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Efficient mass transfer from an acoustically oscillated gas bubble

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Efficient mass transfer enhancements as the result of acoustically oscillated gas bubbles are detected using a microelectrode positioned at variable distances from the gas/liquid interface.

The enhancement in mass transfer as the result of bubble motion is extremely important in many industrial scale electrochemical processes.[1] It is thought to be the result of a number of different mechanisms associated with electrochemical bubble growth, detachment and motion under buoyancy forces away from the solid/liquid interface of an electrode.[2] These mechanisms have been investigated by a number of authors. The work by Whitney and Tobias is particularly noteworthy.[3] These authors studied bubble motion using arrays of microelectrodes produced through photolithographic processing. The individual contribution of single bubbles could be detected from a generator microelectrode. However, in all of these studies the enhancement in mass transfer has involved the motion of bubbles under buoyancy forces alone.

Bubbles are also known to be extremely active acoustically, with the sound of running water (*e.g.* in a small waterfall) largely attributed to bubble entrapment. The subsequent bubble pulsation gives the characteristic 'noise', which is observed.[4] In turn gas bubbles within a liquid interact strongly with incident sound waves. If the sound wave is of the correct frequency and pressure amplitude, then a number of different oscillations of a bubble can be induced. These fall broadly into two classes: a breathing mode (or 'pulsation') where the whole bubble expands and contracts with spherical symmetry about the bubble centre; and a second class which lack spherical symmetry. The shape oscillations called Faraday waves[5] are members of this second class. In the steady state the breathing mode occurs at the frequency of the driving sound field, but in contrast Faraday waves occur at half this frequency. Whilst a breathing mode is always excited, generation of Faraday waves requires the driving field to exceed a threshold amplitude.[6] Both the breathing mode and surface waves move the liquid phase of the media to a greater or lesser extent. Fig. 1 shows a photograph of a gas bubble driven into oscillation by irradiation with sound. The distortions in the surface of the bubble can be clearly seen.

However, the contribution to mass transfer of these modes within the liquid phase has not been reported. Here a microelectrode is used to characterise the mass transfer enhancements produced by an oscillating gas bubble. Microelectrodes were chosen for a number of reasons. These included their ability to operate under steady state conditions, their relatively fast response time and their size.[7,8] In the experiments reported here a microelectrode was positioned close to the gas/liquid interface of an air bubble trapped by buoyancy forces under a solid surface. The liquid phase consists of an aqueous solution[9] of 5 mmol dm^{-3} $[Fe(CN)_6]^{-3}$ in 0.2 mol dm^{-3} $Sr(NO_3)_2$. The microelectrode was positioned close to the gas/liquid interface using an X, Y, Z micrometer and stage. The position of the microelectrode with respect to the gas/liquid interface was verified by monitoring the steady state current recorded in the absence of bubble oscillation. When the electrode (a 25 μm diameter Pt microdisc) was < 125 μm away from the nearest point on the stationary bubble wall, the presence of the gas/liquid interface could be detected as a reduction in the steady state current recorded at the microelectrode.[10–12] This was due to hindered diffusion (negative feedback) as a result of the blocking nature of the gas/liquid interface under the conditions stated. Irradiation of the bubble with sound of the appropriate frequency and amplitude results in oscillation of the bubble surface. This oscillation can be electrochemically detected by the microelectrode positioned close to the gas/liquid interface. The motion of the bubble wall will be detected as an enhancement in mass transfer to the microelectrode as a result of the forced convection of the liquid produced by the oscillation of the bubble wall. Fig. 2 shows the enhancement in mass transfer detected as a function of distance away from the gas/liquid interface. In this case, the bubble was driven into oscillation at a pressure sufficient to generate surface waves on the gas/liquid interface. This was observed in two ways. First, the presence of surface waves on the bubble wall was observed optically as a 'shimmer'. Second, when the microelectrode was positioned close to the bubble wall (*ca.* 5–10 μm) the motion of the bubble wall can be resolved electrochemically. This is shown as an insert on Fig. 2. The insert shows the current and pressure† time traces for a bubble driven to oscillate with surface motion. This clearly shows that the current time trace has a component at $0.5f$ (where f represents the drive frequency, in this case 1.46 kHz). This is characteristic of Faraday waves on the surface of the bubble wall, and is confirmed by the photograph of a bubble under similar conditions shown in Fig. 1. Fig. 2 shows that within the first *ca.* 100 μm, the mass transfer enhancement remains approximately constant. Fig. 2 also shows that the current falls as the distance between the microelectrode and the gas/liquid interface of the bubble increases. However, the perturbation in

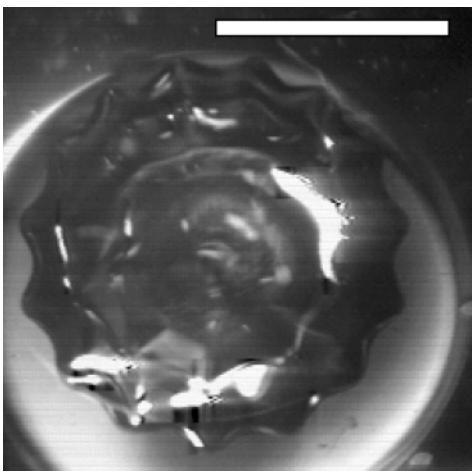

Fig. 1 Photograph taken from below a tethered bubble held by buoyancy forces on the end of a glass rod. The scale bar represents 3 mm. The surface waves can be clearly seen around the perimeter of the gas/liquid interface.

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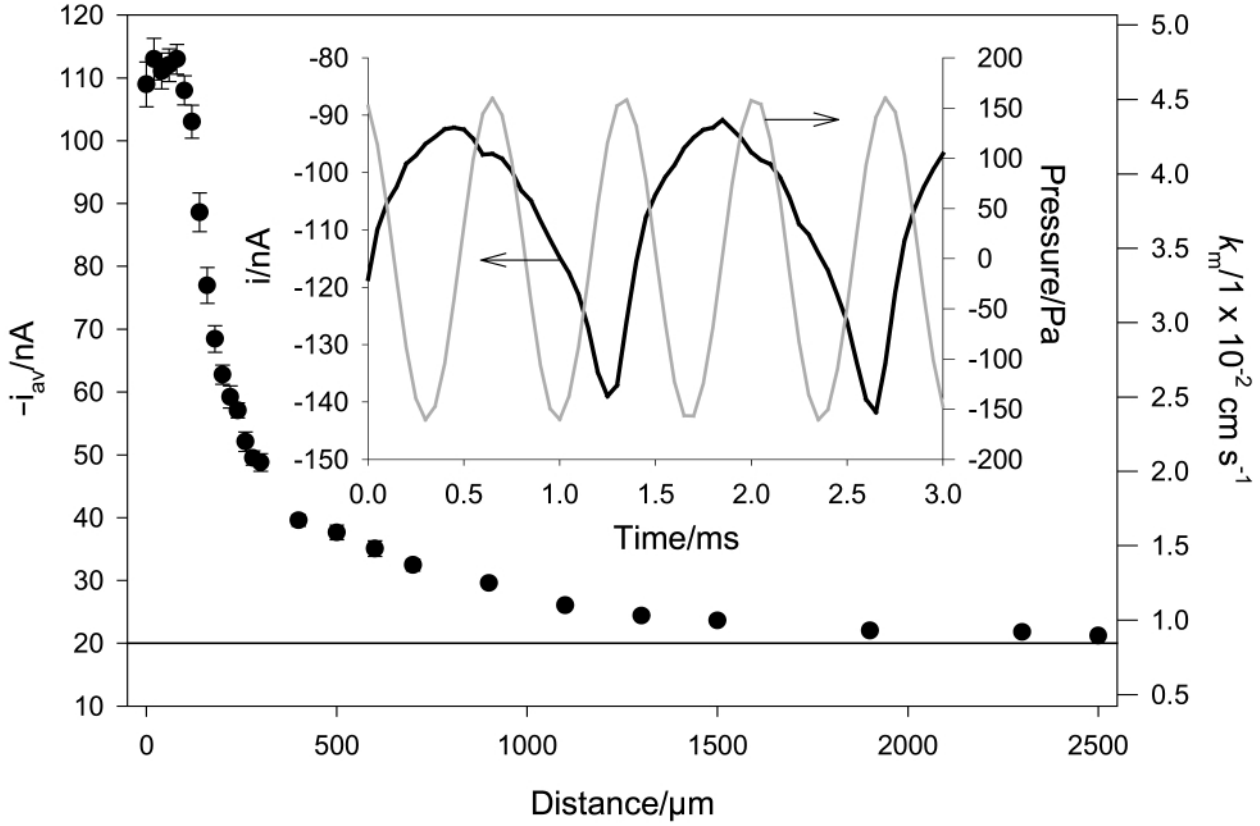

Fig. 2 Plot showing the average current (●) and associated mass transfer coefficient for a single air bubble driven into oscillation by a sound field operating at 1.46 kHz. The solution contained 5 mmol dm^{-3} $[Fe(CN)_6]^{3-}$ in 0.2 mol dm^{-3} $Sr(NO_3)_2$. The error bars show the 95% confidence interval. The insert shows the oscillation in the current (solid line) and pressure† (faint line) as a function of time employing high temporal resolution equipment. The experiment was performed at *ca.* 20–23 °C under aerobic conditions. The solid horizontal line represents the steady state current or mass transfer coefficient for the microelectrode in a stagnant solution.

the mass transfer coefficient can be detected at extended distances away form the gas/liquid interface. A significant enhancement in the time averaged steady state mass transfer to the microelectrode was observed up to distances of *ca.* 2500 μm. This is particularly significant considering that the mass transfer coefficient of the 25 μm diameter platinum microelectrode is already high in stagnant solution (0.008 cm s^{-1}). It is interesting to note that the enhancement in mass transfer as a result of the bubble motion exceeds this value (up to 0.0477 cm s^{-1}) but is brought about by a relatively small pressure amplitude (< 100 Pa). This is a significant point as it clearly demonstrates that enhancing the mass transfer of material to an electrode in this manner would be a significantly more efficient way when compared to the employment of ultrasound to induce cavitation and other high energy phenomena.

Previous studies have shown that ultrasound can enhance mass transfer significantly.[13–15] However, the magnitude of the pressure field required to achieve inertial (transient) cavitation is considerably high. As an example, to generate cavitation in water under standard conditions requires a pressure amplitude in excess of *ca.* 1 atmosphere (101 000 Pa).[4] This is a factor of 1000 higher than the pressures (and in turn a factor of 10^6 in intensity) employed here. Clearly the generation of mass transfer enhancements using acoustically oscillated bubbles, rather than inertial cavitation, would be significantly more efficient. This increase in efficiency is due to the differing mechanisms responsible for the forced convection enhancements observed. The process of inertial cavitation requires that small (*e.g.* of order micron radius) bubbles expand against atmospheric pressure and surface tension forces to a critical radius, before collapsing. However, exciting a large bubble (*e.g.* mm radius) at resonance takes advantage of their exceptionally good acoustic coupling.[4] In turn, the pressure amplitude required to generate surface waves in this case is small, but the enhancement in forced convection is relatively large. As an example, mass transfer coefficients reported from cavitation are on the order[13–15] of 0.1–1 cm s^{-1}. The mass transfer coefficient recorded here is only a factor of 10 less, while the applied pressure is a factor of 1000 less. This is because the excitation of a surface wave does not require a large overall volume change of the bubble, compared to the generation of inertial cavitation.

Notes and references

† Note that the absolute pressure will not be the same as that shown in the insert of Fig. 2 as the presence of the oscillating bubble will alter the measured pressure. The absolute pressure can only be measured when the bubble has been removed from the glass support.

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