

The Effect of Ultrasound on Mass Transport to a Microelectrode

Peter R. Birkin* and Susana Silva-Martinez

Department of Chemistry, University of Southampton, Southampton, UK SO17 1BJ

Ultrasonically generated cavitation events, and their subsequent asymmetrical collapse to form microjets directed at the solid–liquid interface, are observed by recording the electrochemical oxidation of ferrocene at gold microelectrodes irradiated with ultrasound.

The beneficial effects of ultrasound on chemical reactions are well known. Increased reaction rates and altered product distribution have interested many chemists in investigating further the effects of ultrasound on a variety of reactions.^{1–3} The effects of ultrasound have been attributed to the generation of localised intense pressure and temperature regions. These energy regions have been measured experimentally and for short time periods temperatures of up to *ca.* 5000 K⁴ have been observed. These intense energy regions are thought to be the result of cavitation of the solution produced by the ultrasonic wave. Recently, increased attention has been focused on the combination of both ultrasonic irradiation and electrochemistry. However, the employment of ultrasound in electrochemical experiments was studied as long ago as 1963 by Bard.⁵ In more recent work the effects of ultrasound on the product distribution of an electrosynthetic reaction, depassivation and erosion of electrode surfaces and electrochemiluminescence have been reported.^{6–9} The effects of ultrasound on an *EC* reaction have also been reported.¹⁰

Our motivation was to investigate the effect of ultrasound on the mass transport to an electrode surface. In previous work mass transport to macroelectrodes has been investigated.¹¹ However, to our knowledge the effect of ultrasound on mass transport to microelectrodes has yet to be reported in the manner described here.

In order to explain the increased mass transport rates, observed by some researchers at macroelectrodes, it is necessary to understand the formation of microjets, produced as a consequence of asymmetrical cavitation bubble collapse near a solid–liquid interface, directed at the solid–liquid boundary.^{12–15} Degrand *et al.* have attempted to study the ‘micro’ mass transport produced as a result of ultrasonically induced individual cavitation events.¹⁶ In their study high-scan-rate cyclic voltammetry was employed to capture individual events. However, analysis of their current transients has not, to our knowledge, been published. We present here an alternative approach to the study of the cavitation events with the eventual aim of characterising further the effect of ultrasound on mass transport to a solid electrode, specifically the employment of a microelectrode. This enables us to observe individual microjets by monitoring the current produced by the oxidation of a redox-active material, specifically ferrocene, at a microelectrode¹⁷ under ultrasonic irradiation. In essence the microelectrode acts as a target for the imploding cavitation bubbles recording hits and near misses as individual current transients with differing intensity and shape. The employment of a microelectrode leads directly to two advantages. First the small size of the electrode with respect to the cavitation bubbles enables us to record individual cavitation collapse and microjet formation. Secondly measurements of individual microjets can be made under mass-transport-limiting conditions in the absence of any forced convection (*e.g.* a static solution).¹⁸ This second advantage enables easier analysis of the data acquired and direct comparison with conventional electrochemical techniques (*e.g.* wall tube electrodes) in association with the already well developed cavitation theory.^{19,20}

In our system we employed ferrocene as a redox probe dissolved in methanol. In order to obtain reproducible results with this system, a saturated methanol–KCl solution (denoted by SCE*) was used to replace the more common aqueous

saturated KCl solution employed in a calomel reference electrode.

The reversibility of the ferrocene–ferricinium redox couple was tested by cyclic voltammetry recorded using a 10 μm diameter gold microelectrode. A plot of E vs. $-\log[(i_{\text{lim}}/i) - 1]$, obtained from the forward sweep of the cyclic voltammogram, produced a straight line with a gradient of 58.9 mV per decade. This implies that the ferrocene–ferricinium redox couple exhibits reversible behaviour under the conditions stated. The $E_{1/2}$ of the redox couple obtained from this analysis was +324 mV vs. SCE*. The diffusion coefficient of ferrocene under these conditions was calculated as $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

To study the effect of ultrasound on mass transport we recorded the current passed as a function of time at a 25 μm diameter gold microelectrode held potentiostatically at +600 mV vs. SCE* in a methanol solution containing ferrocene (5 mmol dm⁻³) and Et₄NBF₄ (0.1 mol dm⁻³). At this chosen potential the oxidation of ferrocene was mass-transport-controlled. The presence of ultrasound produces microjets directed at the solid–liquid boundary. These microjets or forced convection regions when impinging on or near the microelectrode will increase the mass transport of material to the electrode. Fig. 1 shows some typical results obtained when a 25 μm diameter Au microelectrode was placed directly beneath (*ca.* 2 mm tip to electrode distance) an operating ultrasonic cell disrupter (Microson™ MS-50, 50 W, operating at 23 kHz, tip area 0.08 cm²) and held at +600 mV vs. SCE*. Over the time scale of the trace static-solution mass transport conditions apply (in the absence of any forced convection) and the normalised current was *ca.* 1. However, individual or closely spaced events, denoted by current spikes and decay transients back to a normalised current of *ca.* 1, are observed, strongly implying a microjet or group of microjets impacting on or near the microelectrode resulting in increased rates of mass transport of material to the electrode due to forced convection. Normalised currents of up to *ca.* 70 have been observed under these

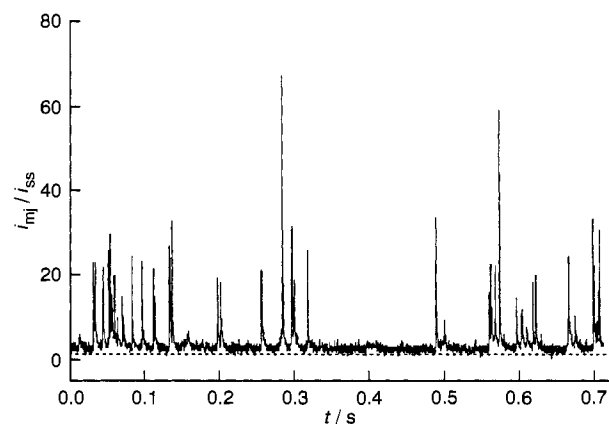


Fig. 1 Normalised current ($i_{\text{mj}}/i_{\text{ss}}$) recorded at a 25 μm diameter Au microelectrode exposed to ultrasound (operating at 20% output). The electrode was held at +600 mV vs. SCE*. The methanol solution contained ferrocene (5 mmol dm⁻³) Et₄NBF₄ (0.1 mol dm⁻³) supporting electrolyte. The dotted line indicates the current recorded for a static solution (i_{ss}) at +600 mV vs. SCE*. The experiment was performed at 25 °C under aerobic conditions.

conditions corresponding to a mass transport coefficient of 1.28 cm s^{-1} for the $25 \mu\text{m}$ gold microelectrode. Single events can be recorded by increasing the time resolution employed in the experiment. Fig. 2 shows a single event recorded at a $10 \mu\text{m}$ diameter gold microelectrode in the presence of ultrasound in a methanol solution containing ferrocene (30 mmol dm^{-3}) and Et_4NBF_4 (0.1 mol dm^{-3}). However, interpretation of these results in terms of fluid jet velocities is not trivial. Comparison of the data with conventional wall tube electrode theory shows us that it is necessary to know the shape, size and position of the microjet as it impacts on the surface of the electrode.²⁰

The normalised current maxima for individual events remained approximately constant when a 10 mmol dm^{-3} or 5 mmol dm^{-3} ferrocene solution was employed implying that the concentration of the probe species had no effect on the observed events in the range we studied. The normalised current maxima for $25 \mu\text{m}$ and $10 \mu\text{m}$ diameter gold microelectrodes were of the same order of magnitude. No current spikes or transients were detected in the absence of ultrasound or at a potential insufficient to oxidise ferrocene. These preliminary results also show that relatively long and uneven time periods can pass between events, from these results up to *ca.* 150 ms, indicating the random nature of the cavitation phenomena. However, increasing the intensity of the ultrasonic source or decreasing the separation between ultrasonic horn and electrode resulted in an increase in the frequency and magnitude of the observed events. These results presumably imply that the intensity of the ultrasonic wave has an effect on the magnitude of the energetics of the cavitation bubble collapse and density of cavitation events.

These results also show the random nature of the cavitation microjet phenomena observed. Fig. 1 shows that over the 0.7 s time period recorded the microelectrode detects *ca.* 36 events. However, during this 0.7 s time period *ca.* 16 000 compression

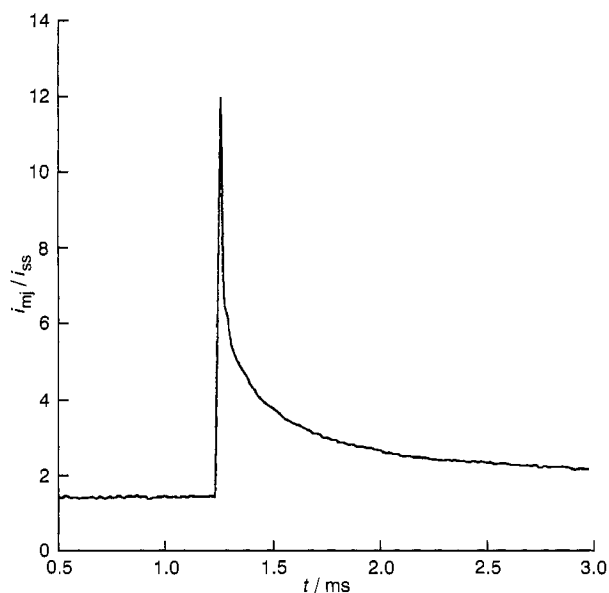


Fig. 2 Normalised current recorded at a $10 \mu\text{m}$ diameter Au microelectrode exposed to ultrasound (operating at 20% output); conditions as for Fig. 1, except for the concentration of ferrocene (30 mmol dm^{-3})

and rarefaction cycles have been produced by the ultrasonic horn. Clearly this indicates that the microjet formation at the solid-liquid boundary relies not only on the ultrasonic wave but also on other parameters, presumably nucleation sites.¹

These well resolved current spikes (*ca.* two orders of magnitude greater than the steady-state mass-transport current produced in the absence of forced convection) were obtained with an ultrasonic horn in a solution with a relatively high vapour pressure (methanol, $25 \text{ }^\circ\text{C}$). We are currently investigating the effect of changing the solvent system and temperature on the shape and height of the current events recorded. Presumably altering the system should allow us to record more energetic cavitation and subsequently increased microjet velocities.

The shape and random nature of the events strongly imply that the results reported here are not due to other erroneous phenomena (*e.g.* stable oscillation and microstreaming).

Employment of the fast response properties of microelectrodes should make it possible to record voltammetry of the solution species in the microjet as they impact onto the microelectrode. We hope to use the data obtained from these microelectrode experiments in conjunction with simulation of cavitation bubble collapse to quantitatively investigate further the cavitation process and the role ultrasound can play in electrochemistry.²¹⁻²²

Received, 27th January 1995; Com. 5/005151

References

- 1 *Sonochemistry, The Uses of Ultrasound in Chemistry*, T. J. Mason, Royal Society of Chemistry, Cambridge, 1989.
- 2 J. P. Lorimer and T. J. Mason, *Chem. Soc. Rev.*, 1987, **16**, 239.
- 3 K. S. Suslick, *Science*, 1990, **247**, 1439.
- 4 E. B. Flint and K. S. Suslick, *Science*, 1991, **253**, 1397.
- 5 A. J. Bard, *Anal. Chem.*, 1963, **35**, 1125.
- 6 A. Chyla, J. P. Lorimer, T. J. Mason, G. Smith and D. J. Walton, *J. Chem. Soc., Chem. Commun.*, 1989, **9**, 603.
- 7 R. G. Compton, J. C. Eklund, S. D. Page, G. H. W. Sanders and J. Booth, *J. Phys. Chem.*, 1994, **98**, 12410.
- 8 H. Zhang and L. A. Coury, *Anal. Chem.*, 1993, **65**, 1552.
- 9 D. J. Walton, S. S. Phull, D. M. Bates, J. P. Lorimer and T. J. Mason, *Electrochim. Acta.*, 1993, **38**, 307.
- 10 R. G. Compton, J. C. Eklund, S. D. Page and T. O. Rebbitt, *J. Chem. Soc., Dalton Trans.*, 1995, 389.
- 11 C. R. S. Hagan and L. A. Coury, *Anal. Chem.*, 1994, **66**, 399.
- 12 B. E. Noltingk and E. A. Neppiras, *Proc. Phys. Soc. London*, 1950, **B63**, 674.
- 13 S. Zhang, J. H. Duncan and G. L. Chahine, *J. Fluid. Mech.*, 1993, **257**, 147.
- 14 F. R. Young, *Cavitation*, McGraw Hill, New York, 1989.
- 15 G. E. Osborne and R. Latorre, *J. Naval Eng.*, 1992, **Jan**, 36.
- 16 J. Klima, C. Bernard and C. Degrand, *J. Electroanal. Chem.*, 1994, **367**, 297.
- 17 R. M. Wightman and D. O. Wipf, *J. Electroanal. Chem.*, 1989, **15**, 267.
- 18 *Microelectrodes, Theory and Application*, I. Montenegro, M. A. Queries and J. Daschbach, 1991, Kluwer, p. 41.
- 19 W. J. Albery and S. Bruckenstein, *J. Electroanal. Chem.*, 1983, **144**, 105.
- 20 J. V. Macpherson, S. Marcar and P. R. Unwin, *Anal. Chem.*, 1994, **66**, 2175, and references therein.
- 21 D. J. Steinberg, *J. Stone Disease*, 1993, **5**, 49.
- 22 S. Zhang and J. Duncan, *Phys. Fluids*, 1994, **6**, 2352.