1

An Introduction to Sonoelectrochemistry

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1.1 Introduction to Ultrasound and Sonochemistry

Ultrasound is defined as sound with a frequency that is beyond the range of human hearing and this is generally considered to be above 20 kHz (20 000 hertz, hertz = cycle per second). The ultrasound frequency range can be broadly subdivided into two categories (Figure 1.1):

 (i) **Diagnostic ultrasound** operates at very high frequencies (above 5 MHz); it is used in foetal scanning and in general for the non-destructive testing of materials. The important feature of diagnostic ultrasound is that the energy involved is too low to produce cavitation in tissues and so is safe to use in medical scanning.
(ii) **Power ultrasound** is mainly in the frequency range between 20 and 100 kHz (but can be extended up to 2 MHz). The energies involved are sufficiently high to produce cavitation in liquids and thus can be used to influence chemistry and processing (see later).

The origins of ultrasound can be traced back to the late nineteenth century with the discovery of the piezoelectric effect by Curie and the ultrasonic whistle by Galton in 1893. However, the first commercial application of ultrasonics did not appear until 1917 with Langevin's echo sounding technique. Langevin's discovery was the direct result of a competition organised in 1912 to find a method of detecting icebergs and so to avoid any repetition of the disaster which befell the Titanic. Essentially all imaging, from medical ultrasound to non-destructive testing (flaw detection), relies upon the same pulse echo type
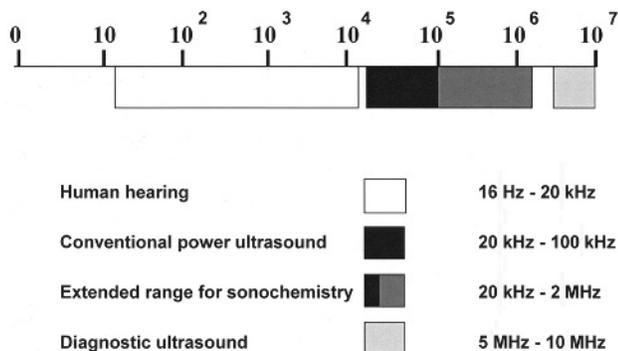
Figure 1.1   *Sound range.*

of approach, that is, a pulse of sound is transmitted through a material and is reflected from a boundary. The time of flight from emission to reception of the echo is then used to compute the distance to the boundary using the speed of sound in that medium. High frequency ultrasound (>1 MHz) is therefore employed for modern medical imaging and non-destructive testing.

The potential of using acoustic cavitation to create changes in materials was identified in the USA in the late 1920s [1–3]. Over the succeeding years some more research went into the applications of ultrasound in chemistry and the first review of this type of work was published in the 1940s [4].

By the 1950s, industry had adopted power ultrasound (which at that time was known as 'Macrosonics') for a range of applications that were gathered together in a series of five publications [5]. At that time there were six general industrial applications and these are listed in order of commercial turnover in Table 1.1.

The majority of the applications shown in Table 1.1 can be considered to be 'engineering' and the whole area of ultrasonic applications in the chemistry laboratory, which had been identified in the 1940s, did not really develop until the 1980s. This renaissance is generally considered to be due to chemists becoming aware of potential alternative uses of ultrasonic equipment which was then appearing in the laboratory in the form of cleaning baths and ultrasonic probes (the latter more commonly in biological laboratories in the form of biological cell disruptors).

From Table 1.1, it can be seen that power ultrasound can be used in two basic ways to bring about changes in a material and these are:

 (i) **Direct** mechanical transmission of vibration from the transducer onto a solid to induce vibrations in the surface of the material.
(ii) **Indirect** transmission of energy via cavitation induced in a fluid by the transmission of acoustic vibrations.

Each of these has a relevance to electrochemistry since (i) can be taken to represent induced vibrations at a solid electrode surface and (ii) can be taken to represent sonication of an electrolyte. In many cases both will occur simultaneously and influence the overall electrochemical process.

Table 1.1 *Industrial applications of macrosonics: the major established areas. Reprinted with permission from Ultrasonics, Macrosonics in Industry 1. Introduction by E. A. Neppiras, 10, 1, 9–13 Copyright (1972) Elsevier Ltd.*

1	**Cleaning**	Dispersing loosely held non-soluble particles and coatings
		Dissolving solid surface coatings
		Degreasing
		Descaling
2	**Plastic Welding**	Remote welding of rigid thermo-plastics
		Insertion
		Staking
		Splicing
		Continuous welding of sheet material
3	**Metal Welding**	Microbonding
		Continuous welding of sheet material
		Bonding metals to non-metals
4	**Chemical Processing**	Extracting: – perfume from flowers
		essential oils from hops
		juices from fruits
		chemicals from plants
		biomacromolecules from cells
5	**Metal Forming**	Wire-drawing
		Tube-drawing
		Plastic-forming of sheet metal
6	**Machining**	Ultrasonic machining with abrasive
		Vibration-assisted ECM
		Vibration-assisted milling, turning, drilling, grinding, polishing
		Teeth descaling
		Vibration-assisted rotary drills

1.2   Applications of Power Ultrasound through Direct Vibrations

The application of power ultrasound through the introduction of direct vibrations onto a solid surface is the basis of many engineering applications including welding, drilling, cutting and tube drawing. The drilling and cutting applications have now also become an important development in surgery.

1.2.1   Welding

A large proportion of ultrasonic equipment currently in industry is devoted to welding or riveting plastic mouldings for the consumer market. The equipment generally operates at around 20 kHz and a shaped tool or horn transmits (and amplifies) the vibrating motion to a shaped die pressing together the two pieces of material to be welded. The vibrational amplitude is typically 50–100 microns (μm).

Ultrasonic welding is generally used for the more rigid amorphous types of thermoplastic. It is particularly important that the vibrational energy is primarily transmitted to the joint rather than be absorbed by the body of the material, producing heat. This is because any

warming of the bulk material can lead to a release of internal moulding stresses and produce distortion. Thermoplastics have two properties which make them particularly suited to ultrasonic welding: (a) low thermal conductivity and (b) melting or softening temperatures of between 100 and 200 °C. As soon as the ultrasonic power is switched off the substrate or bulk material becomes a heat-sink, giving rapid cooling of the welded joint. When the more traditional conductive heating is used for welding, however, the thermal gradient has to be reversed before cooling occurs, leading to long heating/cooling process cycles. Another major advantage of the use of ultrasound is the high joint strength of the weld, reaching 90–98% of the material strength. Indeed, test samples usually break in the body of the material and not at the weld itself.

1.2.1.1 Machining (Drilling and Cutting)

Ultrasonic drilling and cutting were originally introduced and developed for the accurate profiling of brittle materials such as ceramics and glass. It has been used in the aerospace industry since the 1970s for cutting glass and carbon fibre composites and has found many applications in the food industry. In dentistry it is used for removing plaque from teeth and in medicine it is used to improve the efficiency of scalpels and for bone cutting.

Ultrasonic cutting uses a knife-type blade attached through a shaft to an ultrasonic source. Essentially the shaft with its blade behaves as an ultrasonic horn and is normally operated at a frequency of 20 kHz. The cutting action is a combination of the pressure applied to the sharp cutting edge surface and the mechanical longitudinal vibration of the blade. Typically the tip movement will be in the range 50 to 100 microns peak to peak. Several advantages arise from this technology:

 (i) The ultrasonic vibration of 20 kHz applies an intermittent force to the material to be cut and generates a crack (cut) at the tip, controlling its propagation or growth, and thereby minimising the stress on the bulk material.
 (ii) The repeated application of the cutting tip to the product applies a local fatiguing effect which reduces significantly the overall force required to break the bonds of the bulk material.
(iii) In conventional cutting the blade has to compress the bulk material to allow a gap the width of the blade to pass through and this applies a tensile rupturing force at the crack tip. With ultrasonic cutting the whole blade moves or vibrates continuously as it stretches and contracts. This very high frequency movement effectively reduces the coefficient of friction to a very low level, enabling the blade to slide more easily through the bulk material.

1.2.1.2 Metal Forming

This is a rather specialised application of ultrasonics in which the circular die used for tube drawing (or extrusion) is radially vibrated. The vibrations provide an easier passage of the material through the die thus permitting a greater diameter reduction with each pass. It is also claimed that the surface finish produced using this technique is better than that obtained using conventional cold drawing techniques.

1.3   Applications of Power Ultrasound through Cavitation

There are very few references to ultrasound in chemistry from about 1955 to 1970; then in 1970 a major renaissance in the subject began to occur, which then accelerated. This revival of interest is undoubtedly due to the more general availability of commercial ultrasonic equipment. In the 1960s the ultrasonic cleaning bath began to make its appearance in metallurgy and chemical laboratories and in this period biology and biochemistry laboratories also began using ultrasonic cell disruptors on a regular basis. The next major reviews came in the late 1980s [6, 7].

Almost all of the technologies associated with cleaning and chemical processing depend upon the phenomenon of acoustic cavitation. Like any sound wave, ultrasound is propagated via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form. It is the fate of these cavities when they collapse in succeeding compression cycles which generates the energy for chemical and mechanical effects (Figure 1.2). This is a remarkable phenomenon induced throughout the liquid at ultrasonic frequencies that is, 20 kHz or above. In aqueous systems each cavitation bubble acts as a localised 'hotspot' generating temperatures of about 4000 K and pressures in excess of 100 MPa. The implosion happens with a collision density of 1.5 kg cm^{-2} and pressure gradients of 2 TPa cm^{-1}, with lifetimes shorter than 0.1 µs and cooling rates above 10^{10} K s^{-1} are involved.
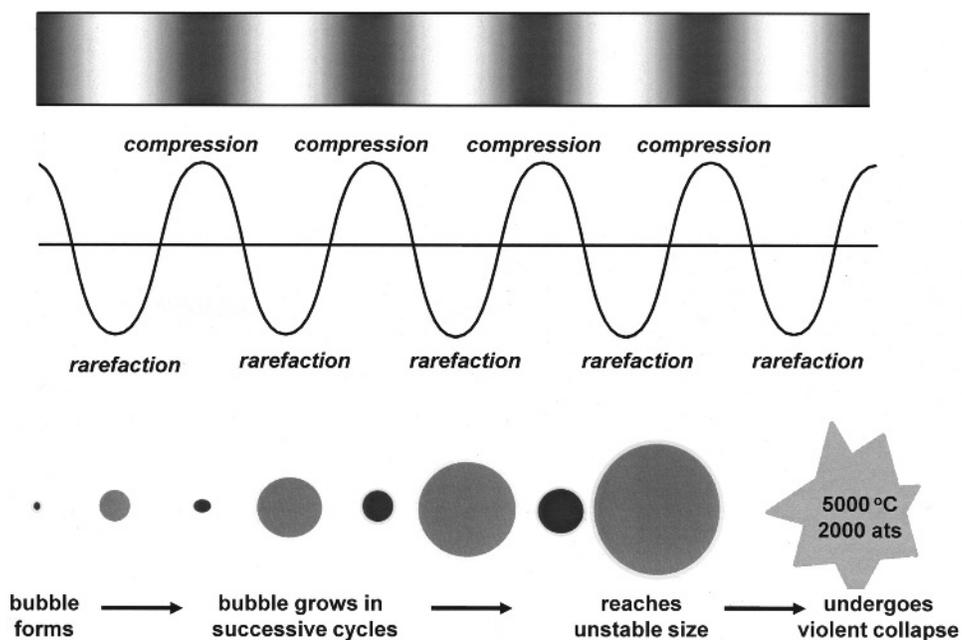

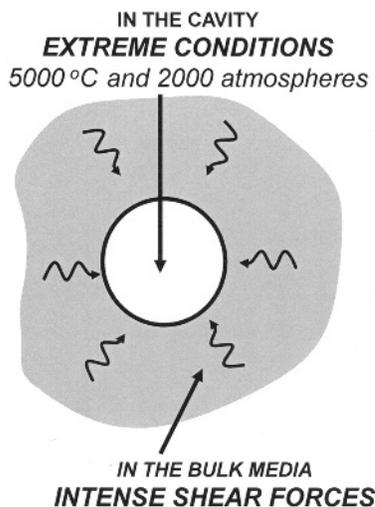*Figure 1.2*   *Sinusoidal wave form and bubble collapse.*

Figure 1.3 *Cavitation collapse in a homogeneous medium.*

1.3.1   Homogeneous Reactions

The mechanical and chemical effects of the collapsing bubble will be felt in two distinct regions: (a) within the bubble itself, which can be thought of as a high pressure and high temperature microreactor, and (b) in the immediate vicinity of the bubble where the shockwave produced on collapse will create enormous shear forces (Figure 1.3).

The cavitation bubble does not enclose a vacuum – it contains vapour from the solvent or any volatile reagent in the solution. Under the extreme conditions generated on collapse of the bubble the molecules in these vapours suffer fragmentation to generate reactive species of the radical or carbene type. The sonochemical decomposition of water into radicals is important in a number of applications. In environmental remediation the hydroxyl radical is a key species in the decomposition of chemical contaminants because it is an extremely strong oxidant and can attack aromatic compounds. Radicals can also attack and kill bacterial cells in sonochemical sterilisation. The generation of radicals can also be used to initiate emulsion polymerisation in aqueous systems, thus avoiding the use of chemical initiators.

1.3.2   Heterogeneous Reactions Involving a Solid/Liquid Interface

When the acoustic cavitation bubble collapses close to or on a solid surface it can only do so asymmetrically due to the surface, which leads to a microjet of liquid being directed towards the surface of the material at speeds of up to 200 m s^{-1} (Figure 1.4). This effect is equivalent to high pressure jetting and is the reason why ultrasound is used for cleaning. The jets can be sufficiently powerful to cause pitting of the surface (erosion). It can also serve to activate solid catalysts and increase mass and heat transfer to the surface by disruption of the interfacial boundary layers. It is primarily as a result of this jet that almost any
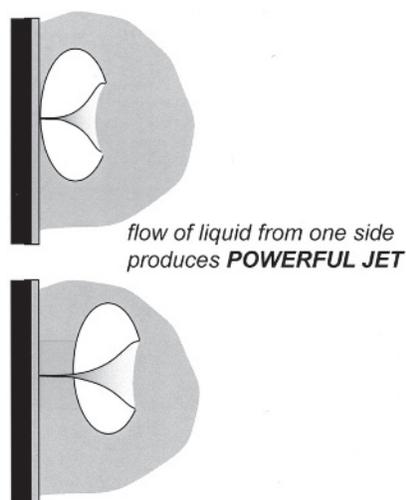
*flow of liquid from one side
produces **POWERFUL JET***

Figure 1.4   *Cavitation collapse near to a surface.*

electrochemical process can be improved by the application of power ultrasound, a field of research which has now become known as **sonoelectrochemistry**.

Cavitation in powder dispersions can cause deaggregation and fragmentation, which can increase the surface area available for reaction and provide efficient mixing.

1.3.3   Heterogeneous Liquid/Liquid Reactions

In any system involving immiscible liquids, cavitation bubble collapse at or near the interface between the two liquids will cause disruption and mixing – resulting in the formation of very fine emulsions. In chemistry such emulsions provide enormous interfacial contact areas between immiscible liquids. For this reason it has been used in conjunction with phase transfer catalysis. Ultrasonic emulsification has also been used for many years in the food industry for the production of tomato sauce, mayonnaise and other similar blended items. Emulsification also has an important role in the plastics industry because a significant proportion of synthetic polymers (over 50% of elastomers) are produced industrially by emulsion polymerisation.

1.4   Electrochemistry

In its simplest form electrochemistry is a study of reactions that take place as the result of applying an electrochemical potential to a chemical system. Electrochemical reactions take place at the interface between an electrode and the electrolyte solution. They involve the transfer of electrons between the electrode surface and the electrolyte or species in solution together with associated chemicals reaction(s) (see Figure 1.5).
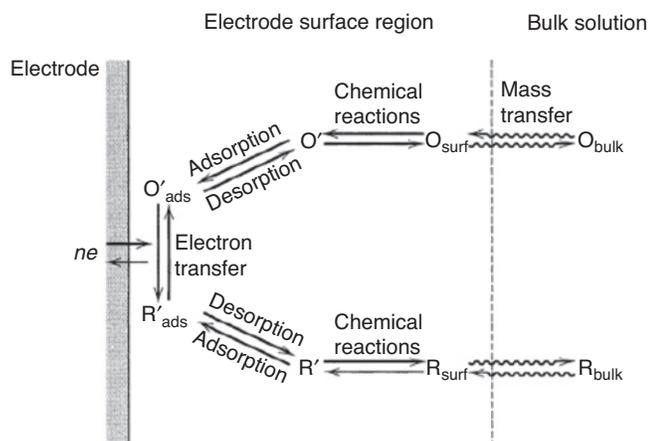
Figure 1.5 *Scheme of the electrochemical processes on the electrode surface.*

1.5 Sonoelectrochemistry – The Application of Ultrasound in Electrochemistry

Sonoelectrochemistry is the coupling of ultrasonic radiation to an electrochemical system. The first application of ultrasound in an electrochemical process dates back to the 1930s and the work of Moriguchi [8] who showed that under sonication water electrolysis using a platinum electrode took place at lower voltages and faster rates than under normal (silent) conditions. In succeeding years research in this field was carried out mainly by metallurgists [9] who were concerned with improving the efficiency of electroplating and the quality of the deposits. However, the term 'sonoelectrochemistry' did not appear in print until 1990 [10].

It might be thought that the effects of ultrasonic irradiation upon an electrochemical process would be limited solely to considerations of the heterogeneous system involving the electrode surface and the electrolyte layer close to this surface, but this is not entirely true. Homogeneous processes that take place in the bulk solution must also be taken into account since the electroactive species in the bulk solution can suffer reactions under the extreme conditions generated during the cavitational collapse and new mechanisms of reaction can arise [11]. In addition, if the electrolyte consists of immiscible liquids then sonication will generate and maintain a very fine emulsion.

The benefits of sonoelectrochemistry have been reported for a number of processes, including electrosynthesis, electroanalysis, bioelectrochemistry, the synthesis of conducting polymers, electroplating, nanomaterial preparation and electrocatalysis [10, 11].

The particular advantages which accrue from the use of ultrasound in electrochemistry include:

(i) degassing at the electrode surface,
(ii) disruption of the diffusion layer, which reduces depletion of electroactive species,
(iii) improved mass transport of ions across the double layer,
(iv) continuous cleaning and activation of the electrode surfaces.

All of these effects combine to provide enhanced yield and improved electrical efficiency.

Given the remarkable effects recorded in the early years of the study of sonoelectrochemistry, it is perhaps surprising that the subject took so long to become accepted. This is almost certainly due to the complexity of the processes induced by ultrasound and the high sensitivity of the results to the experimental conditions such as cell geometry, electrode position and electrode–ultrasound emitter distance as well as the effects of the ultrasonic parameters themselves, such as acoustic power and frequency [12]. However, in recent years, the development of new electrochemical and sonochemical equipment has encouraged a resurgence of this technology and new applications are being developed [13, 14].

There is particular interest in the applications of ultrasound to electrochemistry as a means of making such processes more environmentally friendly. This includes the minimisation of waste and the replacement of toxic components, for example, alternatives to mercury electrodes, and the reduction or replacement of chemical additives. Sonoelectrochemistry can also be used for pollutant degradation and remediation, and to provide more efficient sensors for the detection of various species in water and in the atmosphere.

1.5.1   Ultrasonic Factors that Influence Sonoelectrochemistry

When the ultrasound field intensity is above the cavitation threshold, the collapse of the bubbles is also associated with the formation of shock waves [15] and microflows [16] among other phenomena [17]. In this section the mechanisms that impinge directly on electrochemistry as a result of cavitation will be considered.

1.5.1.1   Acoustic Streaming

When an acoustic wave travels through a medium, part of its energy will be absorbed inducing circular flow in the electrolyte. This phenomena is known as acoustic streaming [17]. Acoustic streaming can occur in three different regions [18]:

  (i) in the bulk solution the pattern is as shown in Figure 1.6(a).
 (ii) on the surface of solids for example, the reactor walls as shown in Figure 1.6(b);
(iii) at the boundary layer as shown in Figure 1.6(c).

The strength of acoustic streaming is directly proportional to the ultrasonic intensity, the attenuation coefficient of the medium and the surface area of ultrasonic emitter, and is inversely proportional to the bulk viscosity of the electrolyte and the speed of sound in the medium [18].

Acoustic streaming can reach parts of the electrolyte away from the direct influence of the ultrasonic emitter because the liquid driven by the radiation pressure can move away from this region [19]. Thus an increase in mass transfer can be observed even when the working electrode is located outside the volume directly affected by high intensity ultrasound [20].

The main effect of the acoustic streaming is to promote the movement of the solution, enhancing mass transfer of electroactive compounds to the electrode surface, and to reduce the diffusion boundary layer [11, 20].

1.5.1.2   Turbulent Flow

The movement of the cavitational bubbles under the influence of the ultrasound field can cause a chaotic and disorderly movement of the solution, giving rise to a turbulent flow. The levels of turbulence are high near to the emitting surface and decrease rapidly with
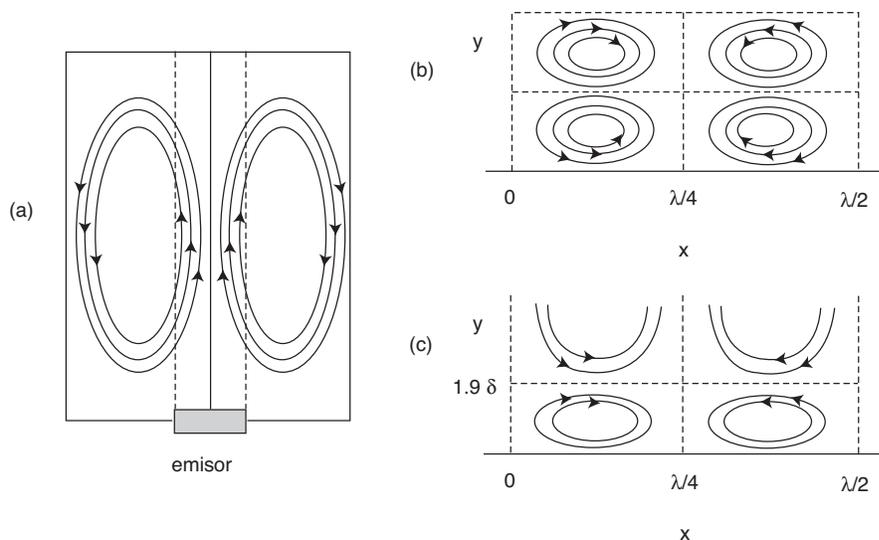
Figure 1.6 *Typical flow patterns of acoustic streaming. Reprinted with permission from Journal of Sound and Vibration, Acoustic Streaming by Sir James Lighthill, 61, 3, 391–418 Copyright (1978) Elsevier Ltd.*

increasing distance from it [21]. Turbulent flow is effective in improving mass transport processes within the solution and at the electrode surface and thus it can cause similar effects to acoustic streaming.

1.5.1.3   Microjets

Microjets are formed at any surface dipped in a liquid when the liquid is subjected to acoustic cavitation (see Section 1.3.2) [22]. If the surface is an electrode and collapse takes place close to the surface the liquid jet will directly impinge upon it, as shown in Figure 1.7 [23].

The formation of the jet and its shape was predicted theoretically by Plesset and Chapman [24] and subsequently confirmed through experimental observation by Lauterborn and Bolle [25]. These studies showed that bubbles that collapsed close to a surface do not remain spherical and so the final temperatures and pressures reached after collapse will be lower in comparison with the values reached during the symmetrical collapse of a bubble in the bulk solution.

Bubbles close to the electrode surface will also give rise to microstreaming (see Section 1.5.1.1) [26]. The combined effects of microjets and microstreaming contribute to the enhanced mass transport of electroactive compounds to the electrode. However, there are two other effects – electrode cleaning and surface activation. These effects will prevent fouling of the electrode surface and can also improve any electrodeposition processes [27].

1.5.1.4   Emission of Shock Waves

There is one more mechanical effect arising from cavitation in addition to shear forces and jetting in the bulk liquid and that is a shock wave generated in the last stages of the violent
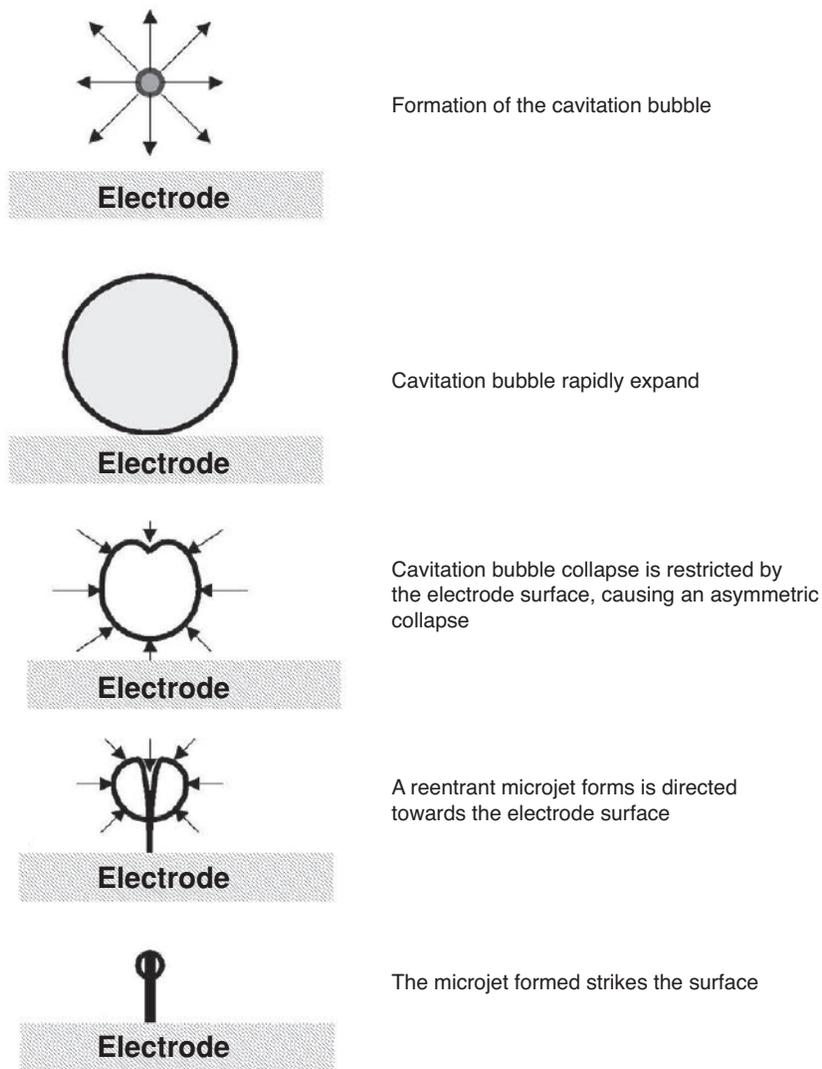
Formation of the cavitation bubble

Cavitation bubble rapidly expand

Cavitation bubble collapse is restricted by the electrode surface, causing an asymmetric collapse

A reentrant microjet forms is directed towards the electrode surface

The microjet formed strikes the surface

Figure 1.7 *Schematic diagram of the cavitating bubble implosion sequence at or near the electrode surface. The arrows indicate fluid pressure.*

collapse [28]. The attenuation of this pressure wave is rapid and so effects on the electrode surface will only take place when the collapse occurs close to it.

1.5.1.5   *Chemical Effects*

In addition to the acoustic effects above, which are mechanical in nature, there will also be sonochemical effects (see Section 1.3). In any liquid medium highly reactive radicals can be formed by the homolytic cleavage of any vapour contained in the cavitation bubble during the bubble's collapse. The nature of these radicals will depend on the solvent used

and the presence of any dissolved gases. In aqueous media and in the presence of oxygen, radicals such as $HO^{\bullet}$, $HO_2^{\bullet}$ and $O^{\bullet}$ have been detected [29].

Sonochemical effects [30–32] associated with the generation of radicals from the sonolysis of the electrolyte have been observed in several electrochemical process, for example, the electrodeposition of lead dioxide on glassy carbon [33] and the oxidation of phenol [34]. However, the influence of chemical effects in sonoelectrochemistry has been relatively little studied in comparison with the physical effects referred to above.

1.6 Examples of the Effect of Ultrasound on Electrochemical Processes under Mass Transport Conditions

The behaviour of simple electrochemistry redox agents such as Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ [30] and Cr^{3+}/Cr^{4+} in aqueous media and ferrocene/ferrocinium in acetonitrile [11, 35] has been studied under the influence of an ultrasonic field. All of these processes exhibit a fast quasi-reversible electron transfer so that the electrode kinetics is considered to be under mass transport control.

Figure 1.8(a) shows the cyclic voltammogram for the electrochemical behaviour of ferrocene on a platinum electrode [35]. This curve presents the typical characteristic behaviour for a reversible one-electron transfer process. Figure 1.8(b) shows the cyclic voltammogram obtained under ultrasonic radiation at 20 kHz with 50 W cm^{-2} directed at the electrode surface with a horn electrode at a distance of 40 mm. Significant changes can be observed as a result of sonication. The mass transport is increased considerably, as evidenced by the greater current density in comparison with the peak current seen under silent conditions,
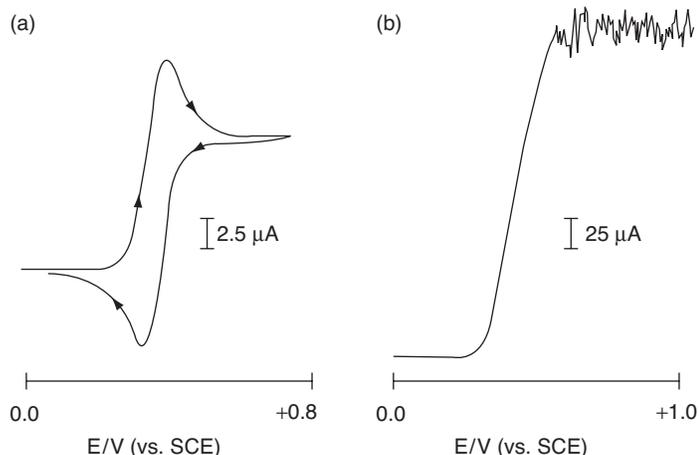

Figure 1.8 *Cyclic voltammograms for the oxidation of 2 mM ferrocene in acetonitrile + 0.1 M NBu$_4$ClO$_4$, platinum electrode (2 mm diameter), 20 mV s^{-1} (a) silent conditions and (b) under 20 kHz, 50 W cm^{-2}, 40 mm electrode–horn distance. Reprinted with permission from Electrochimica Acta, Dual activation: coupling ultrasound to electrochemistry—an overview by R. G. Compton et al., 42, 19, 2919–2927 Copyright (1997) Elsevier Ltd.*
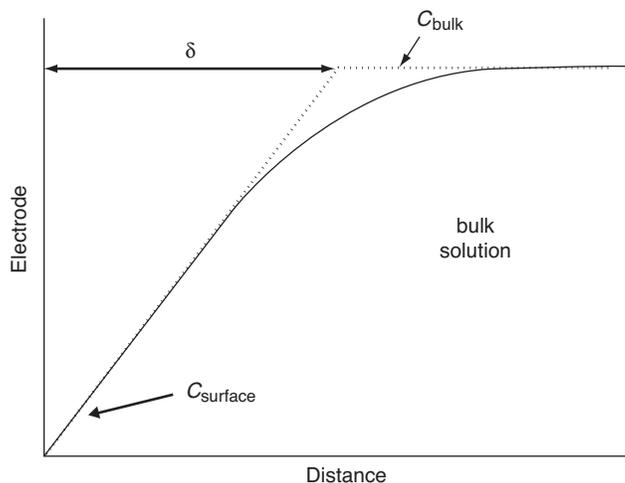
Figure 1.9 *Schematic diagram of the electrode–solution interface according to the Nernst diffusion layer model.*

and also the voltammetric response is qualitatively changed [11, 12]. The typical reversible cyclic voltammogram observed under silent conditions is transformed into a sigmoidal shape indicative of a constant rate of transport of the electroactive species to the electrode surface resulting in a sustained steady current.

The voltametric curve obtained under ultrasonic radiation can be further analysed using the Nernst diffusion layer model [11]. According to this model, the electrolyte can be divided into two zones (Figure 1.9). The closest region to the electrode surface with thickness δ is named the Nernst diffusion layer where it is assumed that there is a totally stagnant layer and thereby diffusion is the only mode of mass transport. In the region outside the Nernst diffusion layer, strong convection occurs and the concentration of all species can be considered to be constant. This model gives an approximate description of the mass transport processes at the electrode–solution boundary assuming a laminar sublayer close to the surface and an approximately linear concentration gradient across a thin layer close to the electrode surface.

The limiting current density (j_{lim}) based on this model is given by Equation (1.1):

$$j_{lim} = \frac{nFD(C_{bulk} - C_{surface})}{\delta} \tag{1.1}$$

where j_{lim} is the limiting current density of the electrochemical process, n is the number of transferred electrons, F is the Faraday constant, D is the diffusion coefficient, C_{bulk} and $C_{surface}$ are the concentration in the bulk solution and in the surface respectively, and δ is the diffusion layer thickness. According to Equation (1.1) the limiting current density increases when diffusion layer thickness decreases.

Marken *et al*. [36] reported that under extreme conditions the minimum diffusion layer achievable in aqueous solution is as thin as 0.7 µm. The limiting currents for the oxidation of ferrocene in the presence of an ultrasonic field was found to increase with increasing
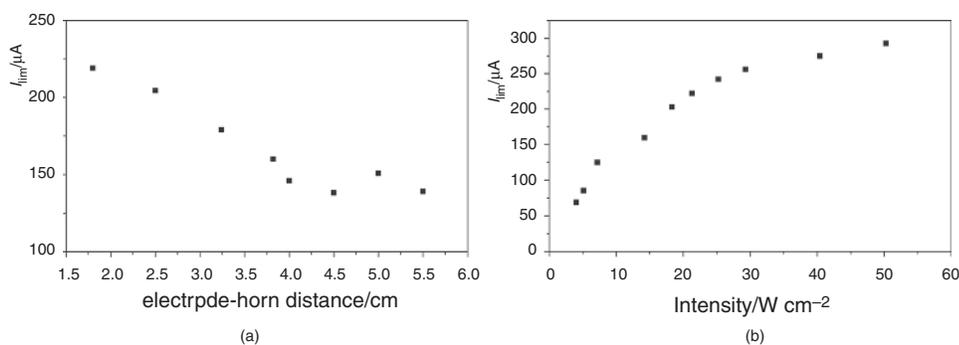
Figure 1.10 *Limiting currents for the oxidation of 2 mM ferrocene in acetonitrile + 0.1 M NBu₄ClO₄, platinum electrode (2 mm diameter), 20 kHz, (a) effect of the electrode surface–ultrasound horn distance and (b) effect of the ultrasonic intensity. Reprinted with permission from Electrochimica Acta, Dual activation: coupling ultrasound to electrochemistry— an overview by R. G. Compton et al., 42, 19, 2919–2927 Copyright (1997) Elsevier Ltd.*

ultrasonic intensity and with decreasing distance between the ultrasonic horn electrode [37], as shown in Figure 1.10. Subsequent studies using other redox couples and a range of ultrasonic configurations produced similar results [11, 38].

In summary, it has been shown that ultrasonic radiation enhances mass transport of electroactive materials to the electrode surface. It has been demonstrated that this enhancement is dependent upon the geometry of the ultrasonic horn relative to the electrode surface.

1.7   Experimental Methods for Sonoelectrochemistry

1.7.1   Cell Construction

A number of experimental arrangements have been used for the introduction of ultrasound into an electrochemical system. The most simple of these is to immerse a conventional electrochemistry cell directly in the water of an ultrasonic bath [11]. This is shown in Figure 1.11 and, in order to maximise the energy transfer of energy from the bath into the electrolyte, the cell should have a flat and thin bottom. Spherical containers are not as good since they will reduce energy transfer through some refection of the acoustic waves [22]. Other workers [39, 40] have used the whole ultrasonic bath as the electrochemical cell by placing the electrodes directly into the bath containing the electrolyte.

Using the simple experimental set-up of an immersed electrochemistry cell, the power transmitted inside is only between 1 and 5 W cm^{-2} and the results obtained depend on the position of the cell within the bath. In addition, the electrodes will interfere with and deflect the acoustic wave and cause an uneven distribution of the ultrasound field [41]. As a general rule it is essential, when using a bath as the source of ultrasound, that all of the operational parameters must be fixed in the experiments otherwise the reproducibility of results will be poor [42]. However, despite these disadvantages, a number of studies have been carried out using this configuration [35] including polymerisation reactions and metal electroplating.
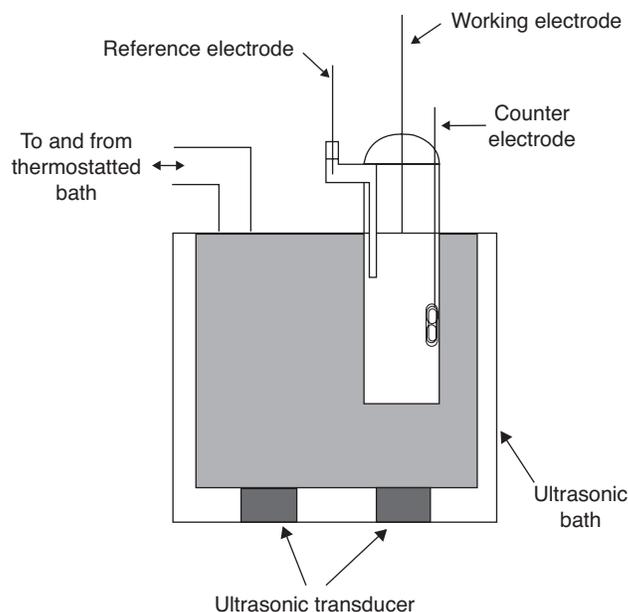
Figure 1.11 *Electrochemical cell dipped in an ultrasonic bath. Reprinted with permission from [33] Copyright (1998) Royal Society of Chemistry.*

A method by which ultrasound can be introduced directly into an electrochemical system is by using an ultrasonic probe dipped into it. An ultrasonic probe consists of a transducer driving an acoustic horn which transmits the vibrational energy to its tip and, in the most used configuration, where both the electrodes and the probe are immersed in the electrolyte solution with the horn tip facing the working electrode at a known distance [43]. This arrangement allows the ultrasonic waves to be directed onto the electrode surface and provides more efficient power control in comparison with the ultrasonic bath. An example of a thermostatted cell with the ultrasonic horn inserted centrally, from the top and opposite the working electrode, is shown in Figure 1.12. This sonoelectrochemistry arrangement allows the ultrasonic intensity and the distance between horn and electrode to be varied [11].

The ultrasonic probe system has several advantages over an ultrasonic bath for sonoelectrochemistry, in particular the fact that the acoustic power applied can be several hundred times higher. This can be applied directly to the electrochemical system and can be controlled by both the amplitude of vibration of the tip and the electrode to probe tip distance. This arrangement does, however, have a few limitations, such as:

(i) Erosion of the horn tip, releasing metal particles (usually titanium alloy) into the system.
(ii) Temperature control due to the heating effect of the horn.
(iii) The need for bipotentiostat control due to the presence of the metal tip of the ultrasound system in direct contact with the electrochemical system [11].
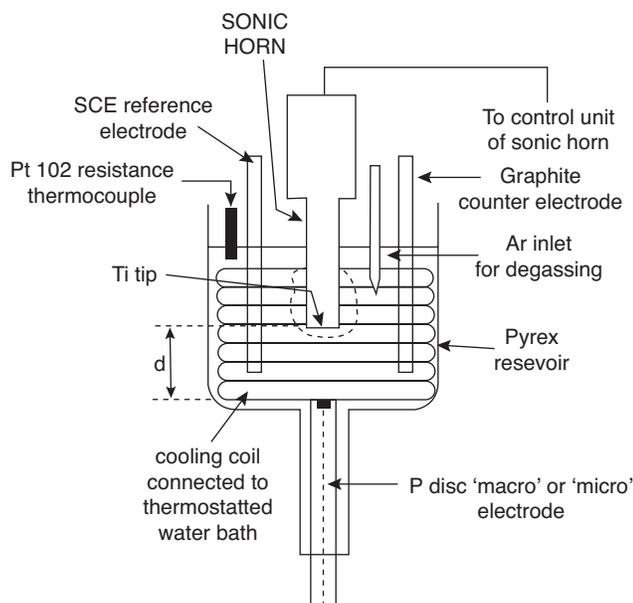
Figure 1.12   *Diagram showing an experimental set-up using an ultrasonic horn in sonoelectrochemistry experiments. Reprinted with permission from Electrochimica Acta, Electrode processes at the surfaces of sonotrodes by R. G. Compton et al., 41, 2, 315–320 Copyright (1996) Elsevier Ltd.*

Another configuration for a sonoelectrochemical cell is to use the horn itself as the working electrode and was first introduced by Reisse *et al*. [44]. Such an electrode is referred to as a sonotrode (or sonoelectrode) [11]. Subsequently the sonotrode system involving consecutive pulses of electrolysis for deposition and ultrasound to release the deposit has been used in the preparation of nanopowders [13]. Figure 1.13 shows the experimental set-up used when a titanium probe (20 kHz) acts both as a cathode and an ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface at the bottom of the horn and the immersed cylindrical part into the electrolyte is covered by an isolating plastic jacket. The ultrasound probe is connected to a generator and a potentiostat using a pulse driver.

Some sonoelectrochemistry arrangements using flow system have also been reported [34, 45].

1.7.2   Stability of the Electrodes Under Sonication

The action of microjets from the collapse of cavitational bubbles on an electrode surface can have both beneficial and deleterious effects. Certainly it can activate the surface and improve the performance of the electrodes by cleaning [10] but it can also damage the electrode surface through erosion [46]. The erosion process can change the surface area of the electrode and so the hardness of the electrode material becomes an important consideration.
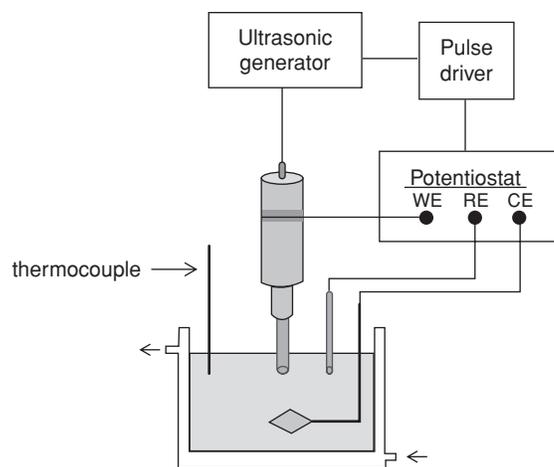
Figure 1.13   *Sonoelectrochemistry set-up used in the production of nanopowders (WE = working electrode, RE = reference electrode and CE = auxiliary electrode).*

Madigan *et al*. [48] reported a study relating to the effects of sonication on common electrodes surfaces at low frequencies (20–30 kHz), including both metals and non-metals [47], analysing the surface after ultrasonic treatment sonication by scanning electron microscopy. Applying an ultrasonic irradiation of 475 W at 20 kHz for 120 s and using 1 mm electrode surface–ultrasound horn distance, non-metals such as glassy carbon and Ebonex were severely pitted in aqueous media. By contrast, metals such as Pt, Au, W and Pd remained largely undamaged and no appreciable surface roughening was observed under the same experimental conditions.

Compton *et al*. [46] investigated the influence of ultrasonic irradiation on the erosion and roughening of Pt and Al, by means of *in situ* AC impedance spectroscopy together with subsequent atomic force microscopy characterisation of the sonicated surfaces. This study was carried out applying 60 W cm^{-2} of ultrasonic intensity at 20 kHz and the electrode was placed 35 mm away. The surface of these electrodic materials was roughed after sonication in 0.1 M TBAP/acetonitrile solution even after an exposure time as short as 120 s. This work corroborated the suggestion that electrode surface roughness increased with increased exposure time and reduced horn–electrode distance.

Several analyses about the effects of an ultrasound field on the surface of a glassy carbon electrode have been reported in the literature [33, 47]. When glassy carbon electrodes were sonicated in water using high intensity (475 W) and very short distance (2 mm) a dramatic change of the electrode surface by pitting was noticeable; by contrast, however, surface roughness did not change appreciably when sonication was carried out in an organic solvent such as dioxane [47]. The explanation for this lies in the difference in cavitation collapse energy between the two solvents. Marken *et al*. analysed the surface state of glassy carbon electrodes immersed in 0.1 M NaOH [48], applying an ultrasonic intensity of 30 W cm^{-2} at 20 kHz and for 1 cm electrode surface–horn distance, no detectable damage was observed after 30 minutes of sonication. Later work [33] carried out with an ultrasound

bath at 30 kHz applying 100 W with the glassy carbon electrodes 6 cm from the transducer showed that the surface of the electrode did not exhibit any signs of superficial pitting or damage after 20 minutes of sonication.

Electrodes made from boron-doped diamond have been widely used in sonoelectrochemistry [49], especially in sonoelectroanalytical applications [50], due to its attractive properties including a wide potential window, low background currents and high resistance to electrode fouling. These electrodes exhibit remarkable resistance to etching and are mechanically stable in sonoelectrochemical applications.

In summary, it has been shown that ultrasound can damage the electrode surface and that the extent of damage depends on the electrode material, intensity of sonication, the distance between the electrode and the source of ultrasound and the duration of the experiment. In electrochemical work it is important that the electrode surface remains undamaged throughout the experiment and this is an even more critical criterion in sonoelectrochemistry where cavitation damage is a possibility and must be avoided. For this reason, it is important to ascertain whether there is any surface damage to the electrodes during sonication in order to make sure that the results are reproducible and quantitative.

1.7.3   Some Applications of Sonoelectrochemistry

Table 1.2 summarises a range of examples of applications of sonoelectrochemistry and some of these will be treated in more depth in the following chapters of this book.

1.7.3.1   *Electro- and Electroless Deposition*

The benefits of the application of an ultrasound field to electrodeposition processes are well established and it has been widely used. Several researchers have demonstrated that employing ultrasound in electroplating baths enhances the deposition rate and the quality of the deposit, increasing thickness, hardness and brightness of the deposited films. Several metallic deposits such as silver oxide [68], silver [66] and tungsten [69], together with bioactive calcium phosphate coating [70] and CdSe film semiconductors [71], have been obtained under ultrasound.

Studies have also been made on the influence of ultrasonic irradiation on the electroless plating of nickel [57], copper [72] and cobalt [73].

1.7.3.2   *Electroanalysis*

Several studies have reported the use of ultrasound for the electroanalytical determination of metals [74] and organic compounds [75] using stripping techniques on different types of electrode and in various complex matrices. For example Banks *et al*. [76] reported the deposition and detection of cadmium using boron-doped diamond electrodes with the aid of anodic stripping with square wave voltammetry in water. The detection limit was 2.5×10^{-8} M in silent conditions and in the presence of ultrasound the detection limit was improved to 3.9×10^{-9} M. The improvement in the detection limit reflected ultrasonically enhanced mass transport of the electroactive species to the electrode surface during the deposition process.

Table 1.2   *Examples of applications of sonoelectrochemistry.*

	Advantages over silent conditions	Examples
Sonoelectroorganic synthesis	Changes the product yield and the selectivity Increases current efficiency Lower voltage applied Avoids electrode fouling	Electroreduction of benzophenone [51] and acrylonitrile [52] Electrooxidation of diacetone-*L*-sorbose [53]
Sonoelectroanalysis	Limiting currents increase due to increased mass transport and electrode surface passivation is prevented	Vitamin C analysis [54] Determination of manganese [55]
Electrodeposition and electroless	Uniform deposits with superior quality are obtained Increases deposit hardness and brightness Decreases of the internal stress and the grain size of the deposit	Electrodeposition of copper [56] and lead [40] Deposition of nickel by electroless [57] Aniline polymerisation [58]
Production of nanomaterials	Avoids the use of reducing agents and surfactants Allows the use of water as a solvent Size of the nanoparticles can be adjusted by varying the operating parameters (ultrasonic power, current density, deposition potential and the ultrasonic vs electrochemical pulse times)	Synthesis of CdSe nanotubes [59] Synthesis of copper [60], platinum [61] and gold nanoparticles [62]
Environmental protection	Enhances mass transport of the pollutant to the electrode surface Avoids electrode fouling Possibility of new paths of degradation	Water disinfection [63] Dye [64] and organochlorine compound degradation [65] Recovery of silver [66] Cyanide degradation [67]

1.7.3.3   Environmental Protection

The application of sonoelectrochemistry to the protection of the environment is an emerging field of research that has been applied successfully for the degradation of a range of important contaminants in water [34, 64, 65]. This technology can be used in combination with other methods including biological treatment, ozonation, photolysis and Fenton processes [77] in order to achieve synergistic effects and reduce the energy cost of the treatment [14].

Sonoelectrochemistry has several advantages over more conventional technologies for the removal of contamination in that it can be carried out under milder conditions, at room temperature and without the need for additional chemical treatment.

1.7.3.4   Electrosynthesis

The benefits of the application of ultrasound to electroorganic synthesis includes activation of the electrode surface, increased yield and the possibility of alteration in the mechanistic pathway together with changed product distribution [53]. A well-known example of product selectivity change induced by sonication is the Kolbe reaction for oxidation of carboxylate anions to hydrocarbons [10].

1.7.3.5   Nanomaterials

Currently the synthesis of nanomaterials is one of the most active fields of research in sonoelectrochemistry [13]. Pulsed sonoelectrochemical techniques [78] have been employed to produce numerous pure metals [79, 80], alloys [81], semiconductors [82] and polymer nanoparticles [83]. The particular attributes of metal powders obtained using this technology are that they are produced in a very finely divided state with high surface area, high chemical purity and with an average particle size of 100 nm [84].

References

(1) Wood, R.W. and Loomis, A.L. (1927) The physical and biological effects of high frequency sound waves of great intensity. *Philos. Mag.*, **4**, 417–436.

(2) Richards, W.T. and Loomis, A.L. (1927) The chemical effects of high frequency sound waves I. A preliminary survey. *J. Am. Chem. Soc.*, **49**, 3086–3100.

(3) Richards, W.T. (1929) The chemical effects of high frequency sound waves II. A study of emulsifying action. *J. Am. Chem. Soc.*, **51**, 1724–1729.

(4) Weissler, A. (1948) Ultrasonics in chemistry. *J. Chem. Educ.*, **25**, 28–30.

(5) Neppiras, E.A. (1972) Macrosonics in industry 1. Introduction. *Ultrasonics*, **10**, 9–13.

(6) Lorimer, J.P. and Mason, T.J. (1987) Sonochemistry Part 1 – The physical aspects. *Chem. Soc. Rev.*, **16**, 239–274.

(7) Lindley, J. and Mason, T.J. (1987) Sonochemistry Part 2 – Synthetic applications. *Chem. Soc. Rev.*, **16**, 275–311.

(8) Moriguchi, N. (1934) The effect of supersonic waves on chemical phenomena (III). The effect on the concentration polarization. *J. Chem. Soc. Jpn.*, **55**, 749–750.

(9) Walker, R. (1990) Ultrasound and electroplating. *Chemistry in Britain*, **26**, 251–254.

(10) Mason, T.J., Lorimer, J.P. and Walton, D.J. (1990) Sonoelectrochemistry. *Ultrasonics*, **28**, 333–337.

(11) Compton, R.G., Eklund, J.C. and Marken, F. (1997) Sonoelectrochemical Processes: A review. *Electroanalysis*, **9**, 509–522.

(12) Compton, R.G., Eklund, J.C., Marken, F., Rebbitt, T.O., Akkermans, R.P. and Waller, D.N. (1997) Dual activation: coupling ultrasound to electrochemistry – an overview. *Electrochim. Acta*, **42**, 2919–2927.

(13) Sáez, V. and Mason, T.J. (2009) Sonoelectrochemical synthesis of nanoparticles. *Molecules*, **14**, 4284–4299.

(14) González-García, J., Esclapez, M.D., Bonete, P., Vargas Hernández, Y., GaeteGarretón, L. and Sáez, V. (2010) Current topics on sonoelectrochemistry. *Ultrasonics*, **50**, 318–322.

(15) Birkin, P.R., Offin, D.G., Joseph, P.F. and Leighton, T.G. (2005) Cavitation, shock waves and the invasive nature of sonoelectrochemistry. *J. Phys. Chem. B*, **109**, 16997–17005.

(16) Klima, J. and Bernard, C. (1999) Sonoassisted electrooxidative polymerisation of salicylic acid: Role of acoustic streaming and microjetting. *J. Electroanal. Chem.*, **462**, 181–186.

(17) Leighton, T.G. (1994) *The Acoustic Bubble*, Academic Press, London.
(18) Frenkel, V., Gurka, R., Liberzon, A., Shavit, U. and Kimmel, E. (2001) Preliminary investigations of ultrasound induced acoustic streaming using a particle image velocimetry. *Ultrasonics*, **39**, 153–156.
(19) Lighthill, S.J. (1978) Acoustic streaming. *J. Sound Vibration*, **61**, 391–418.
(20) Klima, J. (2011) Application of ultrasound in electrochemistry. An overview of mechanisms and design of experimental arrangement. *Ultrasonics*, **51**, 202–209.
(21) Kumar, A., Kumaresan, T., Pandit, A.B. and Joshi, J.B. (2006) Characterization of flow phenomena induced by ultrasonic horn. *Chem. Eng. Sci.*, **61**, 7410–7420.
(22) Mason, T.J. (1999) *Sonochemistry*, Oxford University Press, New York.
(23) Lauterborn, W. (1982) Cavitation bubble dynamics – New tools for an intricate problem. *Appl. Sci. Res.*, **38**, 165–178.
(24) Plesset, M.S. and Chapman, R.B. (1971) Collapse of an initially spherical vapour cavity in the neighbourhood of a solid boundary. *J. Fluid Mech.*, **47**, 283–290.
(25) Lauterborn, W. and Bolle, H. (1975) Experimental investigations of cavitation-bubble collapse in the neighbourhood of a solid boundary. *J. Fluid Mech.*, **72**, 391–399.
(26) Elder, S.A. (1959) Cavitation microstreaming. *J. Acoust. Soc. Am.*, **31**, 54–64.
(27) Mason, T.J. (1989) *Sonochemistry: The Uses of Ultrasound in Chemistry*, Royal Society of Chemistry, Cambridge, UK.
(28) Rayleigh, L. (1917) On the pressure developed in a liquid during the collapse of a spherical cavity. *Philos. Mag.*, **34**, 94–98.
(29) Riesz, P. and Kondo, T. (1992) Free radical formation induced by ultrasound and its biological implications. *Free Rad. Biol. Med.*, **13**, 247–270.
(30) Suslick, K.S. and Doktycz, S.J. (1990) *Advances in Sonochemistry*, Vol. **1** (ed. T.J. Mason), JAI Press, London.
(31) Sáez, V., Frías-Ferrer, A., Iniesta, J., González-García, J., Aldaz, A. and Riera, E. (2005) Characterization of a 20 kHz sonoreactor. Part II: Analysis of chemical effects by classical and electrochemical methods. *Ultrason. Sonochem.*, **12**, 67–72.
(32) Marchante, E., Lana-Villarreal, T., Sáez, V., González-García, J. and Gomez, R. (2009) Sonopotential: A new concept in electrochemistry. *Chem. Commun.*, **27**, 4127–4129.
(33) González-García, J., Iniesta, J., Aldaz, A. and Montiel, V. (1998) Effects of ultrasound on the electrodeposition of lead dioxide on glassy carbon electrodes. *New J. Chem.*, **22**, 343–347.
(34) Trabelsi, F., Ait-Lyazidi, H., Ratsimba, B., Wilhelm, A.M., Delmas, H., Fabre, P.-L. and Berlan, J. (1996) Oxidation of phenol in wastewater by sonoelectrochemistry. *Chem. Eng. Sci.*, **51**, 1857–1865.
(35) Walton, D.J., Phull, S.S., Chyla, A., Lorimer, J.P., Mason, T.J., Burke, L.D., Murphy, M., Compton, R.G., Eklund, J.C. and Page, S.D. (1995) Sonovoltammetry at platinum electrodes: surface phenomena and mass transport processes. *J. Appl. Electrochem.*, **25**, 1083–1090.
(36) Marken, F., Akkermans, R.P. and Compton, R.G. (1996) Voltammetry in the presence of ultrasound: the limit of acoustic streaming induced diffusion layer thinning and the effect of solvent viscosity. *J. Electroanal. Chem.*, **415**, 55–63.
(37) Compton, R.G., Eklund, J.C., Page, S.D., Mason, T.J. and Walton, D.J. (1996) Voltammetry in the presence of ultrasound: mass transport effects. *J. Appl. Electrochem.*, **26**, 775–784.
(38) Kumbhat, S. (2000) Potentialities of power ultrasound in electrochemistry: An overview. *Bull. Electrochem.*, **16**, 29–32.
(39) Walton, D.J., Burke, L.D. and Murphy, M.M. (1997) Sonoelectrochemistry: Chlorine, hydrogen and oxygen evolution at platinised platinum. *Electrochim. Acta*, **41**, 2747–2751.
(40) Agullo, E., González-García, J., Exposito, E., Montiel, V. and Aldaz, A. (1999) Influence of an ultrasonic field on lead electrodeposition on copper using a fuoroboric bath. *New J. Chem.*, **23**, 95–101.

(41) Brett, C. (2008) *Sonoelectrochemistry. Piezoelectric Transducers and Applications* (ed. A. Arnau), Springer-Verlag, Berlin Heidelberg, Germany.

(42) Reisse, J., Vandercammen, J., Yang, D.H., Broeckaert, L., Caulier, T., Fabre, O., Maerschalk, C., Lepoint, Th. and Mullie, F. (1992) *Current Trends in Sonochemistry* (ed. G.J. Price), Royal Society of Chemistry, Cambridge.

(43) González-García, J. (2010) *Sonoelectrochemical Synthesis of Materials. Theoretical and Experimental Sonochemistry involving Inorganic Systems* (eds M. Ashokkumar and A. Kumar), M/S Springer, UK.

(44) Reisse, J., Francois, H., Vandercammen, J., Fabre, O., Kirsch-de Mesmaeker, A., Maerschalk, C. and Delplancke, J.L. (1994) Sonoelectrochemistry in aqueous electrolyte: A new type of sonoelectroreactor. *Electrochim. Acta*, **39**, 37–39.

(45) Esclapez, M.D., Sáez, V., Milán-Yáñez, D., Tudela, I., Louisnard, O. and González-García, J. (2010) Sonoelectrochemical treatment of water polluted with trichloroacetic acid: From sono-voltammetry to pre-pilot plant scale. *Ultrason. Sonochem.*, **17**, 1010–1020.

(46) Compton, R.G., Eklund, J.C., Page, S.D., Sanders, G.H.W. and Booth, J. (1994) Voltammetry in the presence of ultrasound. sonovoltammetry and surface effects. *J. Phys. Chem.*, **98**, 12410–12414.

(47) Madigan, N.A., Hagan, C.R.S., Zhang, H. and Coury, L.A. Jr. (1996) Effects of sonication on electrode surfaces and metal particles. *Ultrason. Sonochem.*, **3**, S239–S247.

(48) Marken, F., Kumbhat, S., Sanders, G.H.W. and Compton, R.G. (1996) Voltammetry in the presence of ultrasound: surface and solution processes in the sonovoltammetric reduction of nitrobenzene at glassy carbon and gold electrodes. *J. Electroanal. Chem.*, **414**, 95–105.

(49) Sáez, V., González-García, J., Kulandainathan, M.A. and Marken, F. (2007) Electro-deposition and stripping of catalytically active ion metal nanoparticles at boron-doped diamond electrodes. *Electrochem. Commun.*, **9**, 1127–1133.

(50) Compton, R.G., Hardcastle, J.L. and del Campo, J. (2007) *Sonoelectroanalysis: Applications. Encyclopedia of Electrochemistry*, Wiley-VCH Verlag GmbH & Co.

(51) Atobe, M., Tonoi, T. and Nonaka, T. (2002) Ultrasonic effects on electroorganic processes. 21. A limiting current study on electroreduction of benzophenone in the presence of a proton donor. *Ultrason. Sonochem.*, **9**, 71–77.

(52) Atobe, M., Sasahira, M. and Nonaka, T. (2000) Ultrasonic effects on electroorganic processes: Part 17. Product selectivity control in cathodic reduction of acrylonitrile. *Ultrason. Sonochem.*, **7**, 103–107.

(53) Cognet, P., Wilhelm, A.M., Delmas, H., Ait Lyazidi, H. and Fabre, P.L. (2000) Ultrasound in organic electrosynthesis. *Ultrason. Sonochem*, **7**, 163–167.

(54) Akkermans, R.P., Wu, M. and Compton, R.G. (1998) A comparison between pulsed sono-voltammetry and low power laser activated voltammetry for the electroanalysis of ascorbic acid in a commercial fruit drink. *Electroanalysis*, **10**, 814–820.

(55) Saterlay, A.J., Foord, J.S. and Compton, R.G. (1999) Sono-cathodic stripping voltammetry of manganese at a polished boron-doped diamond electrode: Application to the determination of manganese in instant tea. *Analyst*, **124**, 1791–1796.

(56) Hong, B., Jiang, C.H. and Wang, X.J. (2008) Effects of ultrasound on morphology of copper electrodeposited on titanium in aqueous and organic solutions. *Mater. Trans.*, **49**, 275–277.

(57) Abyaneh, M.Y., Sterritt, A. and Mason, T.J. (2007) Effects of ultrasonic irradiation on the kinetics of formation, structure, and hardness of electroless nickel deposits. *J. Electrochem. Soc.*, **154**, D467–D472.

(58) Atobe, M., Kaburagi, T. and Nonaka, T. (1999) Ultrasonic effects on electroorganic processes XIII. A role of ultrasonic cavitation in electro-oxidative polymerization of aniline. *Electrochemistry*, **67**, 1114–1117.

(59) Shen, Q., Jiang, L., Miao, J., Hou, W. and Zhu, J.J. (2008) Sonoelectrochemical synthesis of CdSe nanotubes. *Chem. Commun.*, **14**, 1683–1685.

(60) Haas, I., Shanmugam, S. and Gedanken, A. (2006) Pulsed sonoelectrochemical synthesis of size-controlled copper nanoparticles stabilized by Poly(N-vinylpyrrolidone). *J. Phys. Chem. B*, **110**, 16947–6952.

(61) Zin, V., Pollet, B.G. and Dabala, M. (2009) Sonoelectrochemical (20 kHz) production of platinum nanoparticles from aqueous solutions. *Electrochim. Acta*, **54**, 7201–7206.

(62) Aqil, A., Serwas, H., Delplancke, J.L., Jerome, R., Jerome, C. and Canet, L. (2008) Preparation of stable suspensions of gold nanoparticles in water by sonoelectrochemistry. *Ultrason. Sonochem.*, **15**, 1055–1061.

(63) Joyce, E., Mason, T.J., Phull, S.S. and Lorimer, J.P. (2003) The development and evaluation of electrolysis in conjunction with power ultrasound for the disinfection of bacterial suspensions. *Ultrason. Sonochem.*, **10**, 231–234.

(64) Lorimer, J.P., Mason, T.J., Plattes, M. and Phull, S.S. (2000) Dye effluent decolourisation using ultrasonically assisted electro-oxidation. *Ultrason. Sonochem.*, **7**, 237–242.

(65) Sáez, V., Esclapez, M.D., Tudela, I., Bonete, P., Louisnard, O. and González-García, J. (2010) 20 kHz sonoelectrochemical degradation of perchloroethylene in sodium sulphate aqueous media: Influence of the operational variables in batch mode. *J. Hazard. Mater.*, **183**, 648–654.

(66) Pollet, B., Lorimer, J.P., Phull, S.S. and Hihn, J.Y. (2000) Sonoelectrochemical recovery of silver from photographic processing solutions. *Ultrason. Sonochem.*, **7**, 69–76.

(67) Iordache, I., Nechita, M.T., Rosaca, I. and Aelenei, N. (2004) Ultrasound assisted electrochemical degradation of cyanides: Influence of electrode type. *Turkish J. Eng. Env. Sci.*, **28**, 377–380.

(68) Saterlay, A.J., Wilkins, S.J., Goeting, Ch.H., Foord, J.S., Compton, R.G. and Marken, F. (2000) Sonoelectrochemistry at highly boron-doped diamond electrodes: silver oxide deposition and electrocatalysis in the presence of ultrasound. *J. Solid State Electrochem.*, **4**, 383–389.

(69) Goeting, Ch.H., Foord, J.S., Marken, F. and Compton, R.G. (1999) Sonoelectrochemistry at tungsten-supported boron-doped CVD diamond electrodes. *Diam. Relat. Mater.*, **8**, 824–829.

(70) Han, H.M., Phillips, G.J., Mikhalovsky, S.V., FitzGerald, S. and Lloyd, A.W. (2008) Sonoelectrochemical deposition of calcium phosphates on carbon materials: effect of current density. *J. Mater. Sci.: Mater. Med.*, **19**, 1787–1791.

(71) Murali, K.R. and Sasindran, P. (2004) Structural and optical properties of sonoelectrochemically deposited CdSe films. *J. Mater. Sci.*, **39**, 6347–6348.

(72) Touyeras, F., Hihn, J.Y., Bourgoin, X., Jacques, B., Hallez, L. and Branger, V. (2005) Effects of ultrasonic irradiation on the properties of coatings obtaiend by electroless plating and electro plating. *Ultrason. Sonochem.*, **12**, 13–19.

(73) Matsuda, H. and Takano, O. (1993) Influence of ultrasonic radiation on electroless cobalt phosphorus deposition. *Trans. Inst. Met. Finish.*, **71**, 138–141.

(74) Madigan, N.A., Murphy, T.J., Fortune, J.M., Hagan, C.R.S. and Couty, L.A. Jr (1995) Sonochemical stripping voltammetry. *Anal. Chem.*, **67**, 2781–2786.

(75) Hardcastle, J.L., Paterson, C.J. and Compton, R.G. (2001) Biphasic sonoelectroanalysis: Simultaneous extraction from, and determination of vanillin in food flavoring. *Electroanalysis*, **13**, 899–905.

(76) Banks, C.E., Hyde, M.E., Tomcik, P., Jacobs, R. and Compton, R.G. (2004) Cadmium detection via boron-doped diamond electrodes: surfactant inhibited stripping voltammetry. *Talanta*, **62**, 279–286.

(77) Ai, Z., Li, J., Zhang, L. and Lee, S. (2010) Rapid decolorization of azo dyes in aqueous solution by an ultrasound-assisted electrocatalytic oxidation process. *Ultrason. Sonochem.*, **17**, 370–375.

(78) Durant, A., Delplancke, J.-L., Winand, R. and Reisse, J. (1995) A new procedure for the production of highly metal powders by pulsed sonoelectrochemical reduction. *Tetrahedron Lett.*, **36**, 4257–4260.

(79) Aqil, A., Serwas, H., Delplancke, J.L., Jerome, R., Jerome, C. and Canet, L. (2008) Preparation of stable suspensions of gold nanoparticles in water by sonoelectrochemistry. *Ultrason. Sonochem.*, **15**, 1055–1061.

(80) Shen, Q., Jiang, L., Zhang, H., Min, Q., Hou, W. and Zhu, J.J. (2008) Three-dimensional dendritic Pt nanostructures: Sonoelectrochemical synthesis and electrochemical applications. *J. Phys. Chem. C*, **112**, 16385–16392.

(81) Dabala, M., Pollet, B.G., Zin, V., Campadello, E. and Mason, T.J. (2008) Sonoelectrochemical (20 kHz) production of $Co_{65}Fe_{35}$ alloy nanoparticles from Aotani solutions. *J. Appl. Electrochem.*, **38**, 395–402.

(82) Qiu, X., Lou, Y., Samia, A.C.S., Devadoss, A., Burgess, J.D., Dayal, S. and Burda, C. (2005) PbTe Nanorods by sonoelectrochemistry. *Angew. Chem., Int. Ed. Engl.*, **44**, 5855–5857.

(83) Atobe, M., Ishikawa, K., Asami, R. and Fuchigami, T. (2009) Size-controlled synthesis of conducting polymer microspheres by pulsed sonoelectrochemical polymerization. *Angew. Chem., Int. Ed. Engl.*, **48**, 6069–6072.

(84) Reisse, J., Caulier, T., Deckerkheer, C., Fabre, O., Vandercammen, J., Delplancke, J.L. and Winand, R. (1996) Quantitative sonochemistry. *Ultrason. Sonochem.*, **3**, S147–S151.