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Electrochemical, luminescent and photographic characterisation of cavitation

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Abstract

The characterisation of a small sonochemical reactor has been performed using electrochemical, luminescent and photographic techniques. The electrochemical experiments have employed a novel flow system to determine the formation of sonochemical products (in this case hydrogen peroxide) in semi-real time with high sensitivity. The rate of production of hydrogen peroxide is reported as a function of driving pressure amplitude. The degradation of an organic molecule, specifically the organic dye amaranth, within the sonochemical cell is also reported.

Keywords: Hydrogen peroxide; Flow cell; Organic destruction; Frequency

1. Introduction

The generation of cavitation through the application of power ultrasound is an appealing way of accelerating or driving a range of physical and chemical processes [1]. The acceleration and possible alteration of mechanistic pathways are strongly associated with the unusual conditions produced as the result of oscillating or collapsing cavitation bubbles [2]. However because of the complex nature of this particular environment, it is often difficult to determine the extent and the actual effect of cavitation on the phenomena in question. Clearly if cavitation is to be fully exploited and developed as a useful industrial and academic technique, the understanding of the complex and interacting processes that occur within this unusual environment is paramount. It is with this aim in mind that the study presented here was performed.

In the study of sonochemical reactions, many different approaches and experimental set ups have been reported. The range of different ultrasonic frequencies employed best demonstrates this variation in approach to investigating the effects of cavitation on chemical processes [3–9]. Frequency ranges from >1 MHz to 20 kHz can be found as well as differing experimental arrangements such as 'ultrasonic horn' or 'ultrasonic reactor' approaches. However, in many cases the characterisation and consideration of the spatial and temporal nature of the sound field that operates within these environments is lacking. This is unfortunate as without this consideration accurate explanations of the experimental findings are difficult to achieve. It is suggested here that an understanding of the acoustics of the sonochemical reactor is paramount to the appropriate explanation of experimental results.

In the study reported here an electrochemical approach to the detection of a sonochemical product (in this case hydrogen peroxide) has been employed within a small cylindrical sonochemical reactor. The electrochemical detection of hydrogen peroxide is routinely performed in the assaying of enzymatic reactions and the investigation of the mechanism of oxygen electroreduction [10,11]. However, in order to combine electrochemical detection of hydrogen peroxide with the sonochemical system, the technique must satisfy a number of criteria. First, the electrochemical technique must be sensitive enough to detect the low levels of hydrogen peroxide expected. As an example Sato et al. have reported hydrogen peroxide production rates of

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the order of 90 nmol cm^{-3} h^{-1} [5]. Clearly any technique designed to investigate the production of hydrogen peroxide must be sensitive at this level. Second, as hydrogen peroxide is notoriously unstable, rapid assessment of the concentration of this compound is desirable. Lastly, the technique must be reproducible within the sonochemical experimental apparatus employed. These criteria led us to the development of an electrochemical flow cell system attached to the sonochemical cell [12,13]. This system has a number of advantages in comparison to the 'standard' in situ sonoelectrochemistry. If the electrodes are placed within the cell then the mass transfer characteristics are extremely dependent on position and time as the cavitation process tends to generate high localised rates of mass transfer to the electrode surface and in some cases detrimental surface erosion [14–16]. Careful calibration of the system is required prior to determination of sonochemical reaction rates [17]. To meet these challenges we have employed an electrochemical flow cell system coupled to the sonochemical cell. This has a number of advantages. Although the mass transfer coefficients within the cell are small in comparison to those found in cavitation environments, they are steady state and well characterised. In addition because of the small size of the piping involved, little or no disturbance of the sound field within the sonochemical reactor is apparent. Lastly the sonochemical reaction is essentially 'frozen' once the liquid enters the flow system as the wavelength of the sound employed is large compared to the dimensions of the piping leading to a large impedance mismatch. This system has been successfully employed to study a number of sonochemical reactions including the Fricke, the Weissler and the detection of $H^{\cdot}$ [12,13].

Luminescent emission from the sonochemical reactor is also used to characterise the system [18–21]. In this case the light output from multibubble sonoluminescence (MBSL) is used to predict the conditions under which maximum sonochemical effect would be expected. In addition, imaging of the cell enables the sound field to be shown [18]. The results of this study are now presented.

2. Experimental

The experimental set up has been reported in detail elsewhere [12,13,18,19]. The electrochemical measurements of hydrogen peroxide production were recorded in an electrochemical flow cell while the degradation of the organic dye species was followed by using a thin layer flow cell coupled to a diode array spectrometer [22]. The wavelength of the maximum amaranth absorbance (520 nm) was followed as a function of time in the absence and presence of ultrasonic irradiation. Pressure measurements were recorded on a Bruel & Kjaer 8103 hydrophone [1] connected through a Bruel & Kjaer 2635 charge amplifier to a Tektronix TDS 224 digital oscilloscope. The ultrasonic reactor consisted of a double walled glass cylindrical cell (5.8 cm internal diameter, 8.5 cm external diameter and height 12 cm) with an ultrasonic transducer (Morgan Electro Ceramics Ltd., resonance frequency ≈27 kHz) attached to the base using Struers epofix.

Unless stated otherwise all experiments were performed using an aerobic solution (100 cm^3) pH 5.5 citrate/phosphate buffer thermostated at 25 °C [23]. Citric acid (BDH, AnalaR), Na_2HPO_4 (BDH, GPR), Na_2SO_4 (BDH, AnalaR), $FeSO_4 \cdot 7H_2O$ (BDH, AnalaR), H_2SO_4 (BDH, AnalaR), Catalase (Sigma) and Amaranth (Aldrich, 80%) were used as received. All solutions were made up using water purified through a USF Elga Option E10 water purification system. This system produced high purity water with a resistivity >15 MΩ cm.

3. Results

Fig. 1 shows voltammetry of a Pt 0.5 mm diameter electrode depicting the electrochemical oxidation of hydrogen peroxide in a pH 5.5 buffer. The oxidation of hydrogen peroxide can be seen to occur at potentials >+0.3 V vs. SCE. Limiting oxidation of hydrogen peroxide occurred at potentials in excess of +0.6 V vs. SCE. The peak current (0.69 μA) can be compared to the theoretical peak current predicted [24] by Eq. (1) using a diffusion coefficient for hydrogen peroxide of 1.46×10^{-5} cm^2 s^{-1} [25] and $c = 1 \times 10^{-3}$ mol dm^{-3},

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} c \quad (1)$$

where n is the number of electrons (in this case 2), A the electrode area, D the diffusion coefficient, v the sweep rate and c the concentration of hydrogen peroxide employed. Using Eq. (1) a peak current of 1.25 μA is predicted. This deviation may be due to surface limited processes described previously [25].

In order to quantify the electrochemical detection of hydrogen peroxide, a calibration experiment was performed. In this case a 100 cm^3 solution of pH 5.5 citrate/phosphate buffer [23] was pumped through the flow cell. The electrode employed (0.5 mm diameter Pt) was held at +0.8 vs. SCE, a potential that corresponded to mass transfer limited oxidation of hydrogen peroxide (see Fig. 1). The response of the electrode was monitored as a function of time as a known solution of hydrogen peroxide was titrated into the flow system. Fig. 2 shows the current time plot recorded from such an experiment.

[1] It is known that due to the finite size of the element within the hydrophone, pressure measurements within the cell will be subject to spatial averaging [2,18] and the spatial peak (given here as 0 to peak amplitude) will be an underestimate of the real value.

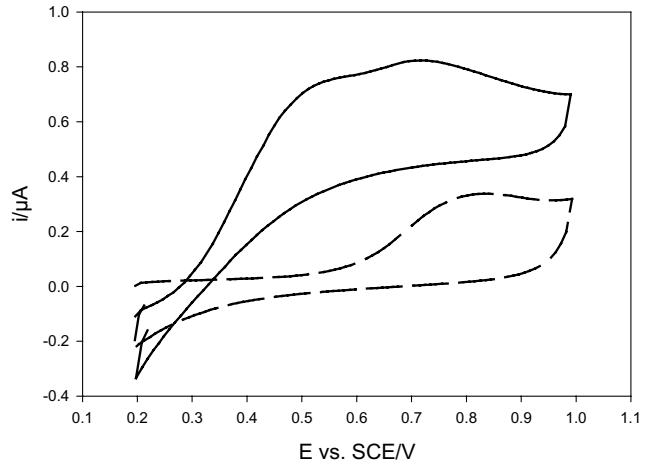

Fig. 1. Plot showing the cyclic voltammograms of a 0.5 mm diameter Pt electrode in pH 5.5 citrate/phosphate buffer. (- - -) represents the voltammetry of the buffer alone while (—) represents the voltammetry of the buffer with 1 mmol dm^{-3} H_2O_2 added. The voltammetry was recorded under aerobic conditions at 50 mV s^{-1} and at 25 °C.

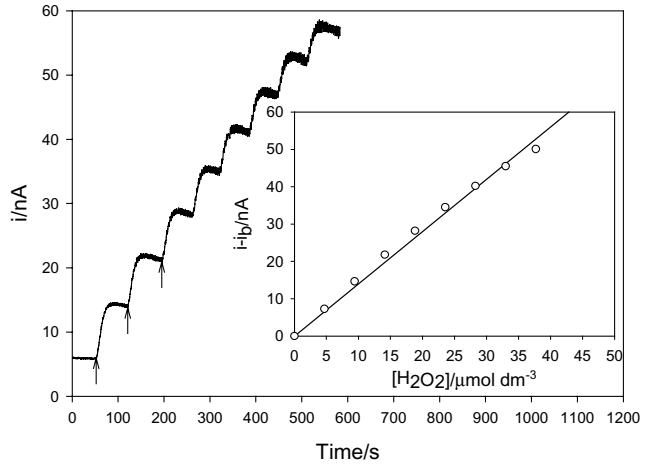

Fig. 2. Plot showing the current recorded as a function of time as hydrogen peroxide was injected into the flow system (the arrows show the first three additions of hydrogen peroxide). The hydrogen peroxide was detected at +0.8 V vs. SCE at a 0.5 mm diameter platinum electrode. Time was allowed for the current to reach a pronounced plateau before additional H_2O_2 was added to the flow system. The insert illustrates the increase in oxidation current as a function of H_2O_2 concentration.

The insert in the figure shows the calibration plot derived from the plateau currents produced by the addition of hydrogen peroxide. An approximately linear relationship between hydrogen peroxide concentration and current can be observed. However, it is known that the oxidation of hydrogen peroxide on platinum relies on a surface process that can be saturated at high hydrogen peroxide concentrations [25]. However, the low level of hydrogen peroxide employed ensures that this effect is not significant but may be responsible for the slight deviation from linearity observed in the calibration plot shown as an insert in Fig. 2. The calibration plot has a slope (CR) of 1.4×10^{-3} A mol^{-1} dm^3. This value can be used to calculate the rate of hydrogen peroxide generation in later experiments.

Fig. 3 shows the luminescent MBSL output of a cylindrical sonochemical cell as a function of frequency from 120 to 128 kHz. A maximum in the light output of the cell occurred at ≈124 kHz. It is known that the rates of sonochemical reactions can be predicted by monitoring the MBSL output of the reactor [19–21]. Hence 124 kHz was chosen for investigation of the sonochemical rate of hydrogen peroxide generation as a function of drive pressure amplitude (see Fig. 5). The insert in Fig. 3 shows images of the cylindrical cell in (a) room light and (b) under dark room conditions used when measuring luminescence. Fig. 3(b) shows a series of bands (as viewed from the side). These are characteristic of the modal sound field present within the cell. Further discussion of the sound field within such a cylindrical cavity can be found elsewhere [18].

Fig. 4 shows the current time trace observed when a pH 5.5 solution was exposed to power ultrasound. In this case the solution initially contained no hydrogen peroxide. Fig. 4 shows that after a ≈30 s delay (caused by the flow path of the solution through the pump system and into the electrochemical cell) an anodic deviation in the current was observed. This was attributed to the production of hydrogen peroxide from the cavitation process and subsequent oxidation on the surface of the platinum electrode. This was further confirmed by the addition of catalase (an enzyme that catalytically decomposes hydrogen peroxide) to the solution. After mixing and the flow system delay time have been passed the current can be seen to return rapidly to the baseline as the enzyme removes the hydrogen peroxide generated by the sonochemical action within the cell. This confirms that the signal observed is the result of hydrogen peroxide generation within the sonochemical reactor. Fig. 4 also shows that the rate of hydrogen peroxide production within the sonochemical cell is linear as a function of time. The gradient of the current time transient recorded (SCR) can be measured and used with Eq. (2) to determine the actual hydrogen peroxide generation rate within the sonochemical reactor.

$$\text{Rate of hydrogen peroxide production} = \frac{\text{SCR}}{\text{CR}} \qquad (2)$$

In this case the maximum rate of hydrogen peroxide is of the order of 100 nmol dm^{-3} s^{-1}.

Fig. 5 shows how the rate of production of hydrogen peroxide varies as a function of the amplitude of the acoustic driving pressure measured within the cell using a calibrated hydrophone. [1] Fig. 5 shows that above pressure amplitudes of ≈1.1 bar the rate of generation of hydrogen peroxide increase rapidly. However, a plateau region at acoustic pressures in the range 2.6–3.2 bar was

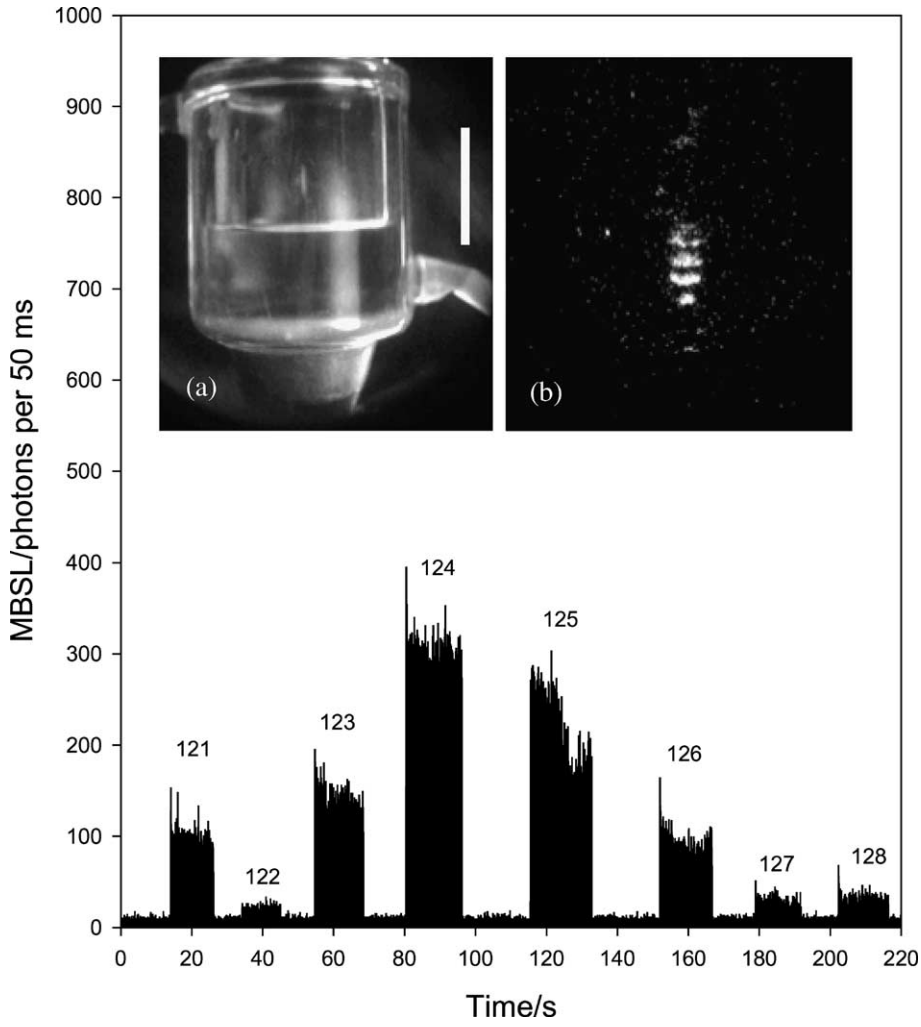

Fig. 3. Plot showing the MBSL output of the cell as a function of time as the ultrasound irradiation of the cell was chopped on and off. The irradiation frequency is reported in the figure (in kHz). The insert in the figure shows images recorded of the sonochemical reactor. Image (a) corresponds to the cell pictured in the light while image (b) shows the MBSL activity at 123 kHz recorded under dark room conditions. The scale bar represents 4 cm.

observed. Clearly at very low acoustic pressures the cavitation is unable to generate the conditions required to drive the pyrolysis of the water vapour within the cavitation bubble. As a result no $OH^{\cdot}$ radicals are formed and in turn no geminate formation of hydrogen peroxide can be detected. The reason for the presence of the plateau region at high acoustic pressures is unclear. One possible explanation could be that at high pressures the dense bubble population shields large volumes of the solution from the true acoustic field. This would cause a saturation mechanism to be triggered. However, further complementary evidence is unavailable at this time. The maximum rate of hydrogen peroxide is $\approx$120 $\mathrm{nmol\,dm^{-3}\,s^{-1}}$ under the conditions stated. This corresponds to 432 $\mathrm{nmol\,cm^{-3}\,h^{-1}}$, which can be compared to the maximum rate of 90 $\mathrm{nmol\,cm^{-3}\,h^{-1}}$ reported by Sato et al. [5]. However, direct comparison between the two results is difficult as they were performed under different experimental conditions. Nevertheless the results reported here show a factor of $\approx$5 increase in the rate of hydrogen peroxide production.

While monitoring the build up of hydrogen peroxide is interesting from a fundamental standpoint of understanding the sonochemistry within a particular reactor, it also has important industrial applications. One such example is the destruction of organic molecules [7,8,21,22]. Ultrasound is known to destroy organics through the generation of cavitation and the subsequent production of the extremely oxidising hydroxyl radical ($OH^{\cdot}$, redox potential +2.8 V [26]). However, the geminate coupling reaction forming hydrogen peroxide clearly removes two radicals for every hydrogen peroxide molecule produced. While this is a potential disadvantage, as the oxidising power of hydrogen peroxide alone is relatively low, destruction of organics using hydrogen peroxide can be efficient if catalysed with a

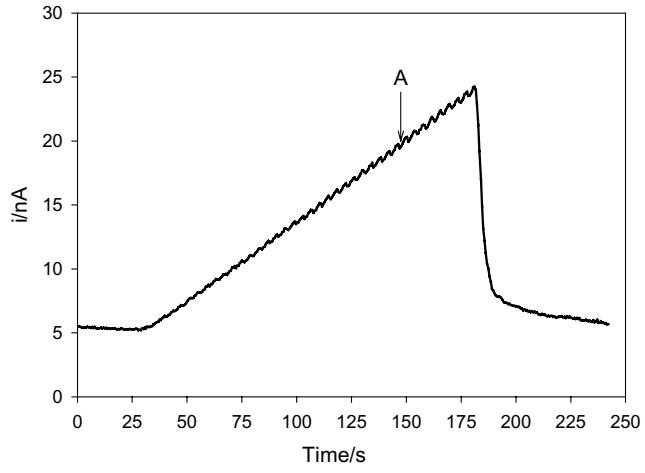

Fig. 4. Plot showing the current recorded as a function of time for the electrochemical detection of sonochemically generated hydrogen peroxide. The ultrasound was turned on at time $t = 0$ s. The potential of the electrode was held at +0.8 V vs. SCE. The ultrasonic frequency was 125 kHz and the voltage amplitude was 110 V corresponding to acoustic pressure amplitude of 2.45 bar. [1] An excess of catalase was added at 'A'.

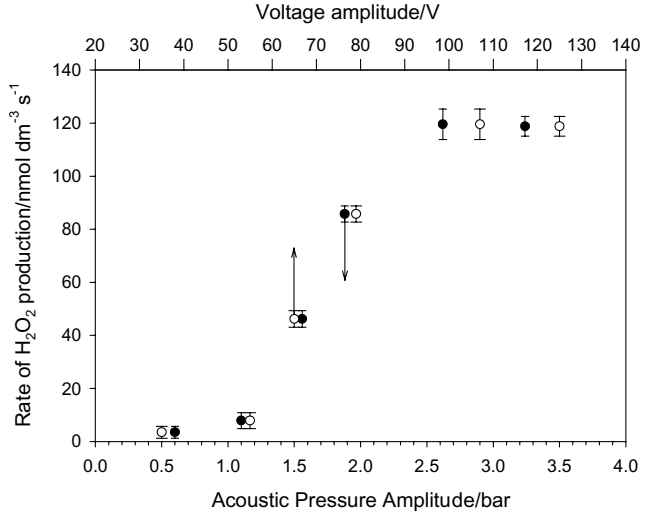

Fig. 5. Plot showing the rate of hydrogen peroxide production as a function of the acoustic pressure amplitude [1] (●) or drive voltage amplitude (○) at 124 kHz. Error bars represent one standard deviation calculated using repeat measurements.

suitable ion. One such system is the employment of Fe^{2+} to produce Fenton's reagent [22,27,28]. Fig. 6 shows the kinetic plot for the destruction of the dye (specifically amaranth) in the presence and absence of Fe^{2+}. Fig. 6 shows that ultrasound can remove the dye molecule from the solution with a rate constant of 2.23×10^{-3} min^{-1} (▲), assuming first order kinetics [29]. However, the addition of Fe^{2+} shows a dramatic increase of an order of magnitude in the rate of destruction of the dye

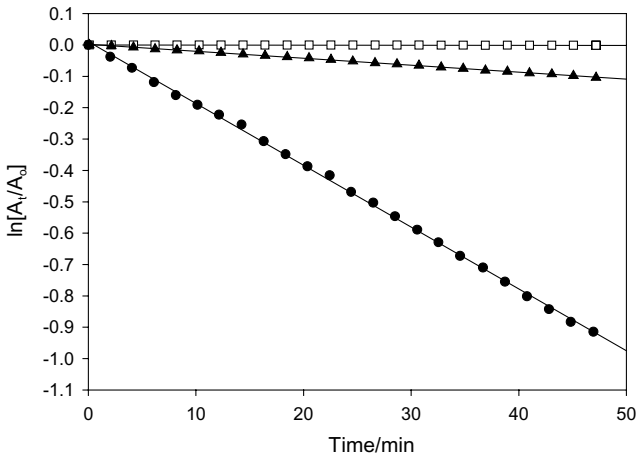

Fig. 6. Plots showing the variation of the normalised plots (considering first order kinetics) as a function of time for various treatment conditions. In each case a 100 cm^3 of an aerobic thermostated (25 °C) solution consisting of 0.1 mmol dm^{-3} amaranth, 50 mmol dm^{-3} Na_2SO_4 and 10 mmol dm^{-3} H_2SO_4 (pH 2) was employed. (□) represents no irradiation of the liquid, (▲) represents ultrasonic irradiation at 125 kHz (3.18 bar) while (●) represents ultrasonic irradiation at 125 kHz (3.18 bar [22]) in the presence of 0.5 mmol dm^{-3} $FeSO_4$.

molecule with an associated rate constant of 1.97×10^{-2} min^{-1} (●). This demonstrates that under the appropriate conditions, the hydrogen peroxide produced through ultrasonic irradiation of a liquid can be activated by the addition of Fenton's reagent thus improving the overall efficiency of the ultrasonic process. This is in agreement with previous studies on other dye systems [22,28].

4. Conclusions

The results presented here show that the production of hydrogen peroxide can be conveniently followed by an electrochemical flow cell technique. The highest rate of hydrogen peroxide generation occurred at 124 kHz under the conditions stated. A maximum rate of hydrogen peroxide production of 120 nmol dm^{-3} s^{-1} was recorded at an acoustic pressure amplitude [1] of 3.2 bar. The production of hydrogen peroxide can be utilised under the correct conditions to enhance the sonochemical degradation of the organic dye species amaranth with a maximum rate constant of 1.97×10^{-2} min^{-1}.

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References

[1] G.J. Price (Ed.), Current Trends in Sonochemistry, Royal Society of Chemistry, Cambridge, 1992;
T.J. Mason (Ed.), Sonochemistry: The Uses of Ultrasound in Chemistry, Royal Society of Chemistry, Cambridge, 1990.
[2] T.G. Leighton, The Acoustic Bubble, Academic press, London, 1994.
[3] H.M. Hung, M.R. Hoffmann, J. Phys. Chem. A 103 (1999) 2734.
[4] Y. Kojima, S. Koda, H. Nomura, Ultrason. Sonochem. 8 (2001) 75.
[5] M. Sato, H. Itoh, T. Fujii, Ultrasonics 38 (2000) 312.
[6] A. Francony, C. Petrier, Ultrason. Sonochem. 3 (1996) S77.
[7] C. Petrier, M.F. Lamy, A. Francony, B. David, J. Phys. Chem.—US 98 (1994) 10514.
[8] M.R. Hoffmann, I. Hua, R. Hochemer, Ultrason. Sonochem. 3 (1996) S163.
[9] C. Petrier, A. Francony, Water Sci. Technol. 35 (1997) 175.
[10] P.N. Bartlett, J.M. Cooper, J. Electroanal. Chem. 362 (1993) 1.
[11] L.Q. Mao, T. Sotomura, K. Nakatsu, N. Koshiba, D. Zhang, T. Ohsaka, J. Electrochem. Soc. 149 (2002) A504.
[12] P.R. Birkin, J.F. Power, T.G. Leighton, A.M.L. Vinçotte, Anal. Chem. 74 (2002) 2584.
[13] P.R. Birkin, J.F. Power, T.G. Leighton, J. Chem. Soc., Chem. Comm. (2001) 2230.
[14] P.R. Birkin, R. O'Connor, C. Rapple, S. Silva Martinez, J. Chem. Soc., Faraday Trans. 94 (1998) 3365.
[15] C.M. Preece, I.H. Hansson, Adv. Mech. Phys. Surf. 1 (1981) 199.
[16] G.O.H. Whillock, B.F. Harvey, Ultrason. Sonochem. 4 (1997) 23.
[17] J.C. Eklund, D.N. Waller, T.O. Rebbitt, F. Marken, R.G. Compton, J. Chem. Soc., Perkin Trans. 2 (1995) 1981.
[18] P.R. Birkin, T.G. Leighton, J.F. Power, A.M.L. Vinçotte, M.D. Simpson, P.F. Joseph, J. Phys. Chem. A, in press.
[19] P.R. Birkin, J.F. Power, A.M.L. Vinçotte, T.G. Leighton, Chem. Euro. J., submitted for publication.
[20] M.A. Beckett, I. Hua, J. Phys. Chem. A 105 (2001) 3796.
[21] A.M.L. Vinçotte, A frequency study of sonoluminescence and sonochemical activity, MPhil Thesis, University of Southampton, UK, 1999.
[22] M.E. Abdelsalam, P.R. Birkin, PCCP 4 (2002) 5340.
[23] R.M.C. Dawson, D.C. Elliott, W.H. Elliott, K.M. Jones, Data for Biochemical Research, third ed., Oxford Science Publications, Oxford, 1986.
[24] A.J. Bard, L.R. Faulkner, Electrochemical Methods—Fundamentals and Applications, John Wiley and Sons, New York, 1980.
[25] S.A.G. Evans, J.M. Elliott, L.M. Andrews, P.N. Bartlett, P.J. Doyle, G. Denuault, Anal. Chem. 74 (2002) 1322.
[26] H.N. McMurray, B.P. Wilson, J. Phys. Chem. A 103 (1999) 3955.
[27] A. Alverez-Gallegos, D. Pletcher, Electrochim. Acta 44 (1998) 853.
[28] J.M. Joseph, H. Destaillats, H.M. Hung, M.R. Hoffmann, J. Phys. Chem. A 104 (2000) 301.
[29] K. Kotronarou, G. Mills, M.R. Hoffmann, J. Phys. Chem. 95 (1991) 3630.