Acoustoelectrochemistry

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Most readers will be familiar with electrochemistry in its simplest form: the insertion of two electrodes into a solution, and the consequent production of an electrical current between them. This is because an oxidation reaction occurs at one electrode, generating electrons there; and a reduction reaction occurs at the other, depleting electrons. The discharge of a car battery is an obvious example. Similarly, electrochemistry can involve the application of a potential difference (voltage) between the electrodes to bring about chemical reactions at them (such as occurs during the re-charging of a car battery).

However, few readers will be aware that such processes can not only be affected by acoustics, but used to probe a range of acoustical phenomena, ranging from the very subtle (surface waves on liquid/gas interfaces) to the complex (cavitation clouds). This ability makes acoustoelectro-chemistry a candidate to probe power ultrasound fields. In these a great range of phenomenon can occur, many of industrial importance (such as cleaning and erosion). The ability of acoustoelectrochemistry to distinguish one from another, and measure their useful effects, is the topic of this paper.

Figure 1. **Photograph showing a cavitation bubble imploding on the surface of a material. The impinging jet can be clearly seen penetrating the bubble to produce a toroidal shape. Reprinted by kind permission of Professor L A Crum.**

Power ultrasound

Power ultrasound has many industrial applications. These include cleaning, disinfection, welding, soldering, machining, the generation of dispersions, and the production and processing of metals, foods and pharmaceuticals [1,2]. Acoustic pressure amplitudes are generally up to a few bar (1 bar = 100 kPa $\cong$ 194 dB re 20 μPa; 220 dB re 1 μPa), and whilst frequencies of a few tens of kHz are most usual, some applications use up to 10 MHz. Usually the ultrasound is applied within liquid.

Most of these industrial processes using power ultrasound rely on the associated phenomena of cavitation. Cavitation itself can be thought of as the generation and collapse of bubbles within a liquid. These collapses can be extremely violent. Even simple calculations, which assume that the gas compresses homogeneously, predict transient high gas temperatures (similar to the surface of the sun, 5000 K) and high pressures (>1 MPa, similar to the pressures found at ocean depths of hundreds of metres)[3].

The incorporation of gas inhomogeneities into the model may increase both by several times [4].

These extreme conditions can produce chemical effects, such as the acceleration of chemical reactions or the production of radical species [5,6]. After reaching minimum size, the bubble re-expands and emits a rebound shock wave. If the bubble wall involutes on collapse, high-speed (100 ms^{-1}) liquid jets can occur *(Figure 1)*. Both rebound shocks and liquid jets can cause mechanical damage *(Figure 2)*. *Figure 3* shows a schematic of bubble growth and collapse and the associated chemical and physical work that can be achieved by each cavitation event.

All these effects, although transient, can be employed to do useful work. *Figure 3* describes three aspects on 'sonochemistry', where acoustics is used to speed up existing reactions or generate new ones, or to activate some interaction between a liquid and surface (such as catalysis).

Sonochemistry is more than just a laboratory phenomenon. One company (L3 Communication ELAC Nautik Gmbh, Kiel Germany) has developed a sonochemical reactor that is designed to treat water effluent. The high intensity sound field produces cavitation, which inactivates micro-organisms, disintegrates cells and breaks up particle clusters. One small plant (16 kW, 40 kHz) is already operational (near Aachen) while a larger plant near Köln (196 kW, 40 kHz), which is designed to inactivate zooplankton, is being installed.

Whilst cavitation erosion in some circumstances (eg. pumps) can be detrimental, it can be beneficial.
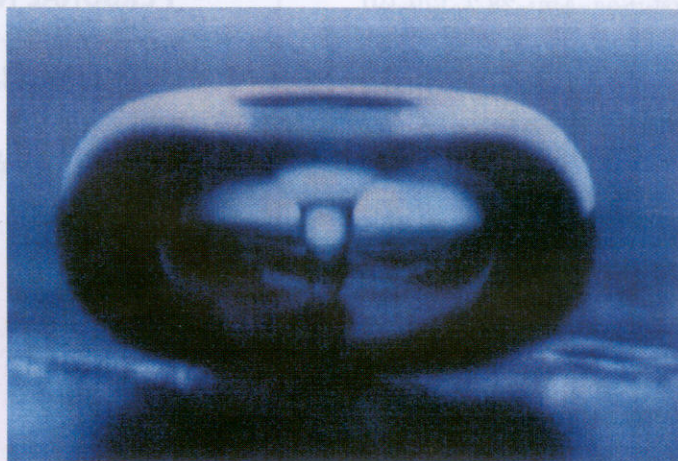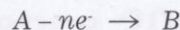

Figure 2. **Picture showing the effect of cavitation induced erosion of an aluminium surface. The aluminium substrate is 2mm in diameter, and was highly polished before immersion in a power ultrasound field.**
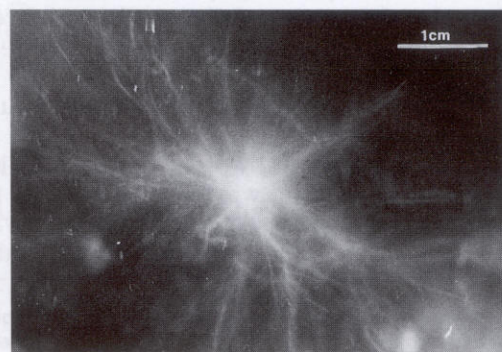
Figure 3. (a) Schematic graph (radius against time) of bubble growth and collapse. (b) The chemical and physical effects of bubble collapse. The boxes show the association between the chemical and physical effects. The orange box shows how gas compression leads to high temperatures, which in turn speed up existing chemical reactions, or generate new ones. The green box shows how the surface damage which results from liquid jets and rebound shocks can clean or erode the surface, or can 'activate' surface-mediated reactions (such as catalysis).

Ultrasonic cleaning is commonplace. It exploits the mechanical damage generated by the shocks and jets associated with bubble collapse. This has the particular advantage that intricate designs can be thoroughly cleaned without the need for complete dismantling of the device.

Because a single ultrasonic field has the potential to generate simultaneously both beneficial and detrimental effects, it is important to be able to monitor these effects. However, the cavitation generated by power ultrasound is almost always complex (*Figure 4*). Within the cavitation cloud, only a proportion of bubbles are likely to produce the effect in question: the others might be ineffective, or might suppress the effect by, for example, scattering sound field [7]. No completely satisfactory way of characterising the cavitation in such clouds has been found.

Acoustoelectrochemistry, the study of the influence of acoustic fields on electrochemical reactions, provides a new and promising opportunity for achieving this goal. Electrochemistry, as its name implies, is a science dedicated to the investigation and facilitation of chemical processes through the application and measurement of an appropriate electrical current. This is usually conducted by ionic species in solution, between two immersed electrodes across which a certain voltage (potential difference) is applied. If we consider a reaction

where a species in solution (*A*) is oxidised at an electrode, it is possible to represent that process as,

$$A - ne^- \rightarrow B$$

where '$-ne^-$' represents the removal of n electrons (e^-) from chemical species *A*, which produces species *B*. In order to maintain charge balance, a reduction process (the addition of electrons) has to occur at the other electrode. The reaction is monitored by recording the current flowing out of (oxidation) or into (reduction) one of the electrodes (termed the working electrode).
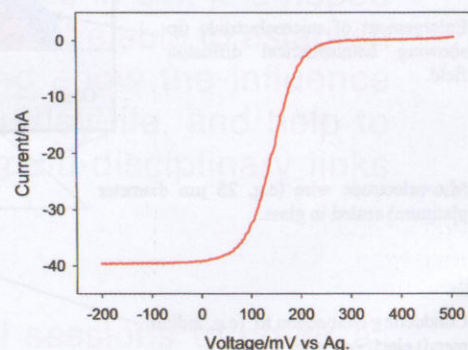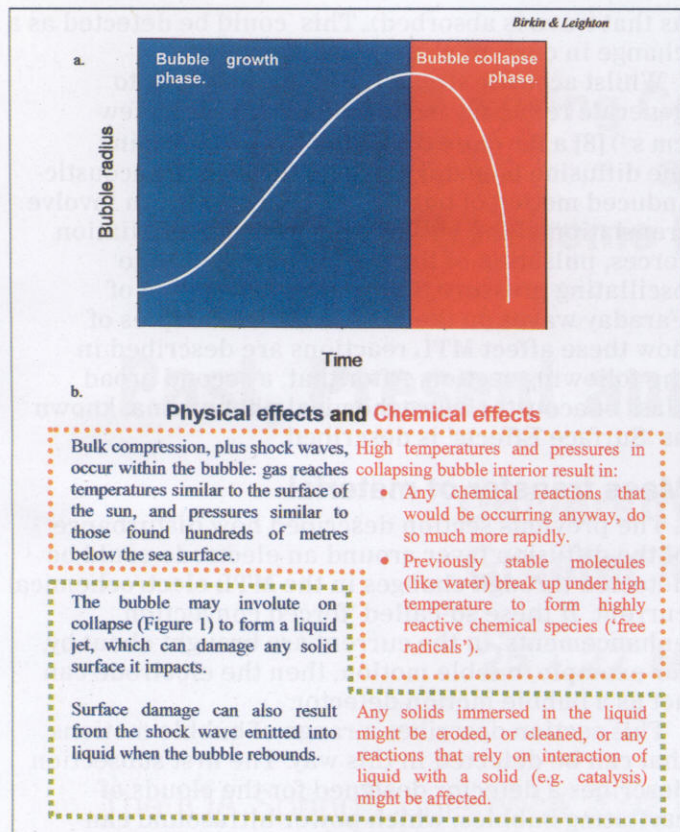
A key measurement is how the current varies in response to changes in the potential applied to the working electrode. This is for two reasons: first, because oxidation or reduction of any particular species requires a critical voltage to be exceeded; second, because the magnitude of the electrical current flow is a direct measure of the rate at which the electrochemical reaction is occurring at the working electrode surface. It is not surprising

Figure 4. Photograph taken in water in a focused 10 kHz sound field (acoustic pressure amplitude at focus is 2.4 bar). The water is 'torn apart' to produce cavitation bubbles. At the focus (centre of picture) is a dense cloud of such bubbles. Cavitation bubbles generated further out from the focus are driven towards it at high speed by acoustic radiation forces, their path giving the appearance of ribbon-like features.

Figure 5. Plot showing the current potential trace recorded for a 25 µm diameter platinum disk microelectrode imbedded in glass. The potential of the working electrode was swept from +0.5 V to –0.2 V at 10 mV s⁻¹. The solution contained a redox active chemical that was reduced (adding electrons) at ca. "+0.2 V vs. Ag". The term 'vs. Ag' represents the use of a silver wire electrode as a reference point to measure electrochemical potentials against. From the figure, this electrochemical reaction requires a voltage of less than about 0.25 V vs. Ag to proceed, and saturates at around 0 V vs. Ag.

therefore, that the most common way of displaying an electrochemical result is to plot the current measured as the voltage applied to the working electrode is varied (*Figure 5*).

There are several ways in which acoustics can affect electrochemical reactions. Most, including the experiments described in this paper, involve bubble

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activity. However, the following thought-experiment is an example of one that does not involve bubble activity.

Consider the class of electrochemical phenomena, which are described as 'mass transfer limited' (MTL). In this case the potential of the working electrode is such that any species arriving at the surface of the electrode is immediately electrochemically consumed (*eg* oxidised). If the liquid around the electrode is stationary, then the rate at which species travel to and from the electrode is usually controlled by diffusion alone. As the reaction progresses in a still solution, a diffusion boundary layer builds up around the electrode. Under these conditions, the population of the chemical species on which the reaction at that electrode is based, becomes partially depleted. Flow in the liquid can disturb this boundary layer and refresh the depleted population there. This enhances the rate of this type of electrochemical reaction, and hence augments the current recorded at the electrode.

One acoustic way of inducing flow around the electrode is through acoustic streaming. Here, the momentum carried by an acoustic wave is transferred to the liquid as that wave is absorbed by the liquid, and so imparts flow (in much the same way as the acoustic energy in a wave causes the liquid to heat up

Figure 6. Diagram showing a schematic representation of a microelectrode. The insert shows the hemispherical diffusion pattern expected under mass transfer limiting (MTL) conditions, the arrows indicating the motion of chemical species within the diffusion boundary layer.
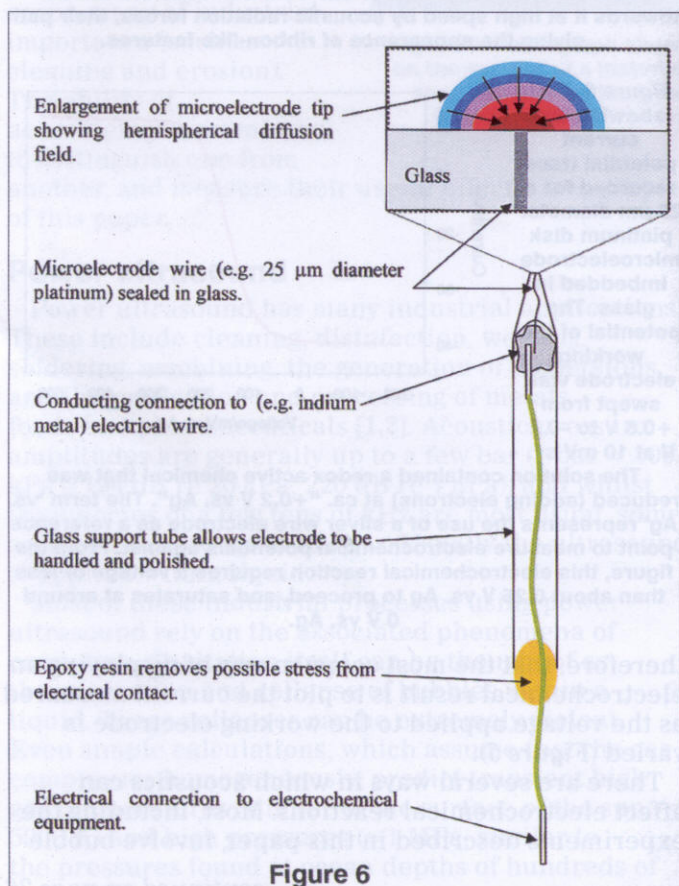

Figure 6

as that wave is absorbed). This could be detected as a change in current at the working electrode.

Whilst acoustic streaming in liquids tends to generate relatively modest flows (of order a few cm s^{-1}) [8] a far more dramatic way of disturbing the diffusion boundary layer is through the acoustic-induced motion of bubbles. Such motions can involve translation of the bubble under acoustic radiation forces, pulsation of the bubble in response to oscillating pressure field, or the generation of Faraday waves on the bubble wall. Examples of how these affect MTL reactions are described in the following section. After that, a second broad class of acoustoelectrochemical phenomena, known as 'Surface Effects' is described.

Mass transfer of material

The previous section described how disturbance of the diffusion layer around an electrode could be detected through changes in the MTL electrochemical current. If these so-called 'forced convection enhancements' in the current are brought about by, for example, bubble motion, then the electrode can act as a bubble motion detector.

This section describes a range of bubble motions that can be detected in this way. The first subsection describes a detector designed for the clouds of cavitating bubbles, which power ultrasound can generate. The second subjection describes detectors designed for less violent bubble activity.

Mass transfer detection in a cavitation cloud

The first sensor detects the short-lived events, which are typical of the sort of power ultrasound fields illustrated in *Figure 4*. As described above, at any one time within any given field, the different bubbles can be exhibiting a wide variety of behaviours. Therefore to obtain an unambiguous signal, one must ensure that the sensor records data from only one bubble at a time. This necessitates high spatial and temporal resolution.

One way of achieving this goal is to employ microelectrodes (electrodes with a critical dimension of less than 50 μm). A typical microelectrode could consist of a 25 μm diameter disk of metal (typically gold or platinum) embedded in an electrical insulator such as glass. *Figure 6* shows a schematic representation of a microelectrode.

If the voltage at this electrode is set to produce MTL conditions, then if the liquid is undisturbed, a steady current is detected. However, these electrodes will detect disturbances in the fluid up to *ca.* 10 radii away from the surface and can be fabricated to dimensions below 1 μm. Clearly this will enable the electrode to have a very small sensing volume within the solution, as required. This fact, coupled with their rapid response time (of ms order), means that microelectrodes can therefore achieve the desired goal, of responding only to motions produced by one bubble at a time, even when deployed in complex cavitation clouds of the type shown in *Figure 4*. Microelectrodes employed in this manner have been able to record [9] cavitation events, which repeat up to 4500 s^{-1}.
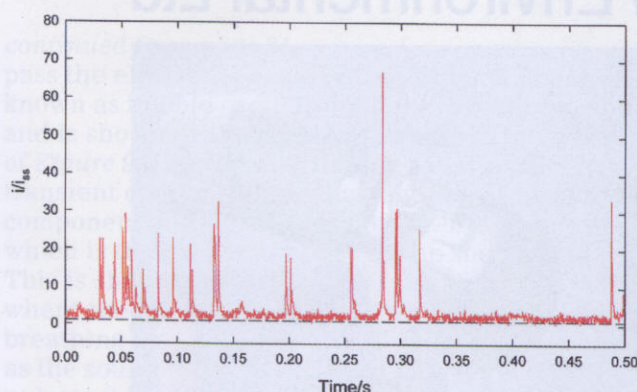
Figure 7. Plot showing the current time trace recorded for a microelectrode held under mass transfer limiting conditions positioned in the cavitation cloud generated from an operating ultrasonic cell disrupter. This axis label 'i/i_{ss}' represents the current recorded normalised to the current in the absence of fluid flow (dashed horizontal line).

Figure 7 shows the current recorded from a microelectrode placed within the cavitation plume of an operating ultrasonic cell disrupter plotted as a function of time [10,11]. The figure shows a series of transient current peaks, each one representing an individual bubble moving the liquid in front of the microelectrode. The area under each peak represents the charge (related to the number of electrons) used up as a consequence of the fluid flow resulting from each of these 'cavitation events', and so gives an absolute measure of the effect of individual bubbles.

There are still, however, ambiguities. A large event, which takes place far from the electrode, could give the same signal as a smaller event, which is close to the electrode. Also, the disturbance of the liquid might result from a number of different possible motions, including bubble pulsation and the rapid bubble translations, which can result from acoustic radiation force effects [12].

This question, of whether a sensor can distinguish between different types of bubble activity, is a key issue. The following subsection illustrates how mass transfer sensors might be designed for the detection of other types of bubble activity, and distinguishes between them.

Mass transfer detection for bubble translation, pulsation, and surface waves

The preceding subsection described a mass transfer detector designed to attempt to monitor individual bubbles in a complex cavitation cloud. This is necessary because of the range of behaviours, which can occur simultaneously. Even so, some ambiguities remain as to what type of bubble activity generated the signal. Therefore this section shows how in principle acoustoelectrochemical techniques can be used to distinguish between different types of bubble motion. Three motions are studied in laboratory circumstances, which facilitate their isolation: the rise of bubbles under buoyancy in the absence of a sound field; the pulsation of bubbles in a sound field; and the acoustic excitation of Faraday waves on the walls of pulsating bubbles.

Figure 8 shows the current transients generated when bubbles, previously injected into a cell through a gas porous material ('frit'), rise under buoyancy and pass close to the microelectrode (the apparatus is shown as an inset in *Figure* 8). The important feature in the current time histories is the number of peaks. Since each peak corresponds to the buoyant passage of a bubble close to the electrode, then as expected the number of peaks tends to increase with gas flow rate.

The results described in *Figure* 8 do not involve any acoustics. The importance of such measures becomes clear when one realises that, by adding an imposed acoustic field to the system shown in *Figure* 8, it could be tuned to monitor the oxygen content in the ocean which results from dissolving air bubbles, a measure of great environmental significance [13].

The contribution to the dissolved oxygen made by bubbles of a specific size could be assessed by exploiting the following effect: if sound of a specific frequency is projected into the region around the electrode, then those bubbles which are of the radius required to resonate at that frequency will, as they
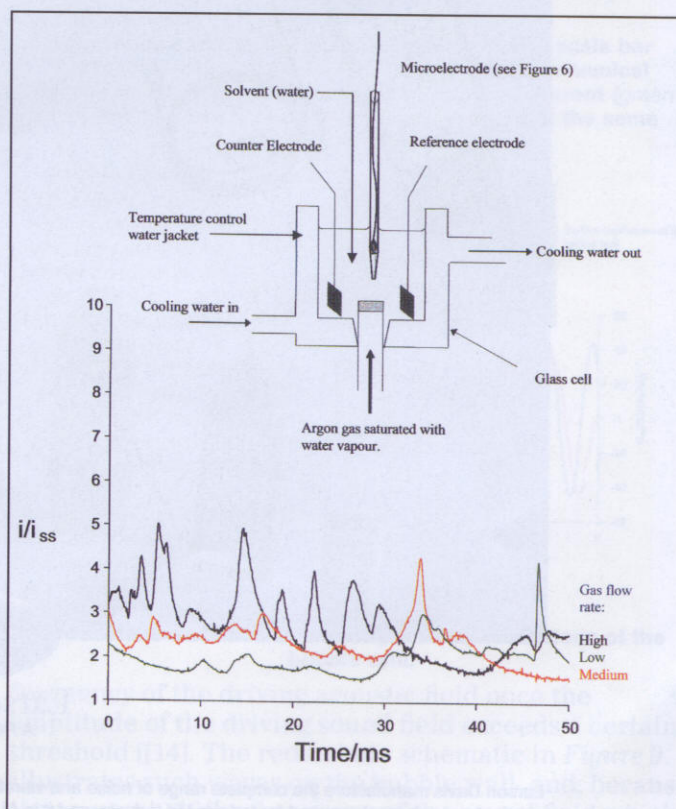
Figure 8. Plot showing the MTL current time trace recorded for a microelectrode, as argon bubbles are injected through a porous injector ('frit') into the solvent (water), which is temperature-controlled by use of water flowing through a jacket. The apparatus is shown in the inset. The buoyant rise of the bubbles disturbs the diffusion layer about the microelectrode, which is detected as peaks in the current i (shown normalised to the steady state current, i_{ss}). Data are displayed for three gas flow rates: High (*black line*, 80 cm³ s⁻¹), Medium (red line, 40 cm³ s⁻¹), and Low (*green line*, 10 cm³ s⁻¹). The two other electrodes allow stable conditions: the 'counter electrode' (which uses a mesh to increase its surface area) supplies an opposite current to that detected at the microelectrode, so as to maintain charge balance in the liquid; the 'reference electrode' provides the stable datum against which electrical potentials are measured.
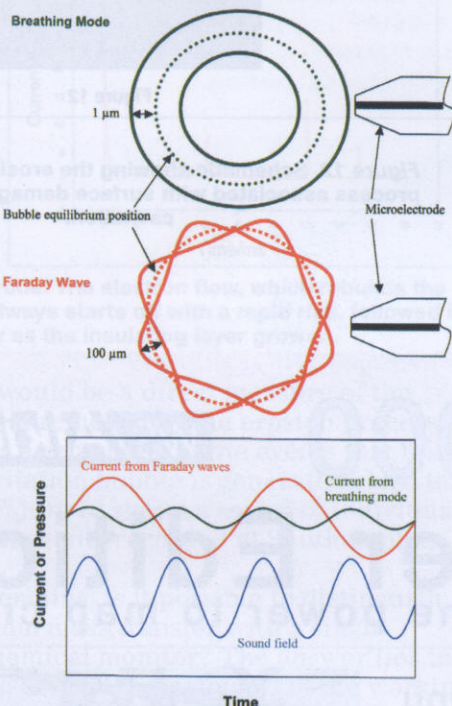
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pass the electrode, be pulsating. Such pulsation is known as bubble oscillation in the 'breathing mode', and is shown by the green schematic at the top of *Figure 9*. Hence superimposed in the current transient caused by their passage would be a current component at the frequency of the 'breathing mode' which is the same frequency as the sound field. This is shown schematically at the base of *Figure 9*, where the microelectrode current resulting from the breathing mode (green) is at the same frequency as the sound field, which drives the bubble to pulsate (blue). Bubbles of other sizes, which were not resonating with the sound field, would exhibit no such modulation.

Such a technique would rely on the ability of resonant bubble pulsation to generate a component in the measured current at the same frequency as the acoustic field. This is demonstrated in *Figure 10*,

Figure 9. The upper part of the plot schematically shows the positions of the bubble wall at equilibrium (dotted line), and at the two extreme displacements, during the oscillatory cycle of: the pulsation (or 'breathing') mode (green); and the mode corresponding to the generation of Faraday waves on the bubble wall (red). Note that the amplitude of wall oscillation for the Faraday wave mode is around 100 times greater than for the pulsation mode in these experiments. The lower graph is a schematic showing the expected current time plots for the two measured modes of oscillation of a bubble irradiated with sound. The *blue line* corresponds to the driving sound field, and is at the same frequency as the current resulting from the pulsation mode (*green line*). The current resulting from the Faraday wave mode is at half this frequency (*red line*).

using a bubble, which is held motionless under a glass rod to remove buoyant rise motion. This assists photography, and keeps the geometry of the bubble fixed with respect to the electrode and the sound source. In the absence of a sound field, the MTL current is steady. However, when exposed to an acoustic field, the bubble begins to pulsate. This induces an oscillating convection of the fluid close to the electrode, detected as a current component at the frequency of the acoustic field (see schematic in *Figure 9* and *Figure 10c*).

Indeed, the system can even detect the Faraday waves on the bubble wall, generated at half the
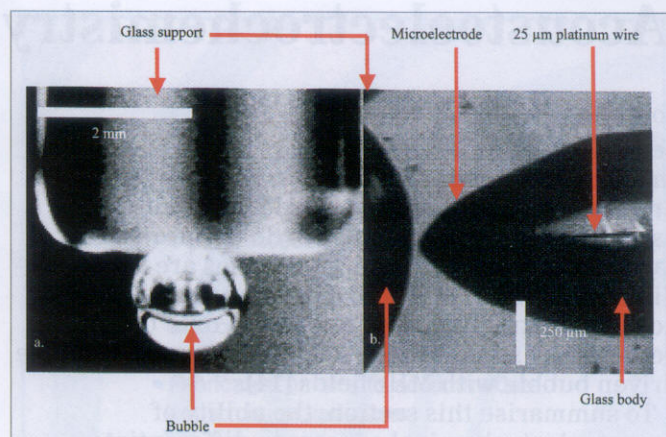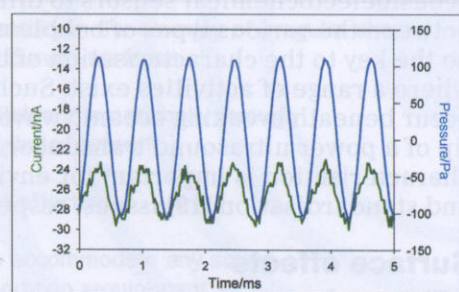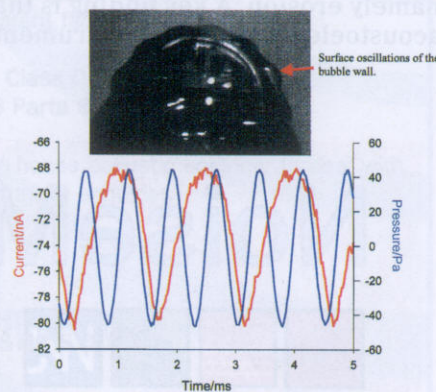

Figure 10. (a) Photograph showing a tethered bubble held beneath a glass rod. The scale bar indicates 2 mm. **(b)** Close up picture of a bubble wall with a microelectrode positioned close to the air/liquid interface. The scale bar represents 250 µm. **(c)** Plot showing an electrochemical measurement of the breathing mode. Here the current (*green line*) and the pressure (*blue line*) signals occur at the same frequency (1.4239 kHz).

Figure 11. Plot showing the current time trace (*red line*) and pressure (*blue line*) recorded in the presence of the bubble. The bubble was driven to oscillate by a 1.3509 kHz sound field. The current time trace demonstrates the electrochemical detection of Faraday waves. The inserted photograph shows a high-speed picture of a oscillating bubble viewed from below. The surface waves can be clearly seen as distortions of the bubble wall.

frequency of the driving acoustic field once the amplitude of the driving sound field exceeds a certain threshold [[14]. The red bubble schematic in *Figure 9* illustrates such waves on the bubble wall, and, because they are at half the frequency of the sound field which drives the bubble, the current shown in the schematic at the base of *Figure 9* (red) is at half the applied acoustic frequency (blue). Successful implementation of this technique is shown in *Figure 11*. Because the wall displacement amplitudes of these Faraday waves (*ca.* 50 microns) is so much greater than that of the pulsation (having micron order), once they are excited the existence of the relevant frequency component (at half the driving frequency) is very clear in the electrode current signal (*Figure 11*).

There is a fascinating post-script to this experiment. Although the amplitude of wall motion associated with Faraday waves exceeds that due to bubble pulsation by

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several orders (*Figure 9*), the acoustic emission from the bubble is dominated by the monopole pulsation emission. The subharmonic multipole emissions associated with Faraday waves do not propagate to distance, and therefore such waves are very difficult to detect acoustically. Prior to acoustoelectrochemistry, this has to date only been achieved by stimulating a complex interaction of the driven bubble with MHz fields [14].

To summarise this section, the ability of acoustoelectochemical sensors to differentiate between the various types of bubble motion may be the key to the characterisation of bubble clouds where a range of activities exist. Such clouds occur beneath breaking oceanic waves, or at the tip of a power ultrasound transducer, where their characterisation is important for environmental [18] and standardisation [19] issues, respectively.

Surface effects

The previous section showed how acoustically-induced bubble effects can affect electrochemically-measured mass transfer. In this section, acoustoelectrochemistry is used to monitor a different, more violent, effect of acoustic cavitation, namely erosion. A key finding is that a single acoustoelectrochemical instrument can be used to
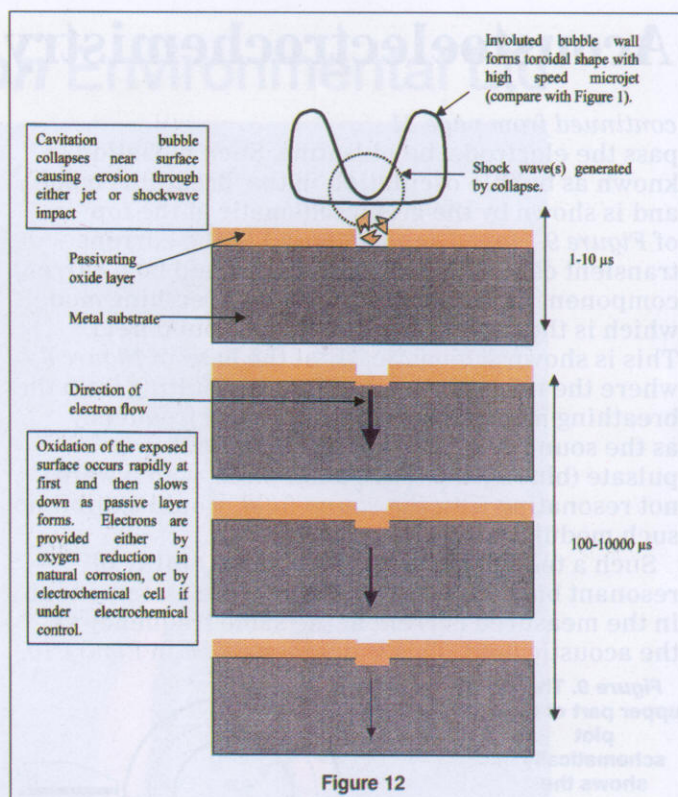

Figure 12. Schematic showing the erosion and corrosion process associated with surface damage as the result of cavitation.

monitor, and distinguish between, mass transfer and erosion when they occur simultaneously.

The ability of cavitation to damage surfaces, through rebound shocks and microjets, was explained at the start of this paper. Most solid surfaces of metals are coated with an oxide layer (eg. rust), produced by the corrosive reaction of the metal with oxygen and water from the surrounding atmosphere or liquid. Cavitation damage can generate small pits in this oxide layer (for example, where the jet impacts the solid), exposing bare metal to the liquid. The subsequent rapid reformation of the oxide layer is an oxidation process ('repassivation'), and results in excess electrons, which in natural corrosion are consumed by oxygen reduction at another site on the metal. However, if the layer were on the exposed surface of a microelectrode, the electrons produced by the reformation of the passive layer would produce a measurable current rather than reduce oxygen. The

Figure 13. Plot showing single current time events recorded for a passivated electrode exposed to transient (collapsing bubbles) cavitation bubbles produced by power ultrasound. Each transient represents an individual cavitation bubble removing part of the surface of the passivated electrode. The electron flow, which rebuilds the passivating layer, always starts off with a rapid rise, followed by decay as the insulating layer grows.
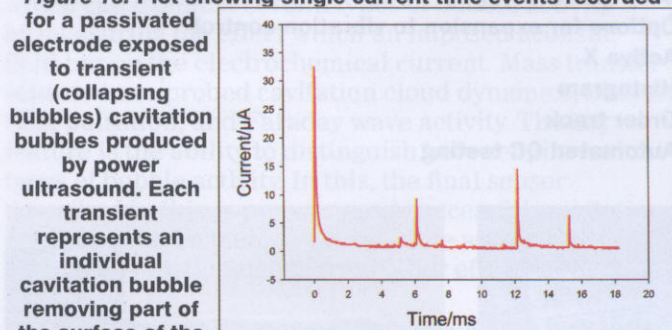
charge involved would be a direct measure of the amount of material removed by the erosion process.

Figure 12 shows a schematic of the events that take place when a cavitation bubble is generated close to a solid surface. *Figure 13* shows a series of individual cavitation erosion events recorded at Southampton [15].

The question remains: is it possible to distinguish erosion events from mass transfer with a single acoustoelectrochemical monitor? The answer lies in the ability both to control the potential of the working electrode, and to exploit the temporal characteristics of the mass transfer and surface erosion sensing techniques. As an example, mass transfer sensors are sensitive to a broad range of phenomena (acoustic streaming, bubble motion and bubble oscillation), while erosion sensors are sensitive to both the jetting and shocks associated with bubble collapse. If a microelectrode is held at a potential required to detect mass transfer, it will be sensitive to the entire range of phenomena that will cause fluid flow. In turn the current time trace would reflect this in recording a large number of events per second. Each of these events would be of the order of ms in duration.

However, the potential of that microelectrode can be changed so that it is insensitive to mass transfer, but rather detects the surface repassivation which immediately follows erosion. It is now a detector only of those bubble collapses, which are capable of causing erosion. In the latter case the current time
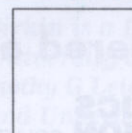
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transients would be less frequent (reflecting the fewer mechanisms responsible for erosion) and of shorter duration (100-10000 μs; *Figure 13*). In both cases the position of the microelectrode need not be changed, and so an accurate idea of both bubble population and type of bubble character could be distinguished [16].

Conclusions

This paper has shown how electrochemical sensors, based on electrodes immersed in liquids, can detect two phenomena; the arrival at the electrode and subsequent reaction of ionic species present in solution (mass transfer); and the reformation of an oxide surface on a metal in response to erosion (repassivation). Both processes can be influenced by acoustically-induced bubble activity. As a result, sensors have been designed which can examine certain types of bubble activity, by measuring the effect which an imposed acoustic field has on the electrochemical current. Mass transfer sensors have probed cavitation cloud dynamics; buoyant rise; pulsation; and Faraday wave activity. The key feature is the ability to distinguish between the various types of bubble activity. In this, the final sensor described in this paper was most successful: cavitation erosion could be monitored real-time and *in situ,* and readily distinguished from other effects of bubble activity.

One might ask: What use is acoustoelectrochemistry? The ability to monitor cavitation erosion *in situ*, and real-time, clearly has potential. BP Amoco estimates that *ca.* $200,000,000 has been spent to replace eroded pipelines and equipment since 1987 [17]. Ocean bubbles have a major role in contributing to the levels of dissolved oxygen, and other gases, in the oceans (more than 1000 million tonnes of atmospheric carbon alone dissolves into the oceans each year) [12]. This has great environmental significance, [18] and acoustoelectrochemical techniques offer a unique opportunity to study this [13].

There is in the UK, and elsewhere, an interest in monitoring bubble activity during ultrasonic cavitation in order to achieve standardisation of power ultrasound instrumentation [19]. In this, electrochemical techniques may play a role in distinguishing between types of cavitation. Other applications, not described in this paper, include analytical chemistry (the measurement of specific chemical compounds), and beneficial mechanical effects on sample pre-treatment [20,21]. Even though cavitation and its applications have enjoyed 90 years of attention from scientists and engineers, it still has the ability to raise new questions and provide us with novel phenomena to study [22]. The new field of acoustoelectrochemistry may help to answer some of these very old questions.

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