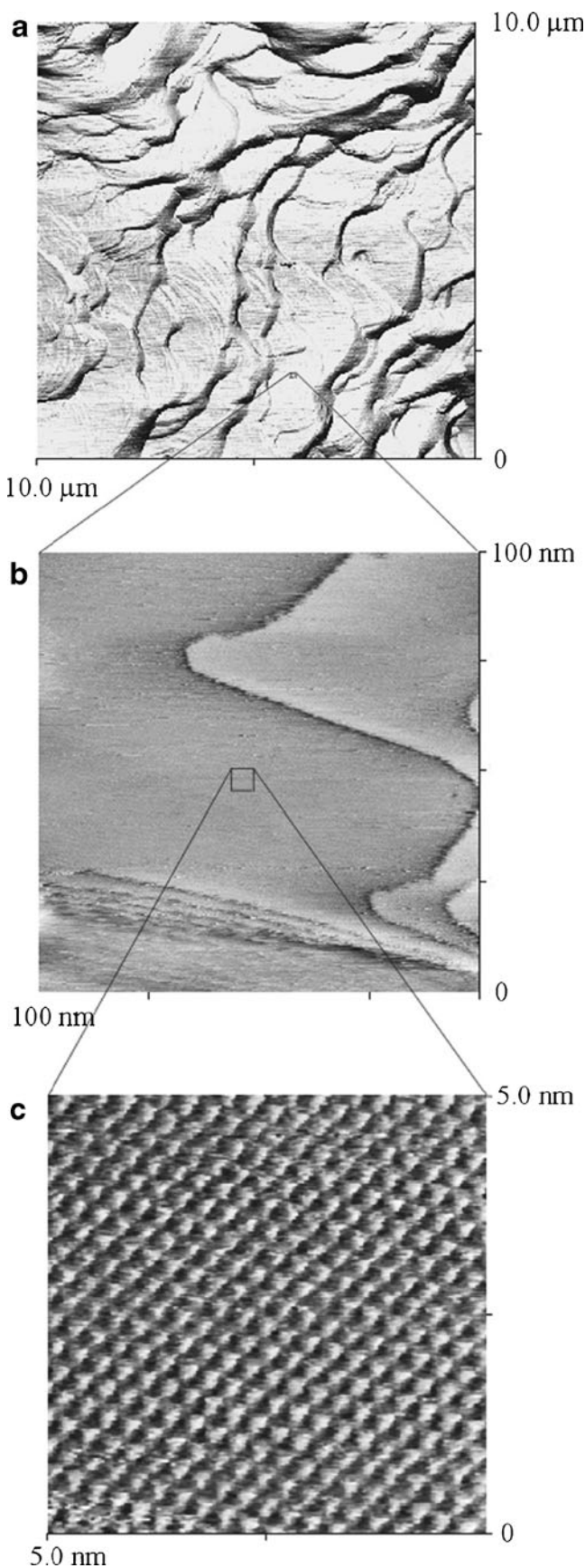


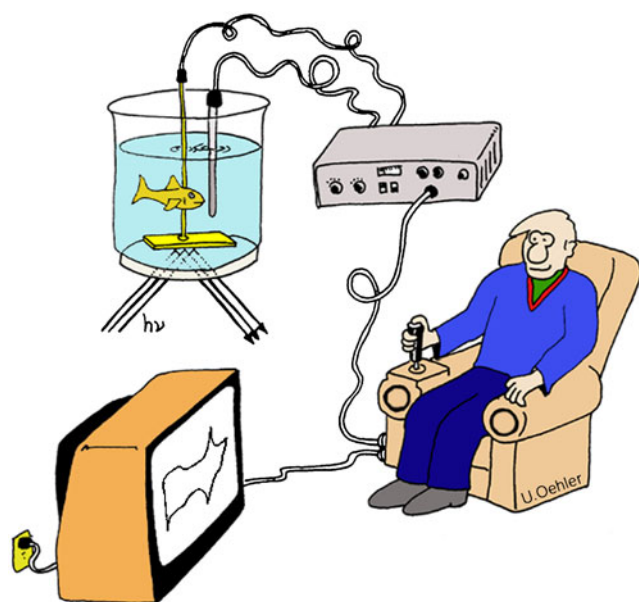
**Fig. 2** Experimental set up for X-ray absorption of an electrode surface at the Cornell High Energy Synchrotron Source. Inset an X-ray absorption spectrum of a monolayer of copper deposited at the gold electrode surface

optical window so that only a thin (a few micrometers thick) layer of the electrolyte is trapped between the electrode surface and the window. Fig. 2 shows a picture of such a cell used for in situ X-ray absorption spectroscopy at the Cornell High Energy Synchrotron Source (CHESS). The last but not the least, scanning probe microscopies, such as atomic force and STM provide real-time and real-space images of the interface with atomic resolution [10]. These imaging techniques reveal the real morphology of the electrode surface. The solid surface is no longer seen as a hard wall, but as Fig. 3 shows, it consists of terraces, steps and kinks. In electrochemistry, these spectroscopic, diffraction and surface imaging methods are frequently referred to as non-traditional techniques. Today, by careful combination of traditional and non-traditional methods, one can provide an atomistic picture of interfacial phenomena.

In an electrochemical environment, one may charge the solid surface. This charge generates a field on the order of  $10^7$ – $10^8$  V/m that drives ions and dipolar molecules. By turning a dial on a control instrument, one can manipulate ions and molecules present at the interface. As the cartoon in Fig. 4 shows, electrochemistry provides surface science with a “joystick” that can be used to force ions and molecules to adsorb or desorb, to form ordered or disordered adlayers, change their surface orientation, spread them into a uniform film or group them together into surface aggregates. In contrast to classical surface science where one works in vacuum and out of equilibrium, surface

**Fig. 3** STM image of a real gold electrode surface: **a** image of a  $10 \times 10$ - $\mu\text{m}$  section of the surface showing multiple terraces, **b** zoomed in image showing surface topology of a single terrace, **c** atomic resolution image of a section of the single terrace surface showing characteristic structure of a gold single crystal surface



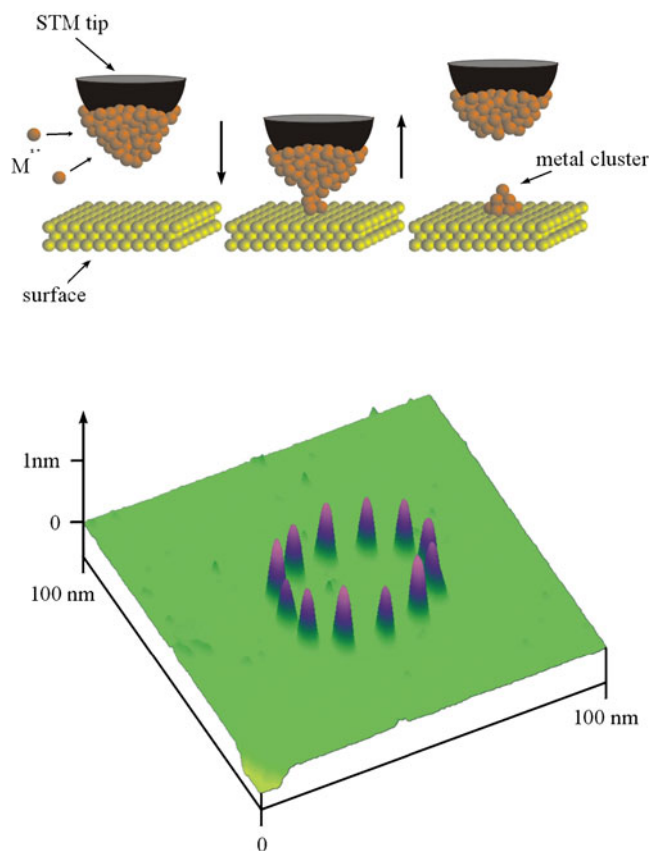


**Fig. 4** Surface electrochemistry—surface science with a joy stick

electrochemistry may be employed to study processes at equilibrium and at ambient conditions.

Surface electrochemistry makes significant inroads into other disciplines such as materials science, and it is my personal opinion that in the near future, surface electrochemistry will play a significant role in biomimetic research. Electron and ion transfer are involved in the activity of biological membranes. These processes also play a central role in electrochemical science, and electrochemistry is well equipped to study these reactions. It is already known that phospholipid bilayers may be deposited onto nonconductive solids, and we have just learned that they may also be coated onto a metal electrode surface [11–13]. The macroscopic and microscopic techniques of surface electrochemistry may therefore be employed to study membrane processes [13].

The methodological progress has spawned new disciplines such as electrochemical nanotechnology [14]. Several groups have recently demonstrated that the STM tip may be used not only for imaging surfaces but also for nanostructuring the surface. One of these methods is shown in Fig. 5. Copper is electrochemically deposited on the STM tip and then the tip approaches the gold surface until a contact between the tip and the surface is established. When the tip is withdrawn, a small cluster of copper (having an average height 0.8 nm) remains on the gold surface. These clusters display remarkable stability with respect to anodic dissolution. By controlling the movement of the tip, this procedure may be used to print various patterns at the electrode surface. A corral of only 12 clusters is shown in Fig. 5, but amazingly, a field of 10,000 clusters was recently created [15]. Other interesting development in



**Fig. 5** *Top panel*, principle of tip-induced copper cluster deposition. *Bottom panel*, a corral of 12 copper cluster formed at an Au(111) electrode surface. Courtesy of D. M. Kolb [9]

electrochemical nanotechnology is the demonstration that nanowires may be used as electrochemical sensors [16] and measurements of conductivity through individual molecules or through ensemble of molecules [17, 18]. The new field of molecular electronics is emerging from these studies.

The examples given above constitute the tip of the iceberg. There are many other important areas of electrochemistry that are in the process of impressive methodological and scientific changes. They include dramatic progress in batteries and fuel cells research [19], solar energy conversion [20, 21], development of sensors, biosensors and molecular recognition devices [22–25]. Electrochemistry has tremendous potential to solve numerous environmental problems by offering viable methods of toxic waste disposal [26] and also finds application in thin-film technology. Electrochemistry finds applications in many industrial technologies and commercial products. Batteries (electrochemical power sources) are omnipresent in our daily life. Many metals such as copper, nickel, zinc and aluminum are produced electrolytically. The value of the yearly production of these metals in Canada is in excess of \$5 billion. Copper electroplating is used to print conductive circuits in microelectronic devices. Fuel cells, the environmentally

clean power sources for the auto industry, are at the brink of great commercialization, which will change our automobiles and bring fresh air to our cities.

On the map of science, electrochemistry is located at the crossroad of many disciplines. The knowledge gained from electrochemical studies is relevant to other fields such as analytical chemistry, energy storage and conversion, biology and medicine, materials science and microelectronics. This interdisciplinary character makes electrochemistry a particularly valuable teaching tool. The education provided in an electrochemical laboratory is broad and the graduate student has an opportunity to integrate and to apply most of the knowledge he/she has learned in undergraduate school. His/her project will require development of software and hardware for scientific instrumentation, training how to combine spectroscopy with electrochemical measurements, and occasionally, he/she will have to perform synthetic or preparatory work. The student may travel to synchrotrons or neutron beam sources to perform dedicated experiments, and this will give him/her an opportunity to mingle with physicists, biologist and materials scientist coming from over the world and to get the flavour of a truly interdisciplinary and international science.

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