



The role of nanoelectrochemistry in nanotechnology

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Nanotechnology and chemistry

The rapid progress in scientific and technological developments in recent years has been very much associated with advances in nanotechnology, nanoengineering and instrumentation.

What is the role of chemistry in this progress? This question was briefly addressed in J.J. Ramsden's article on nanotechnology in the first issue of this journal.¹ A chemist's perspective of the structure of matter starts from the molecular level, which means at sub-nanometre dimensions.² However, the discovery and design of large molecules such as the sphere-like fullerenes, which are entirely made of carbon atoms,³ pave the way for the formation of supramolecular structures and architectures of nanometre dimensions, through bonding and cooperative effects between molecules, with consequent molecular ordering. Many biomolecules are of nanometre dimensions and can exhibit similar properties: as one simple example, the dimeric glucose oxidase enzyme has the dimensions of $7 \times 5.5 \times 8$ nm.

Furthermore, instruments have been invented which allow the examination of solids and surfaces down to the atomic scale both in air and liquids. Techniques such as scanning electron microscopy and transmission electron microscopy require the use of a high vacuum. The new family of microscopies—collectively known as scanning probe microscopy—encompasses techniques such as scanning tunnelling microscopy (STM), atomic force microscopy (AFM), scanning Kelvin microscopy (SKM) and scanning electrochemical microscopy (SECM).⁴ All of these require accurate positioning of a nanometric-sized probe, often to within less than 0.1 nm, and rely for their positioning on the change in dimension of piezoelectric crystals, which occurs in a linear fashion with applied electric field.

¹ J.J. Ramsden, "What is nanotechnology?", *Nanotechnology Perceptions* **1** (2005) 3–17.

² The unit traditionally used by the chemist to denote molecular dimensions is the Ångström (Å) corresponding to 0.1 nm or 10^{-10} m.

³ R.F. Curl Jr., H. Kroto and R.E. Smalley won the Nobel Prize for Chemistry in 1996 for their discovery of fullerenes. Buckminsterfullerene, C_{60} , is a carbon cage with 60 carbon atoms in the form of a sphere with a diameter of approximately 0.7 nm.

⁴ G. Binnig and H. Rohrer won the Nobel Prize for Physics in 1986 for their invention of the scanning tunnelling microscope, which led to the development of many other forms of scanning local probe microscopes.

The chemist is, of course, not only concerned with examining systems in a stationary state. He or she is also interested in probing the changes of a system with time and the reactions that can occur between molecular species. These reactions take place either in a highly localized region between molecules or ions inside a phase or at interfaces, which can be between a solid and liquid, a solid and a gas, two immiscible liquids or between a gas and a liquid. Many of these interfacial phenomena are highly important at an industrial level in the catalysis of chemical processes, and it is often found that tiny catalyst particles are far more effective and efficient than large ones.

This article is concerned with the role of electrochemistry in nanotechnology and will indicate some of the exciting contributions that electrochemistry is making to the field.

What is electrochemistry?

Electrochemistry is concerned with chemical phenomena associated with charge separation, usually in liquid media.⁵ The separation of charge often leads to charge movement in order to try to annul the electric field which is created—this can occur in solution or within a solid. Alternatively, charge can be transferred from (or to) a chemical species in solution to (or from) another phase such as a solid (electrode) surface, leaving the chemical species with a more positive or a more negative charge than before—this transfer is usually of electrons. In order to ensure a net charge of zero in the whole process (electroneutrality), two or more charge transfer reactions involving different chemical species need to take place simultaneously, in opposing directions: oxidation (loss of electrons and increase in charge) and reduction (gain of electrons and decrease in charge). In the case of charge transfer reactions at solid surfaces, the oxidation and reduction are spatially separated, usually occurring at different electrodes immersed in solution in a cell.

When the sum of the energy changes due to oxidation and reduction reactions corresponds to a net decrease in energy of the system, energy is released. This energy can be harnessed as electrical energy, such as occurs in batteries and fuel cells. The electrodes where the reactions occur are linked by conducting paths both in solution (via ionic transport) and externally (via electrical wires) so that charge can be transported and the electrical circuit completed. On the other hand, if external electrical energy is supplied to the system then the naturally occurring reactions can be forced to go in the opposite direction and convert chemical substances, which is electrolysis. Important large-scale examples can be found in the chloralkali industry to produce caustic soda and chlorine and in the production of aluminium metal from the aluminium oxide mineral bauxite. Finally, sometimes uncontrolled spontaneous oxidation and reduction reactions can occur on conducting surfaces, usually metals, which can lead to their dissolution—normally referred to as corrosion.

Fig. 1 shows some of the areas in which electrochemistry is important. A number of these can be clearly related to nanoscale phenomena. Control and investigation of these charge transfer processes using modern electrochemical instrumentation and complementary techniques is now possible down to the nanometre dimension.

⁵ See, for example, C.M.A. Brett and A.M. Oliveira Brett, "Electrochemistry. Principles, methods and applications", Oxford: Oxford University Press (1993).

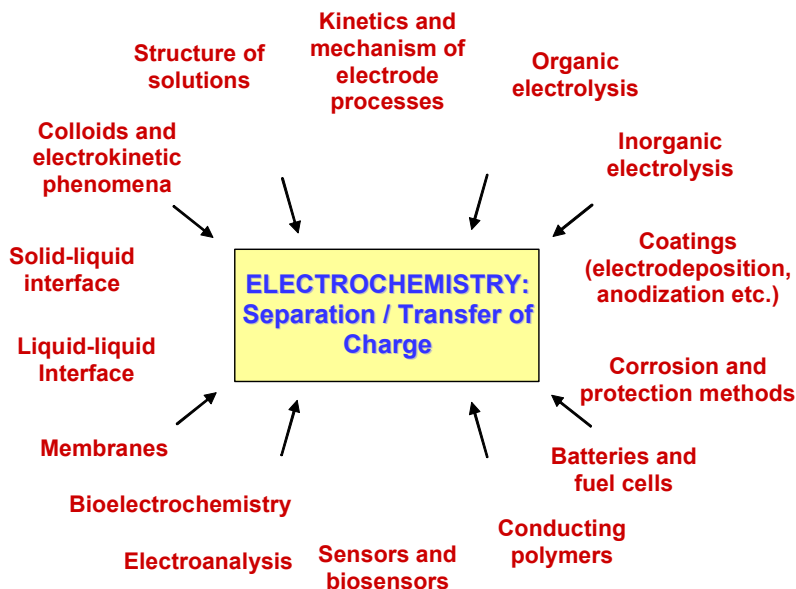


Figure 1. Areas of research and applications involving electrochemistry

Nanoelectrochemistry

Nanoelectrochemistry represents the control and investigation of electrochemical processes at the nanometre level.⁶ It is intimately linked with the use and development of nanomaterials, and helps in bridging the gap between materials at the macroscopic/microscopic level and those at the molecular level. This can be done through a top-down or a bottom-up approach. At dimensions of a few nanometres only, the number of molecules involved can be sufficiently small that the macroscopic physical and chemical behaviour is no longer valid and quantum effects have to be taken into account. Investigation and exploitation of this phenomenon is still in its infancy.

Some of the exciting possibilities and potentialities of nanoelectrochemistry are now beginning to come to fruition and will be examined in the following sections.

Nanostructures: nanomachining, nanoelectrodeposition and nanocorrosion

A common aspect of nanostructures is their control and investigation by scanning probe microscopies, as will be seen.

Nanomachining has used techniques such as extreme ultraviolet lithography to enable the construction of features down to a size of approximately 15 nm using ultraviolet radiation of a wavelength of 13 nm—this represents the size limit of this technique. However, nanoelectrochemical machining should reach smaller dimensions, as will be further discussed below. In contrast to nanomachining, nanoelectrodeposition involves the nucleation and growth

⁶ M. Hugelmann, P. Hugelmann, W.J. Lorenz and W. Schindler, “Nanoelectrochemistry and nanophysics at electrochemical interfaces”, *Surf. Sci.* **597** (2005) 156–172.

of new phases beginning at the molecular level. Nanomachining can be regarded as a top-down and nanoelectrodeposition a bottom-up approach.

A uniform acid etching of surfaces can lead to the revelation of their nanostructure, which can then be examined by scanning probe microscopy, see example in Fig. 2.⁷ For metals and alloys, this can give important information on the effect of details of the fabrication process and heat treatment on the nanostructure, and suggest which methodologies are the most beneficial in order to minimize corrosion and lead to the desired physical and chemical properties.

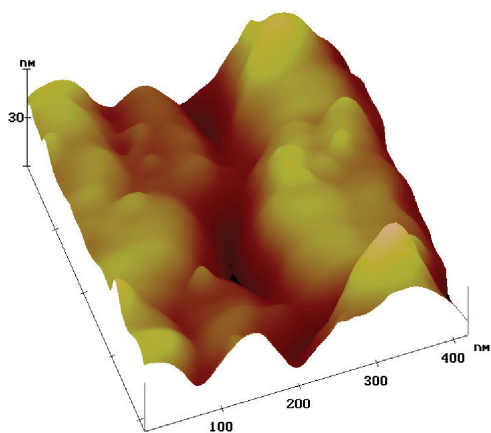


Figure 2. Three-dimensional AFM topographical image of chromium steel tempered at 450 °C after etching in a solution of nitric acid in ethanol. The small 40 nm particles are attributed to chromium carbides (reprinted from ref. 7, with permission from Elsevier).

In a different type of strategy, controlled electrochemical etching of wires of micrometre dimensions leads to nanowires that eventually break where the wire is least thick, monitored by a sudden decrease in conductivity, leaving a gap of molecular dimensions.⁸ Molecules can then be inserted in this gap and the transport of electronic charge by individual molecules investigated. This holds much promise for the future, particularly in probing the recognition molecules used in sensor applications and in molecular electronics.⁹

By the judicious use of electrochemistry, electrochemical etching (i.e. forced corrosion) and electrochemical deposition at the nanometre level can both be carried out with a combination of scanning tunnelling microscopy and scanning electrochemical microscopy.¹⁰ In this way, etched features of the order of 10 nm in diameter can be made by the scanning probe tip. By altering the control conditions, protruding features of the size of a nanoelectrode probe

⁷ V.A. Alves, A.M. Chiorcea Paquim, A. Cavaleiro and C.M.A. Brett, “The nanostructure and microstructure of steels: electrochemical Tafel behaviour and atomic force microscopy”, *Corros. Sci.* **47** (2005) 2871–2882.

⁸ H.X. He, S. Boussaad, B.Q. Xu, C.Z. Li and N.J. Tai, “Electrochemical fabrication of atomically thin metallic wires and electrodes separated with molecular-scale gaps”, *J. Electroanal. Chem.* **522** (2002) 67–72.

⁹ J.R. Heath and M.A. Ratner, “Molecular electronics”, *Physics Today*, May 2003, pp. 43–49.

¹⁰ O. Sklyar, T.H. Treuler, N. Vlachopoulos and G. Wittstock, “The geometry of nanosized electrodes and its influence on electrolytic currents and metal deposition processes in scanning tunnelling and scanning electrochemical microscopy”, *Surf. Sci.* **597** (2005) 181–195.

tip can be deposited on a conducting substrate as a nanodot. This type of combination can be predicted to be used in the future for the nanopatterning of surfaces and the construction of nanodevices.

Nanocorrosion is the loss of material due to environmental degradation at the nanoscale, and is particularly important in nanostructured materials. This is a new field, because rather than features such as inclusions that cause corrosion in conventional materials, defects at the nanometre scale become the major cause. Again, the methods that will be necessary to investigate and control nanocorrosion must be *in situ* nanoprobes.

Carbon nanotubes

Scientists have long been interested in carbon nanotubes, and this interest continues, attested to by the large number of publications on the theme.

Carbon nanotubes¹¹ are tubular structures, typically of nanometre diameter and many micrometres in length, with a very large surface area per volume. Single walled nanotubes (SWNT) are like a sheet of graphite (a hexagonal lattice of carbon) rolled up into a cylinder, and which can have semiconductor or metallic conductivity. Bundles of SWNTs can be formed, referred to as ropes, or with a bamboo-like structure. Multiwalled nanotubes (MWNT), consisting of at least several and up to tens of concentric cylinders with a spacing between them of 0.3 to 0.4 nm, can also be synthesized. Which type is produced depends on the synthesis method and experimental conditions: methods used are arc-discharge, laser ablation or chemical vapour deposition.

From an electrochemical point of view carbon nanotubes can be regarded as true nanoelectrodes, with diameters that can be less than one nanometre. Often they are employed to modify the surfaces of larger electrodes¹² and modification strategies can be used such that they are all aligned perpendicular to the electrode surface. In these cases they can be applied in electrochemical sensors and have favourable properties in the measurement of key analytes such as ascorbic acid (vitamin C) and dopamine (an important neurotransmitter). The surfaces of the carbon nanotubes themselves can be modified by attaching other molecules to them such as enzymes and other redox proteins.¹³ The larger surface area leads to a higher sensor response and direct electron transfer has also been observed.

Nanotubes of metals and of crystalline compounds can be made using ordered porous membrane templates such as anodic alumina, but application are far fewer up until now.

Nanoparticles and nanowires

Nanoparticles possess physical and chemical properties that make them potentially applicable in optoelectronics, information storage, catalysis, biological labelling, photonics,

¹¹ K. Gong, Y. Yan, M. Zhang, L. Su, S. Xiong and L. Mao, "Electrochemistry and electroanalytical applications of carbon nanotubes: a review", *Anal. Sci.* **21** (2005) 1383–1393.

¹² J.J. Gooding, "Nanostructuring electrodes with carbon nanotubes: A review on electrochemistry and applications for sensing", *Electrochim. Acta* **50** (2005) 3049–3060.

¹³ E. Katz and I. Willner, "Biomolecule-functionalised carbon nanotubes: applications in bioelectronics", *Chem. Phys. Chem.* **5** (2004) 1084–1104.

photography and battery production. They also offer excellent prospects for chemical and biological sensing, particularly in the form of colloidal gold and semiconductor quantum dot nanoparticles, in which electrochemistry plays an important part.¹⁴ Their power can be enhanced by associating them with biological recognition reactions.¹⁵ As with nanotubes, the amount of research being undertaken is evidenced by the immense number of publications.

Nanosized particles are usually prepared by one of two routes. One is from supersaturated solutions containing organic surfactants, which impede growth of the particles once they are formed. The other is by controlled electrodeposition in which nanoparticles are nucleated by a short high voltage pulse and then a lower voltage is used to grow the particles at a slower rate to their final dimension—the benefit is that the size of the nanoparticles can be precisely controlled. Usually the particles are spherical, examples being gold, silver and nickel. Under carefully controlled experimental conditions it is possible to regulate the particle growth in two dimensions only, leading to the formation of nanowires.

A more convenient method to form nanowires is by the use of porous templates, which consist of a regular ordered array of submicrometre-sized pores, for example porous alumina membranes. This technique is known as templated electrodeposition and involves the deposition of the metal within the pores forming wires, followed by membrane dissolution.

The goal of much of the research being undertaken is to make novel commercial devices based on assemblies of nanoparticles. By immobilizing the nanoparticles on an electrode surface, usually by self-assembly, electrochemistry offers an easy route of coupling nanoparticle activity to an external circuit. This immobilisation is often in multilayers, exploiting the fact that the nanoparticles are charged and using self-assembling intermediate layers of ions or large molecules of the opposite polarity. This layer-by-layer (LbL) approach is easy to carry out and is currently the object of much fundamental research.

One example of an application is in dye-sensitized solar cells using titanium dioxide nanoparticles, which offer a very high surface area and thence a much higher solar conversion efficiency. Another is in electrochemical sensors, where again the existence of a very large surface area allows much higher sensitivities and thence the reduction of detection limits.

Nanosensors

Nanometre-sized sensors can be used in situations in which would otherwise be impossible to introduce a sensor, owing to the minute space available or the tiny volume of analyte, progress in nanomaterials and instrumentation having made it possible. A recent example uses polyaniline conducting polymer (doped with poly(acrylic acid) to ensure that it has high conductivity) to bridge a gap of 20–60 nm between two nanoelectrodes and onto which the enzyme glucose oxidase is immobilized.¹⁶ Glucose molecules in the analyte are oxidized

¹⁴ D.J. Riley, “Electrochemistry in nanoparticle science”, *Curr. Opin. Colloid Interface Sci.* **7** (2002) 186–192.

¹⁵ E. Katz, I. Willner and J. Wang, “Electroanalytical and bioelectroanalytical systems based on metal and semiconductor nanoparticles”, *Electroanalysis* **6** (2004) 19–44.

¹⁶ E.S. Forzani, H. Zhang, L.A. Nagahara, I. Amlani, R. Tsui and N. Tao, “A conducting polymer nanojunction sensor for glucose detection”, *Nano Lett.* **4** (2004) 1785–1788.

catalytically by the enzyme with consumption of oxygen and production of hydrogen peroxide. The peroxide reacts with the polyaniline causing an increase in conductivity, which is measured between the two nanoelectrodes. Due to its small size, the sensor response is extremely fast; such tiny sizes are needed for future *in vivo* real-time monitoring of glucose levels.

Nanobatteries

Batteries are electrochemical power sources. In order to supply energy for the operation of nanometre-size electrochemical, optical etc. nanosensors, a robust power source is necessary, which has to be a nano-sized battery. One interesting potential application is a nanobattery to power an artificial retina.¹⁷ The secret of operation is to have a small gap between the two electrodes of the battery, this gap being filled with a porous membrane with the pores containing battery electrolyte.

Challenges for the future

As has been seen, nanoelectrochemistry is playing, and will continue to play, an important role in many developments in nanotechnology. Adaptation of scanning probe microscopy strategies, in particular, has a very important potential not only as an investigative technique but also as a way of producing tiny nanostructures. Future progress will require developing ways for greater control and investigation of the processes that are necessary to produce new nanomaterials for diverse applications.

¹⁷ D. Teeters, N. Korzhova and L. Fisher, "Nano-battery systems", U.S. Patent 6586133 (2003).