Measurement of species flux from a bubble using an acousto-electrochemical technique

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Abstract

An acousto-electrochemical technique is presented which, for the first time, offers the potential for measuring the flux of dissolved species in a liquid resulting from bubbles of a specific chosen size in the population. Laboratory trials are presented, but the device itself was damaged in the surf zone and no data was obtained from the ocean deployment. Nevertheless, the preceding laboratory tests demonstrate the viability of the technique. The device responds to perturbations of the fluid around a small electrode. Three such sources of motion must be characterised if it is to achieve the objective stated above. First, the perturbations resulting form the translatory motions of bubbles in the liquid. To obtain bubble radius resolution in the measurement of mass flux, however, it is necessary to apply to driving ('pump') sound field. Bubbles close to resonance will, in addition to a translatory motion, impart to the liquid a component of mass flux at the pump frequency. This is detected. However to show that this is the result of bubble wall pulsation, and not some other coupling, the amplitude of the pump field is increased until the electrochemical sensor detects Faraday waves on the bubble wall. Not only does this prove the relation between mass flux to bubble wall motion, it provides a second route by which the radius-resolved component of mass flux might be identified. In these preliminary laboratory tests, electrochemical detection of these motions was achieved through the observation of current produced by the reduction of a suitable redox agent present within the liquid phase of the solution employed. Preparations were made to obtain preliminary data from the Hurst Spit 2000 surf zone trial, but the device was damaged by the environment.

1. Introduction

The significance of flux of mass, momentum and energy between the atmosphere and the oceans has been recognised for several decades. The importance of subsurface oceanic bubble populations to the mass flux is known, but quantification is not simple. The ability to measure the mass flux which results from bubbles of any chosen size within a population would greatly increase our ability to test models of the bubble-mediated flux. This paper describes for the first time a technique which, after further development, would be capable of providing this measurement.

The principle of the technique is as follows. Motion within a liquid will distort the diffusion boundary layer about an electrode, and so give rise to an electrical signal which can be use to quantify the molar amount of that species detected by the electrode. Whilst many such processes (e.g. turbulence) can give rise to such time-varying signals, so too can the motion of nearby bubbles. However it is not the translation of such bubbles that is of primary interest. This is because the electrochemical effect of bubble 'fly-by' is relatively insensitive to the bubble size. Of more importance is the fluid motion caused by acoustically-generated motion of a bubble wall. Hence if the region around an electrode is insonified by a single ('pump') frequency, then the pulsation of near-resonant bubbles in the proximity of the electrode will give rise to a component of the time-varying electrical signal which is at the pump frequency. This can then be related to the flux of that species which results from those only those bubbles that are close to resonance. By varying the pump frequency, it is possible in principle to interrogate the bubbly liquid to determine the contributions of bubbles of various sizes to the mass flux. Use of a suitable model, which incorporates the contributions to fluid motion at the pump frequency of both the resonant and off-resonant bubbles, will eventually provide a measurement, resolved for bubble radius, of the mass flux from a population of bubbles across a wide size range.

In this way, this acousto-electrochemical detection is similar to the combination frequency method [1]. Both rely on the excitation of the bubble pulsation through insonification at a 'pump' frequency. However both avoid making measurements of the effect of the bubble motion on the pump sound field, and in doing so avoid the ambiguities which the presence of, for example, large off-resonance bubbles can create [1]. Instead, they both rely on detection of some other signal which is affected by the motion of the bubble wall. In the case of the combination-frequency system, this 'other signal' is the scatter of the high frequency 'imaging' field. In the case of the acousto-electrochemical system, it is the electrochemical reactions which take place at the electrode.

Given the similarities of the two techniques, it is perhaps not unsurprising that one of the first discoveries made using the combination-frequency technique, the detection of Faraday waves on the bubble wall [2, 3], should readily be replicated using the acousto-electrochemical technique. These surface waves occur on the bubble wall with a period of twice that of the pump field [4, 5]. Other acoustic methods, which rely solely on the use of a pump field, are on the whole insensitive to Faraday waves, because the wavelength of the latter are several orders of magnitude smaller than the wavelength of the pump field. The detection of Faraday waves by the acousto-electrochemical technique is described for the first time in this paper.

The importance of a technique for measuring bubble-mediated mass flux, and especially one with the capability to resolve the contributions made by the bubbles of various radii, is not limited to the ocean. The mass flux resulting from the generation and motion of bubbles within industrial processes, for example the chloralkali industry, has been recognised as being important in the overall efficiency of the process. Bubbles produced in this manner are thought to affect the efficiency of the overall system. In many instances the production of bubbles reduces the overall efficiency of the electrochemical system. However, electrochemically generated bubbles are also considered to enhance the transfer of material from the bulk phase of the solution within the cell to the electrode itself. Understandably, considering the scale of these industrial processes the study of bubble population within the cell is extremely important. The motion of electrochemically generated bubbles during their generation and subsequent release from the electrode has been studied intensively to understand the contribution of these processes to the mass transport of material to the electrode surface. In order to understand the mechanisms responsible for the enhancement in mass transfer to the electrodes a number of electrochemical investigations have been reported. Among these studies the work by Tobias *et al.* [8] is noteworthy. These authors used electrochemical generation and electrochemical detection of the effects of bubble release and motion to assess the various aspects of the factors contribution to mass transfer of material to an electrode surface. In order to achieve these measurements Tobias *et al.* [8] employed an array of microelectrodes to electrochemically image the motion of individual bubbles. Microelectrodes are well suited to the study of bubble motion through a liquid. The impact of individual bubbles on the hemispherical diffusion pattern characteristic for microelectrodes of a critical dimension has been reported by a number of authors. The application of microelectrodes and electrochemical techniques enables not only the study of bubble motion but also enables the investigation of higher energy process associated with inertial cavitation. Birkin *et al.*[9] and Leighton *et al.* [10] showed that it was possible to measure the effects of individual cavitation bubbles. These examples of the industrial and environmental impact of bubble phenomena demonstrate the need to improve and quantify the effects of bubbles on both natural and manmade processes.

In this paper, we report here for the first time the development of the acousto-electrochemical technique for the detection of bubble-mediated mass flux in liquids. Since the technique responds to the effect on the dissolved species of motions of the bubble wall, three sources of signal must be characterised if it is to achieve the objective stated above. First, the perturbations resulting form the translatory motions of bubbles in the liquid. These are examined in Sections 2.1 and 3.1, in the so-called ‘fly-by’ tests. However to obtain bubble radius resolution in the measurement of mass flux, it is necessary to introduce a second factor, through the application of a ‘pump’ sound field which will drive bubbles into pulsation. Bubbles close to resonance will, in addition to a translatory motion, impart to the liquid a component of mass flux at the pump frequency. This oscillatory signal is detected, the bubbles being tethered to remove the translatory component in these preliminary tests (Section 3.2). The third component, also detailed in Section 3.2, of the tests exploits the generation of Faraday waves on the bubble wall. These are parametrically excited once the amplitude of wall pulsation (and hence, for a given bubble size, the amplitude of the pump field) exceeds a threshold value [7]. Faraday waves impart, to the oscillatory electrochemical signal generated by the bubble pulsation, a component at the subharmonic of the pump frequency. In these preliminary laboratory tests, electrochemical detection of these motions was achieved through the observation of current produced by the reduction of a suitable redox agent present within the liquid phase of the solution employed. Preparations were made to obtain preliminary data from the Hurst Spit 2000 surf zone trial, but the device was damaged by the extreme conditions in the field.

2. Laboratory tests: Experimental

To develop and test the technique, prior to the Hurst Spit 2000 sea trial [1], a series of three laboratory experiments were undertaken. The fly-by test employed a specific cell (Sections 2.1 and 3.1), whereas the electrochemical detection of bubble pulsation and Faraday waves used tethered bubbles (Section 3.2). Whilst these tests employed specific chemicals for ease of analysis (Section 2.3), the system was adapted to be chemically non-invasive for ocean use (Section 4).

2.1 ‘Fly-by’ apparatus

Figure 1 shows a schematic of the fly-by experimental cell employed to detect the motion of bubbles through the cell. The cell enabled the injection of bubbles from a needle at the base. In addition a hydrophone enabled monitoring of the acoustic emission associated with bubble injection. At the top of the cell a 25 µm diameter platinum microelectrode was positioned within the path of the bubbles directly in front of a Sonitron sound source. A two-electrode arrangement was employed with a homebuilt current follower enabling both high gain (up to 1 x 10^8 V A^{-1}) and low noise acquisitions of the experimental data.

The observation of surface oscillations of the bubble wall was achieved by the development of a novel cell fabricated from a Mylar speaker and Perspex. This enabled sufficient room for a glass rod to support a bubble, a hydrophone, electrodes and visual observation of the phenomena occurring within the cell. Further description of this experimental set-up will be reported elsewhere.

2.2 Associated equipment

That electrochemical data, which required only low temporal resolution, was recorded on a Computer Boards DAS08/16 ADC card. The equipment was interfaced to at PC using a Quick Basic interface program. The results of experiments requiring higher temporal resolution were recorded using a Gould 465 digital oscilloscope. The data was transferred to a PC through a RS 232 cable and commercially available software. A saturated calomel electrode (SCE) or a silver wire were used as a reference electrode were stated. The sound source consisted of a Sonitron piezoelectric transducer driven by a EG&G function generator. A Bruel and Kjear 8103 hydrophone and a Bruel and Kjear 2635 charge amplifier were used to measure and amplify pressure signals where reported. All electrochemical experiments were performed in a Faraday cage in an effort to reduce electrical noise.

2.3 Chemicals

Potassium chloride, KCl (BDH, AnalR) and Ruthenium (III) hexaamine trichloride, $[Ru(NH_3)_6]Cl_3$ (Strem, 99%) were obtained commercially and used without further purification. All solutions were made up from water purified though an Elga Elect 5 water system which produced water with a resistivity above 15 MOhms cm^1.

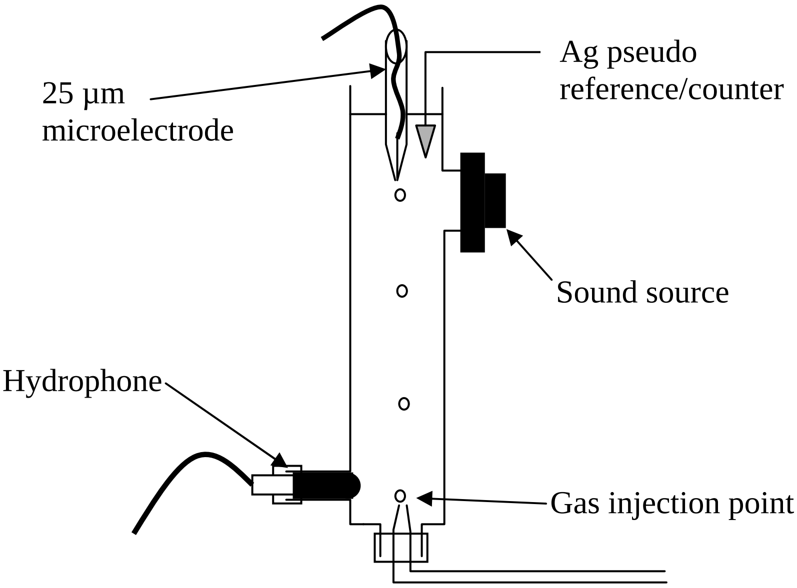

Figure 1. Schematic representation of the 'fly by' cell developed at Southampton. This cell enabled both the acoustic emission associated with bubble injection to be monitored and additional electrochemical data associated with the motion of the injected bubbles close to the electrode surface.

3. Results

3.1 'Fly-by' Experiments

If bubbles driven into oscillation were to pass within close proximity to an electrode surface, the additional mass transfer of the signal would provide a measurement of the effect on dissolved species of bubbles.

As discussed in Section 2.1, the apparatus designed to record such novel data (Figure 1) relies on the injection of bubbles through a needle placed at the base of the water column. The bubbles size is estimated from the passive emissions detected by the hydrophone upon injection (with corrections for the effect of the changing hydrostatic head as the bubble rises). After its passage up the column, the bubble approaches electrode, where the additional mass transfer as the result of bubble motion through the bulk liquid will be detected as a series of current time transients. As bubbles 'fly-by' the electrode, the diffusion layer is perturbed and a transient current spike is produced. Figure 2 shows some initial results of the apparatus showing both the hydrophone and electrochemical signals.

The hydrophone signal (solid line) detects a bubble 'signature' [11] each time one is injected. Eight bubbles are injected at regular intervals, as can be seen by the 1 s hydrophone time series of Figure 2. However the microelectrode signal responds to only one of these (at around 0.2 s). This is because the bubbles need to pass very close (of order 100 microns) to the electrode to cause a signal, making it a good local detector. The paths of the other bubbles in the figure do not result in a sufficiently close passage.

It should be noted that the fly-by cell was fitted with a transducer to supply a pump field to drive the bubbles into pulsation. Examination of that component of the electrochemical signal which is at the pump frequency, is the basis of the principle of obtaining measurements of mass flux resolved for bubble radius. However those tests were not completed prior to writing.

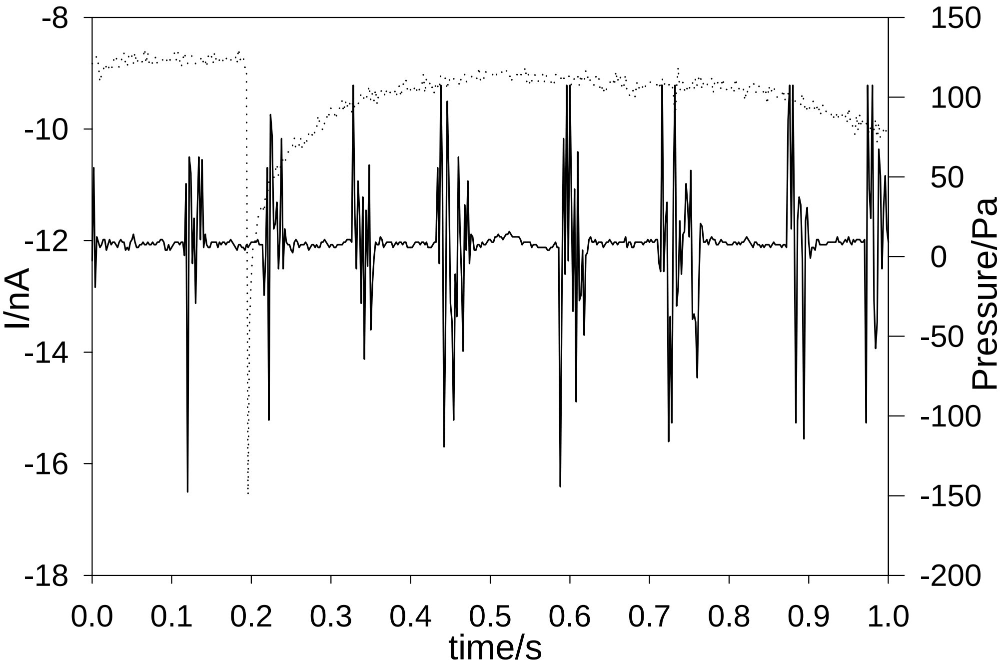

Figure 2. Plots showing the current and pressure signals recorded as a function of time. The electrochemical signal was recorded using a 25μm Pt microelectrode while the pressure was recorded using a hydrophone. The cell contained a solution of an aerobic solution of 0.1 mol dm^{-3} KCl. The potential of the electrode was held at -1.3 V versus Ag wire. The solid line represents the hydrophone response while the dotted line represents the current.

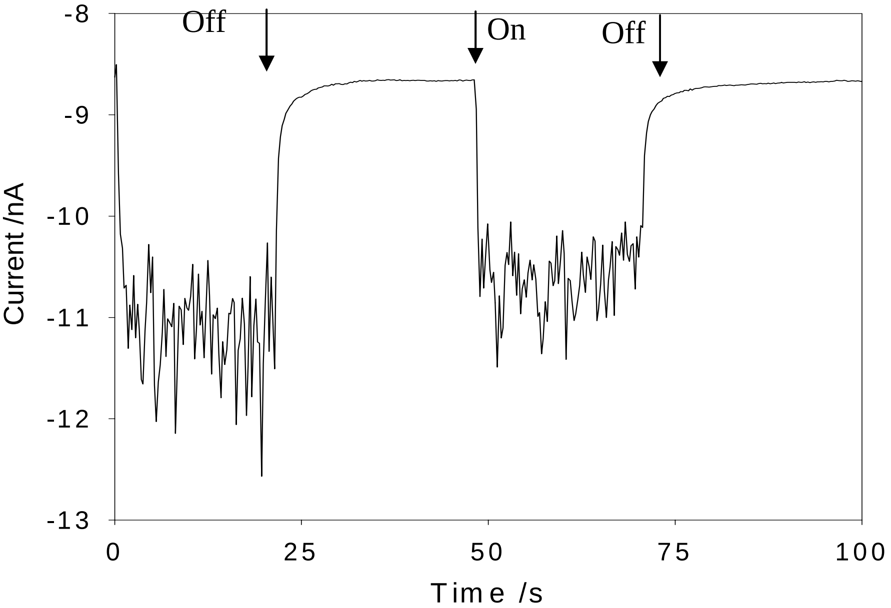

Figure 3. Current time plot obtained for an argon bubble irradiated with sound. The surface motion was detected by a 10 μm diameter Pt microelectrode. The solution contained 5 mmol dm^{-3} [Ru(NH$_3$)$_6$]Cl$_3$ in 0.1 mol dm^{-3} KCl. The solution was initially purged with argon. The potential of the electrode was maintained at –0.6 V vs. SCE. The temperature of the solution was 20-22 ^{o}C. The sound was initially on. The arrows indicate the other times during the experiment where irradiation with sound was terminated or initiated.

3.2 Electrochemical experiments in the presence of a pump field

3.2.1 Experiments with low temporal resolution

Figure 3 shows a low temporal resolution measurement of the effect of bubble oscillation on the mass transfer of a 10 μm diameter Pt microelectrode positioned within close proximity to the wall of an argon bubble. In this experiment the bubble wall held beneath a glass rod (see Figure 5), in a solution contained 5 mmol dm^{-3} [Ru(NH$_3$)$_6$]Cl$_3$ in 0.1 mol dm^{-3} KCl. The microelectrode was held at a potential sufficiently negative to reduce [Ru(NH$_3$)$_6$]$^{3+}$ ions, in this case –0.6 V vs. SCE (saturated calomel reference electrode), at a mass transfer limited steady state. In this experiment the solution had been saturated with argon gas to remove dissolved oxygen, which is also electrochemically active at this potential. In the absence of irradiation of the bubble with sound a steady state current depicting the mass transfer characteristics of the microelectrode under normal stagnant conditions. In this case and under these conditions the steady state current (8.7 nA) implies that the diffusion coefficient of the $[Ru(NH_3)_6]^{3+}$ species was 9 x 10^{-6} cm^2 s^{-1}. This value was calculated from Equation (1):

$$i_{ss} = 4nFaDc \tag{1}$$

where i_{ss} represents the current recorded under mass transfer steady state conditions, n the number of electrons exchanged per molecule of $[Ru(NH_3)_6]^{3+}$ arriving at the surface of the electrode, F Faraday's constant, a the radius of the microelectrode, D the diffusion coefficient of the $[Ru(NH_3)_6]^{3+}$ species within the solution and c the concentration of $[Ru(NH_3)_6]^{3+}$ within the solution employed. The value of D obtained under these conditions is in agreement with the literature quoted values. In the presence of the irradiation of the bubble with sound a clear increase in the steady state current can be seen. This is attributed to the additional mass transfer as the result of convective flow of solution driven by the oscillation of the bubble wall. This noise like nature of the signal is as expected considering the time scale of the experiment and the frequency of bubble oscillation expected from a bubble irradiated at this drive frequency. The enhancement in mass transfer can be calculated from (2).

$$i = nFAk_m c \tag{2}$$

where i represents the current, k_m represents the mass transfer coefficient of the system, A the electrode area and all other terms as previously defined. In this case a mass transfer coefficient of the order of 0.029 cm s^{-1} was recorded. This is a significant number considering the already impressive mass transfer figure of 0.023 cm s^{-1} for a microelectrode in stagnant solution. This indicates that the solution around an oscillating bubble is moving relatively quickly on the electrochemical timescale employed. It was also noted that as the microelectrode was positioned further away from the surface of the bubble wall the effect of bubble oscillation showed a marked decrease.

3.2.2 Experiments with high temporal resolution

In order to temporally resolve the oscillations of the surface of the bubble wall it was necessary to employ a larger microelectrode. This was necessary particularly considering the current scale and the relatively small signal detected for the bubble wall oscillations themselves in this system. Figure 4 shows an experiment performed with a 25 µm diameter Pt microelectrode held at –0.6 V *vs.* SCE. Figure 4 contains higher time resolution data than Figure 3, again for a bubble held beneath a galss rod. It shows the current detected as the pressure amplitude of the pump field applied to an air bubble was increased. In this case the pressure close to the bubble wall was measured with a hydrophone. Though to a first approximation the hydrophone signal monitors the field which drives the bubble into pulsation, note should be made of the ability of the bubble itself to affect the signal detected at the pump frequency [6].

The solution employed in this experiment contained only 0.1 mol dm^{-3} KCl and hence only oxygen electrochemistry could be observed at the surface of the Pt microelectrode. Figure 4a shows a largely noise signal as a result of pick-up between the acoustic transducer and the high gain (1 x 10^8 V A^{-1}) electrochemical equipment used in this investigation. As the pressure was increased (see Figure 4b and Figure 4c) a strong signal associated with the visible oscillation of the bubble surface was observed. However, the frequency dependence of the signal was clearly different to the drive frequency (in this case 1.593 kHz). Figure 4b and figure 4c show a clear emergence of a signal a half the driving frequency (in this example 796 Hz). This we attribute to the excitation of Faraday waves on the surface of the bubble wall: the amplitude of the pump field required to generate this signal agrees with the amplitude theoretically required to excite Faraday waves [7]. The additional fluid motion, as a result of these surface waves, is detected as the additional mass transfer enhancement shown in Figure 3. These results show for the first time that the detection of wall motion of a stationary tethered bubble is possible using an electrochemical approach employing microelectrodes and a suitable redox system.

Figure 5 shows two images of a bubble tethered to a glass rod within the electrochemical cell employed in this study. Figure 5a shows an image of the bubble in the absence of irradiation with sound, while Figure 5b shows the same bubble driven to oscillate by an applied sound field. In this case the bubble can be clearly seen to display equatorial surface waves (which in the video sequence oscillate in the expected manner). These Faraday waves give the bubble a segmented appearance.

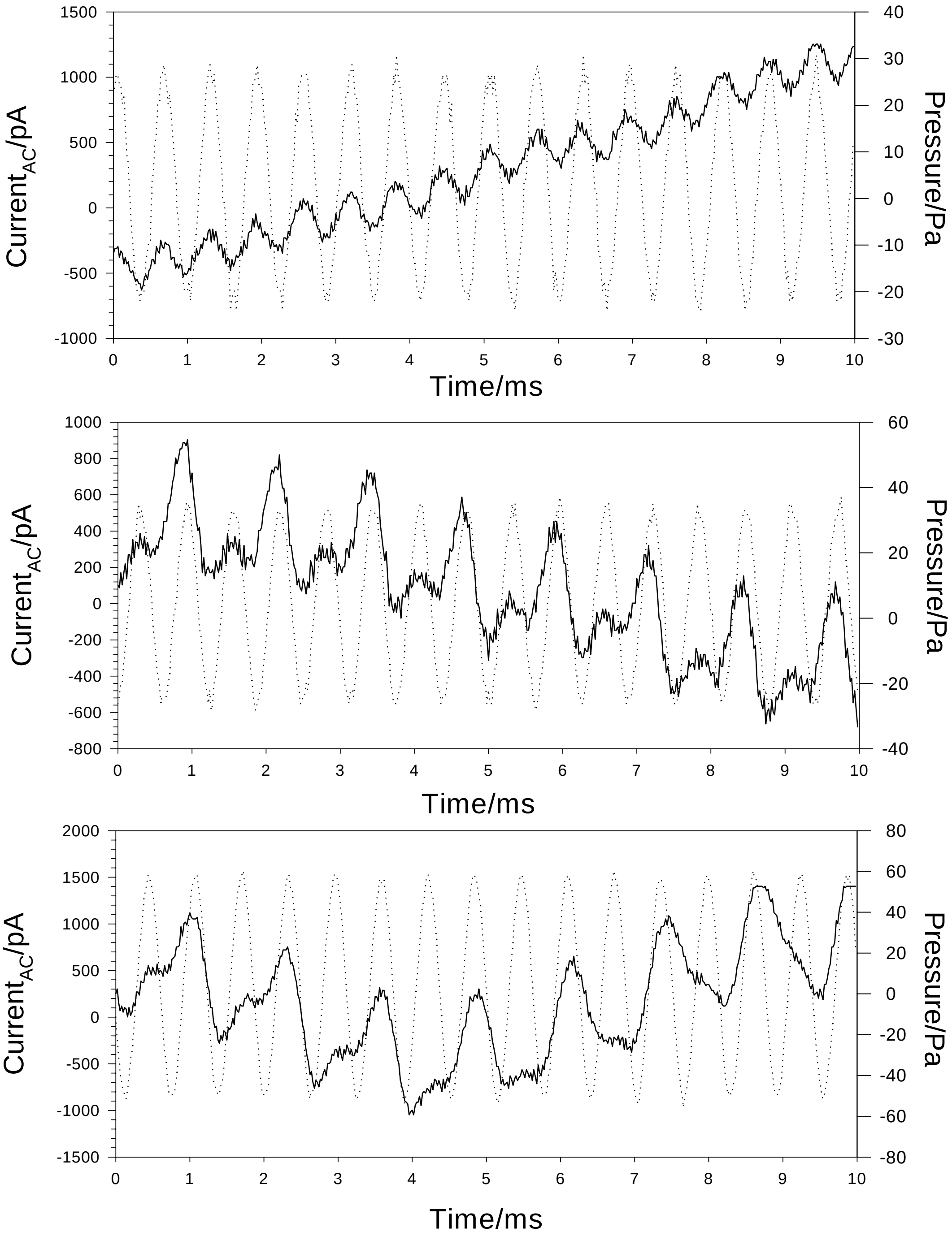

Figure 4. Plots showing the current and pressure signals recorded as a function of time as the acoustic pressure is successively increased through 'a' to 'c'. The electrochemical signal was recorded using a 25 μm Pt microelectrode while the pressure was recorded using a hydrophone. The cell contained of an aerobic solution of 0.1 mol dm^{-3} KCl. The sound irradiation frequency was 1.593 kHz. The potential of the electrode was held at -0.6 V vs. SCE. The temperature was 20-22 ^{o}C. The solid line represents the current while the dotted line the hydrophone response. Whilst the bubble clearly pulsates in sympathy with the driving field, as the amplitude of the latter is increased the generation of Faraday waves on the bubble wall is indicated by the inclusion of a component at the subharmonic of the driving frequency.

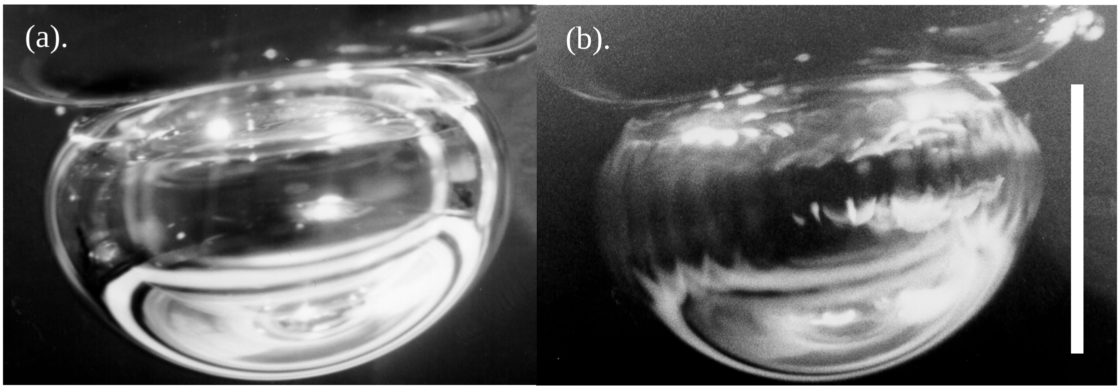

Figure 5. Image taken of a tethered bubble. Image 'a' shows a bubble in the absence of irradiation with sound while image 'b' shows the same bubble driven into oscillation by an acoustic field. Faraday waves are clearly visible about the bubble equator. The image was recorded using a Gallenkamp stereomicroscope and RICOH SLR camera and flash. An aqueous solution was employed at 20-22 ^{o}C. The white scale bar (shown as a vertical line in part 'b') is 2.5 mm long.

4. Sea Trial

The apparatus illustrated in Figure 6 was developed to determine electrochemically bubble populations at the Hurst Spit 200 sea trial [1]. It consists of a 25 μm Pt electrode set inside a copper tube, which acted as both a counter/reference electrode. The potential was held at -1.3 V vs. Ag to enhance the electrochemical signal for deployment at sea. However, the sensor was damaged by the extreme conditions present in the surf zone [1].

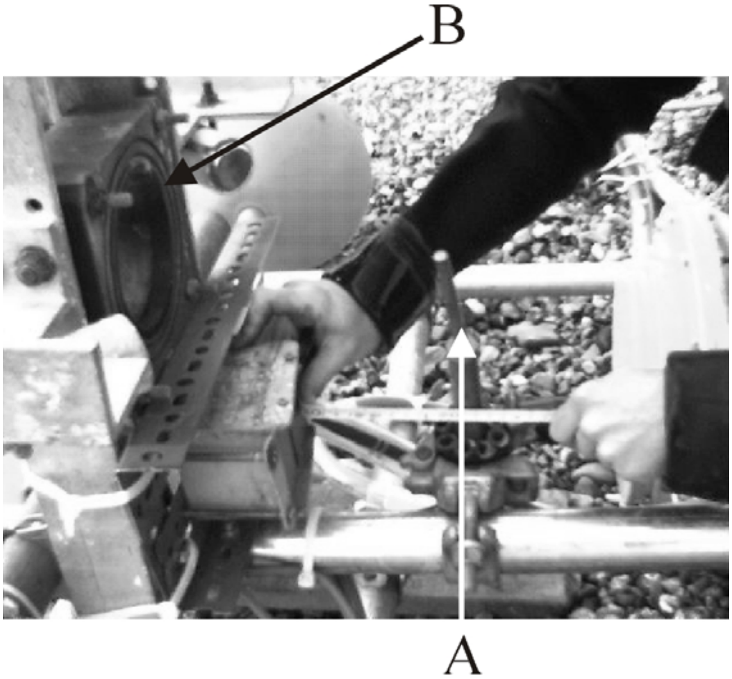

Figure 6. The sensor developed electrochemically to determine bubble populations, shown amidst in the Hurst Spit 2000 sea trial rig. The electrode tip is the white dot in centre of picture, and its shaft is labelled A. The pump frequency source (on either side of which are the combination frequency transducers) is labelled B.

5. Conclusions

An electrochemical signal resulting from the passage close to an electrode of a bubble has been reported, and the local nature of the detector illustrated. The detection of bubble oscillation as the result of acoustic irradiation of a stationary bubble has been reported for the first time. Electrochemical evidence for subharmonic motion on the surface of the bubble, associated with the well-known phenomena of Faraday waves, has been reported for the first time. Details of how to adapt this system to the ocean are given, but no ocean data was obtained because of damage. Further laboratory tests, including 'fly-by' tests in the presence of a pump field, and a bubble population covering a wide radius range, are planned prior to the next sea trial. To date only the first half of Objective (ii) from Section 3 of Leighton *et al.* [17] has been accomplished.

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