Sonovoltammetry at platinum electrodes: surface phenomena and mass transport processes

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Application of simultaneous ultrasound to representative solution-phase reversible voltammetric couples produce a step-shaped voltammogram at platinum electrodes of both 'macro' and 'micro' dimensions. The limiting current increases with ultrasonic power, but is not markedly affected by ultrasonic frequency in the 20–800 kHz region. In contrast the complex voltammetry of a platinized platinum electrode surface within the hydrogen adsorption regime in aqueous acid medium is very little affected by sonication. Factors affecting the reproducibility of sonoelectrochemical experiments when employing ultrasonic sources are discussed.

1. Introduction

In a continuing study into the simultaneous ultrasonic irradiation of electroorganic reaction systems we have observed a range of useful effects, including altered reaction pathway and product mix, enhanced chemical yields and current efficiencies, diminution of cell voltage and power requirements, minimization of electrode fouling and other procedural enhancements depending on the reaction system [1, 2]. These results have mainly concerned the electrooxidation of carboxylate anions (the Kolbe reaction) with ultrasound in the 20–60 kHz region and we have recently extended this study into the relative high-frequency region of 800 kHz, and have also examined the influence of ultrasonic power upon electrosynthetic systems [3].

We have also investigated the effect of ultrasound upon electrochemiluminescence, and have observed markedly enhanced quantum efficiencies from the ruthenium bipyridine and luminol systems [4] and also found previously-unreported electrochemiluminescence from arylacetate electrooxidation [5].

To underpin these results we report the influence of ultrasound upon model electroanalytical systems. The application of ultrasound within electrochemistry was first studied some time ago [6] and, for example, the effects of insonation upon mass transfer have been discussed [7]. There have been other studies on the

effects of mechanical agitation upon electroanalysis, for instance the development of vibrating-wire electrodes for polarography [8, 9]. There is also hydrodynamic modulation voltammetry [10]. Ultrasound is also well known to produce benefits in electroplating systems [11]; while the use of ultrasound to pretreat electrodes is also well known [12]. However, it is fair to say that reports on sonovoltammetry have been sporadic until very recently, when there has been an upsurge of interest [13–15]. The Kolbe reaction occurs most effectively at current densities above $100 \, \text{mA cm}^{-2}$ and is not amenable to traditional voltammetry. However, our synthetic studies have been performed at platinum electrodes, and to identify sonoelectrochemical phenomena that might be relevant to these results we have examined other representative test systems at platinum for our voltammetric studies. We now compare the behaviours under ultrasound of the well-known reversible solution-phase couples, ferrocyanide/ ferricyanide in aqueous medium, and ferrocene/ ferrocinium in acetonitrile, at conventional platinum wire electrodes and also at platinum microelectrodes (dimensions close to μm); and contrast this with the complex redox voltammetry of a platinized platinum surface in acidic media, in order to distinguish between the effects of ultrasound upon solution-phase and upon surface-immobilized processes. We also exploit recent developments in ultrasonic methodology to give preliminary results on the influence of ultrasonic power and frequency upon selected systems.

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2. Experimental

2.1. *Studies on platinum wires or microelectrodes*

Voltammetry of potassium ferrocyanide (30 mM) in aqueous nitric acid (0.5 M) at a platinum wire electrode (1 cm × 0.3 mm) was performed in a two-compartment cell with a platinum foil counter electrode (2 cm^2) and saturated calomel reference (SCE) electrode. Platinum electrodes were cleaned by heating to red heat and quenching prior to each experiment.

All reagents were of the highest grade available and solutions were degassed with nitrogen for 20 min prior to test, the gas was then passed over the solution surface during the experiment.

An EG&G model 173 potentiostat/galvanostat was employed, driven by a Thompson model DRG16 ramp generator outputting to a JJ Instruments PL1500 chart recorder. Scan rates employed were either 50 mV s^{-1} or 25 mV s^{-1} unless otherwise stated.

Ultrasound was provided by either a Walker ultrasonic bath (25 kHz and 24 W cm^{-2} fixed power output) or a K. W. Meinhardt high frequency bath (800 kHz, power output variable approx. 18 to 61 W cm^{-2}. The electrochemical cell was placed at various places in these baths to determine maximum cavitation prior to test. For the Walker bath the typical depth of liquid in the bath was 15 cm and the cell was immersed such that the platinum electrode was approximately 3 cm below liquid level. For the Meinhardt bath the cell fitted closely into the focussed resonant cavity, the electrode being some 4 cm below the liquid level. For both systems cooling was provided by circulation of water at a constant temperature of 5 °C. The ultrasonic power delivered into the reaction vessel was calculated calorimetrically [16]. In this method the electrochemical cell system was exposed to ultrasound for a fixed time without voltammetry, and the rise in temperature measured without cooling procedure.

Voltammetry of ferrocene (2 mM) in acetonitrile containing tetrabutylammonium perchlorate [TBAP] (0.1 M) was performed in a cell in which an ultrasonic horn was immersed in the solution of interest at a known distance, typically about 40 mm, above an electrode of a chosen (variable) radius ranging from 2.5 µm to 0.4 cm. Three separate horns were employed and were supplied by Heat Systems (model W380) and Sonics & Materials (models VC385 and VCX400) and were equipped with titanium tipped horn probes (of diameter 13 mm) extended by 127 mm and operating at 20 kHz. Power levels up to and including 63 W cm^{-2} were employed and calibrated calorimetrically [16]. Thermostatting of the electrochemical cell was accomplished by means of a copper cooling coil inserted in the solution through which water was circulated from a constant temperature bath. By limitation of the sonication time to less than one minute this arrangement enabled the voltammetric
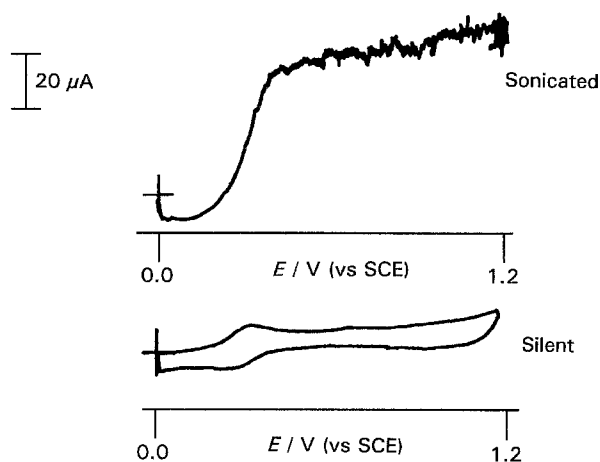

Fig. 1. Effect of ultrasound (38 kHz bath) upon the voltammetry at platinum wire (0.3 mm × 1.0 cm) of ferrocyanide (3 mM in 0.5 M HNO$_3$). Both traces are on the same current scale. Scan rate: 25 mV s^{-1}.

measurements to be conducted at constant temperature (estimated as within 2 °C).

Platinum microdisc electrodes were obtained from Bioanalytical Systems (West Lafayette, USA) and had radii of 2.5, 5.1, 13.6, 29.0 and 60.0 µm as measured electrochemically under steady state conditions. Macroelectrodes of radii 0.05, 0.1, 0.15, 0.21 and 0.39 cm were mounted in an insulating Teflon sheath. All electrodes were carefully polished before hand using diamond lapping compounds (Kemet, Kent, UK) of decreasing size down to 0.25 µm.

Voltammetric measurements were carried out using a Solartron 1286 electrochemical interface three-electrode potentiostat under computer control or an Oxford Electrodes potentiostat. The counter electrode was a carbon rod and a saturated calomel electrode acted as the reference.

Acetonitrile (Fisons, dried and distilled) was used with tetrabutylammonium perchlorate and ferrocene (used as received from Aldrich (99%)). Solutions were thoroughly purged of oxygen by bubbling through the solution argon that had been dried with calcium chloride and then presaturated with acetonitrile.

2.2. *Studies on platinized platinum*

Platinized platinum (1.0 mm diam. wire; Johnson-Matthey, Puratronic grade) of an exposed area of ~1 cm^2 was employed. This was platinized by
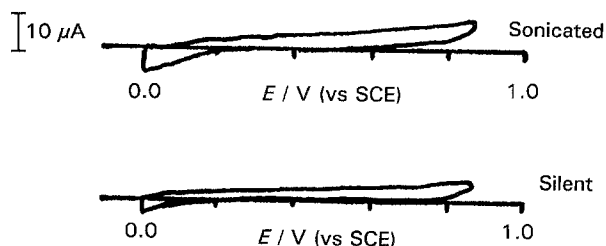

Fig. 2. Cyclic voltammetry of background electrolyte (as for Fig. 1) without redox species at platinum wire in the absence and presence of ultrasound (38 kHz bath). Scan rate: 25 mV s^{-1}.
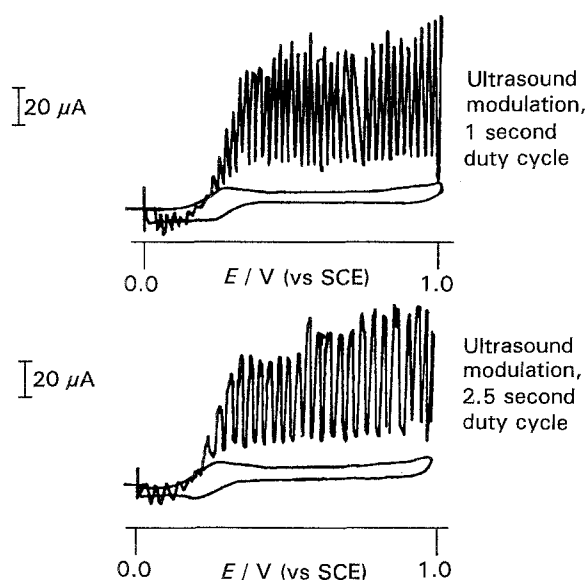
Fig. 3. Effect of superimposed modulation duty-cycle upon the insonation of ferrocyanide voltammetry. Conditions as for Fig. 1.

cathodizing at room temperature at a current density of $50\,mA\,cm^{-2}$ for 1 min in a solution containing 1 g of H_2PtCl_6 in 100 ml of 0.1 M HCl.

A Wenking model PG6881 potentiostat was employed for cyclic voltammetry and was programmed by a function generator (Metrohm VA scanner, model E612). Traces were recorded on a Rikadenki (RW-21) X–Y recorder. Ultrasound was provided by a Julabo USF ultrasonic bath (38 kHz and nominally $2 \times 150\,W$ output).

3. Results and discussion

Figure 1 contrasts voltammetry of potassium ferrocyanide at platinum wire in dilute aqueous nitric acid with and without ultrasound. Both scans are at $50\,mV\,s^{-1}$ sweep rate and are on the same current

scale. Ultrasound is provided by a sonic bath. The silent trace shows the typical shape of a reversible couple; while the insonated trace has the characteristic 'step' shape of a system at limiting current. This limiting current is some eight times greater than the diffusion-controlled maximum, confirming the greater sensitivity of ultrasonically-assisted voltammetry, already reported [10, 13, 14]. It is the faradaic component that is most affected by ultrasound, as shown in Fig. 2 where background scans in the absence of electroactive solute are compared with and without sonication (note magnified current scale).

An experimental sophistication is to superimpose a pulsed duty cycle upon the ultrasonic source. This has been previously reported as 'ultrasonic hydrodynamic modulation voltammetry' [10]. Many ultrasonic sources have inbuilt duty cycles, and this technique can also avoid the development of appreciable temperature differentials in the cell during scan. Control of duty cycle also provides an additional time-dependent variable, and we show this in Fig. 3 for two scans at $50\,mV\,s^{-1}$, one with an ultrasonic duty cycle of 1 s the other at 2.5 s, all other conditions being equivalent. We find that the limiting current is unaffected by duty cycle, and we also observe a minimum in the envelope at which the direction of current pulse inverts (here evident at about 1 V). This minimum has previously been tentatively connected to the potential of zero charge [10]. We intend to further investigate this phenomenon, which cannot be observed from the continuously-sonicated trace (Fig. 1), and requires imposition of a pulsed duty-cycle on the ultrasonic source. A useful practical benefit of imposing an ultrasonic duty-cycle is that it can help to clarify the limiting current value, which is not always straightforward to achieve during continuous sonication (vide infra, Fig. 10).
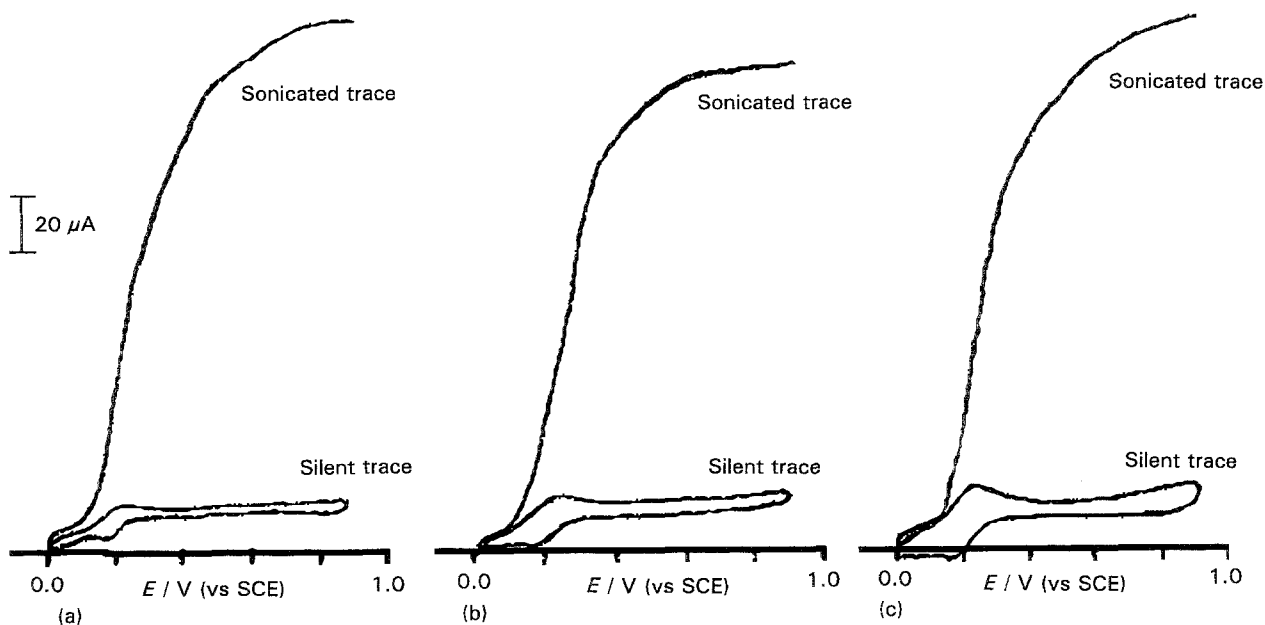
Ultrasonic irradiation has been shown to increase

Fig. 4. Scan rate independence of voltammetry of ferrocyanide (3 mM in 0.5 M HNO_3) at platinum wire (0.3 mm × 1.0 cm) under fixed insonation conditions (38 kHz bath) upon voltammetry. Both traces are on the same current scale. Scan rate: (a) 12.5, (b) 25 and (c) 50 mV s^{-1}.

the rate of mass transfer to the electrode thereby raising the limiting current density mainly by reducing the diffusion layer thickness [17, 18]. The limiting current at constant ultrasonic power should thus be independent of scan rate, and we show this to be so, over the scan rate regime of 12.5 to $50\,mV\,s^{-1}$, in Fig. 4, where insonation is again provided by a bath, the traces all being obtained at the same ultrasonic power level. The expected increase of i_{max} with scan rate of the silent system is included for comparison, on the same current scale. The scans were performed with a superimposed duty cycle of 1 s, (cf. Fig. 3), but currents shown are smoothed maximum values for each sonic pulse, the rest of the envelope being omitted for clarity.

Similar enhancements in limiting current were obtained from the ferrocene couple in acetonitrile at both macro and microelectrodes.

Figure 5 shows voltammograms obtained in the absence of ultrasound at disc electrodes of radius $13.6\,\mu m$ and $0.10\,cm$, respectively. The former has the characteristic sigmoidal shape expected from a microdisc electrode[19]. In contrast the macroelectrode displays the cyclic voltammogram expected for a reversible one-electron oxidation. In both cases the current/voltage waveshapes and magnitudes were consistent with the simple reversible process and provided a value of $D = 2.3 \times 10^{-5}\,cm^2\,s^{-1}$ for the diffusion coefficient of ferrocene in agreement with the literature value [20].

Figure 6 shows measurements analogous to those given in Fig. 5 except that 20 kHz ultrasound of intensity $44 \pm 5\,W\,cm^{-2}$ has been directed at the electrode surface with a horn electrode separation of 40 mm.

For the case of the microelectrode the mean transport limited current is somewhat enhanced as compared to the silent case (Fig. 5(a)) but the form of the voltammogram is otherwise unaltered except for the presence of a measured 20 kHz a.c. signal superimposed on the voltammetric wave (as discussed below). In contrast the macroelectrode response is qualitatively changed from that of a familiar cyclic voltammogram to a sigmoidal shape indicative of a constant rate of transport of the electroactive species to the electrode surface so as to sustain a steady current. Again a 20 kHz a.c. current was found to be imposed on the basic form of the voltammogram. This was also observed in the aqueous ferrocyanide voltammogram (cf. Fig. 1). The magnitude of the current in the sonicated trace is considerably greater than that of the peak current seen under silent conditions and would correspond to a rotation speed of approximately 200 Hz were the electrode rotated in the absence of ultrasound to achieve an equivalent steady-state current.

3.1. Effect of ultrasonic frequency

The preponderance of recent reports on sonoelectrochemistry have concerned ultrasound in the 20–60 kHz frequency region, due to the ready availability of laboratory ultrasonic baths. There is also a body of work into the medical effects of ultrasound at substantially higher frequencies in the region beyond 2 MHz; but there has been little study at relatively high powers in the frequency region in between. However, with recent availability of modern apparatus this region is now readily attainable, and in Fig. 7 we contrast the voltammetry of ferrocyanide in
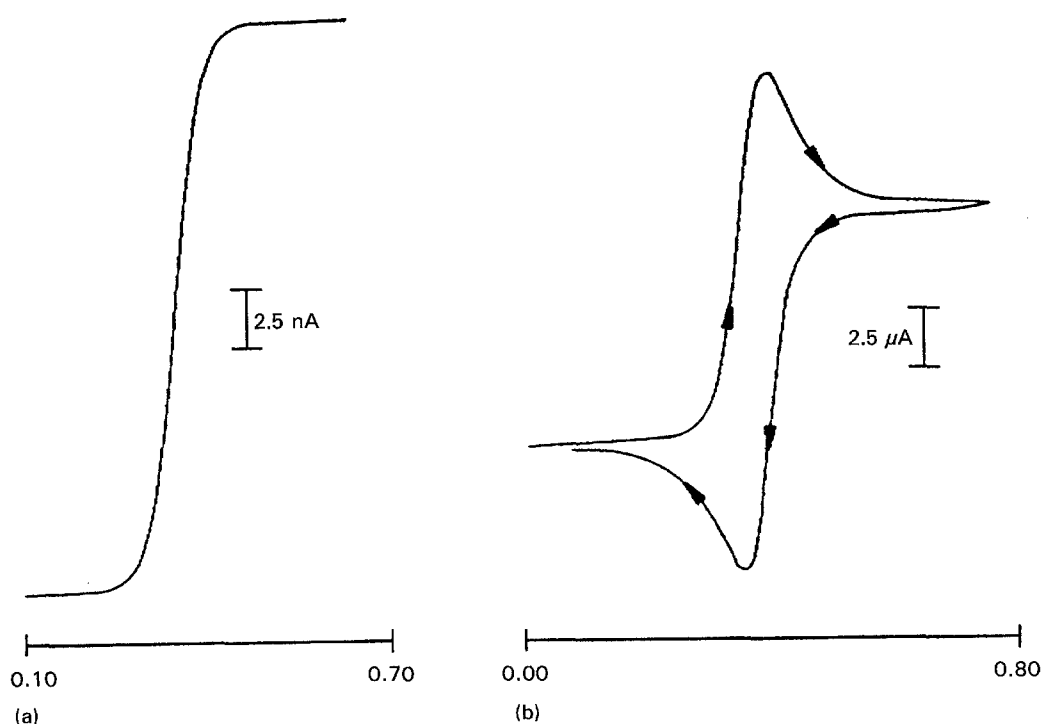

Fig. 5. Voltammograms recorded in the absence of ultrasound for the oxidation of Cp_2Fe (2.0 mM) in acetonitrile/0.1 M TBAP for (a) a microdisc electrode of radius $13.6\,\mu m$ and (b) a macro-electrode of radius 0.1 cm. In the latter case a voltage sweep rate of $20\,mV\,s^{-1}$ was used.
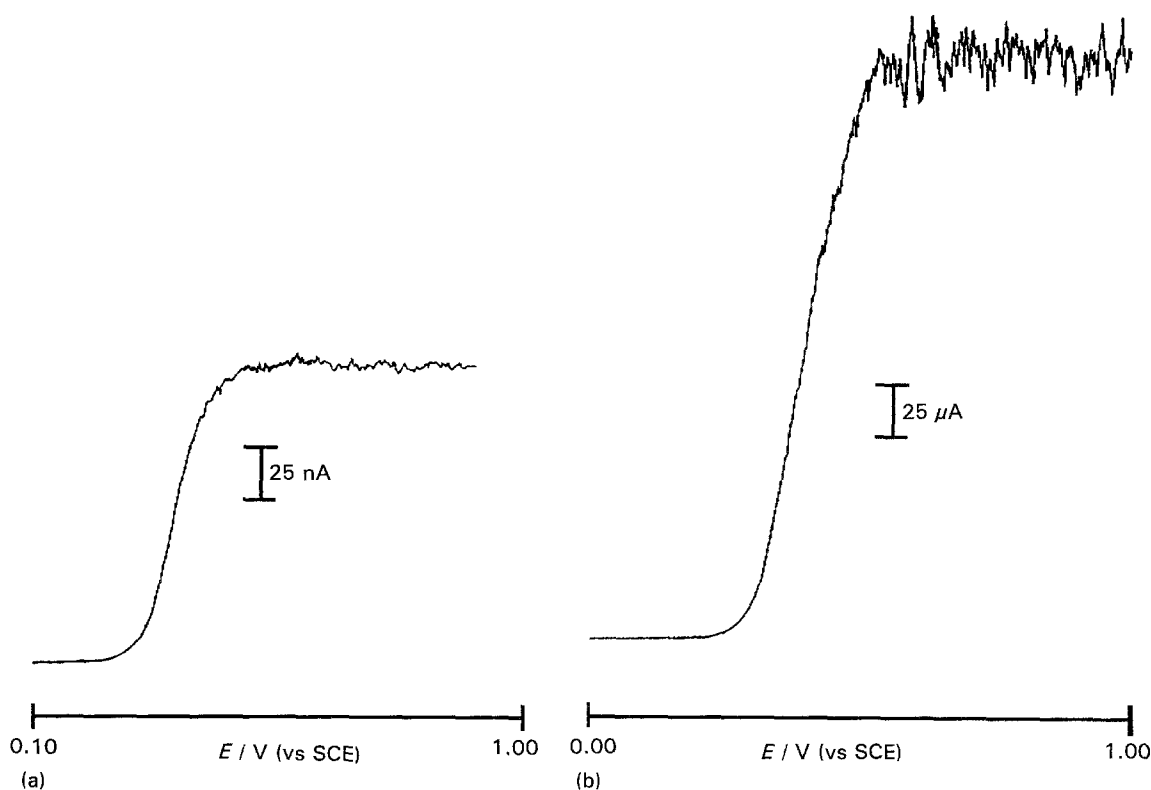
Fig. 6. Voltammograms recorded in the presence of ultrasound (20 kHz; intensity $44 \pm 5 \, \text{W cm}^{-2}$) for the oxidation of Cp_2Fe (2.0 mM) in acetonitrile/0.1 M TBAP for (a) a microdisc electrode of radius $13.6 \, \mu m$ and (b) a macro-electrode of radius 0.1 cm.

dilute aqueous solution under ultrasound at both 25 kHz and 800 kHz. Both experiments were performed at similar power levels (as indicated by the method of initial temperature changes [16]). However it should be noted that the two ultrasonic sources have different geometries, as do the electrochemical cells involved, but despite this the similarity in the sonicated traces is evident, at least in overall shape and in the limiting current value. It is seen that there is a shift in potential between the two traces, despite the thermodynamically reversible nature of the couple. We believe that the potential shift may reflect a combination of temperature effect upon the couple (despite external cooling, localized temperature effects are well known in sonochemistry) with perhaps some measure of reaction introduced by ultrasonic generation of hydroxyl radicals in aqueous solutions. These can chemically oxidize ferrocyanide anions. We

are further studying this frequency effect upon half-wave potentials [21]. The similarity of voltammetric behaviour at 25 and 800 kHz mirrors a similarity of frequency effect upon electrosynthetic experiments [3], where if anything, the electrooxidation of cyclohexanecarboxylate is enhanced at the higher frequency. This throws into question the role of cavitation in sonoelectrochemical phenomena, since cavitation processes vary across the 32-fold frequency range [16]. An expression for the enhanced diffusion leading to increased limiting current has been proposed [22] involving three dimensionless terms, amplitude number, diffusion length number, and cavitation damping number; but our frequency results show that the limiting current is not markedly dependent on frequency over the range examined.
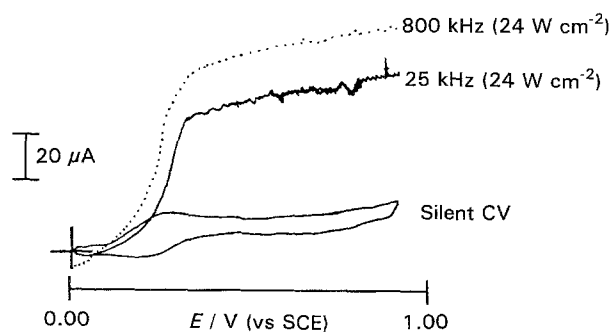

Fig. 7. Effect of ultrasonic frequency (at fixed power, from 800 kHz bath and 25 kHz probe sources) upon ferrocyanide (30 mM in 0.5 M HNO_3) on voltammetry at platinum wire (0.3 mm × 1.0 cm).
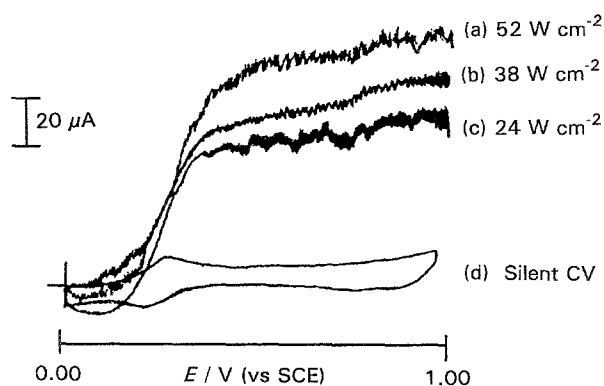

Fig. 8. Effect of ultrasonic power (at fixed frequency 800 kHz) upon ferrocyanide voltammetry at platinum wire (0.3 mm × 1.0 cm). Scan rate $50 \, \text{mV s}^{-1}$. Other conditions as for Fig. 1.

3.2. *Effect of ultrasonic power*

A more significant factor upon the limiting current is the ultrasonic power at fixed frequency. Figure 8 shows the ferrocyanide/ferricyanide couple in aqueous HNO_3 at a platinum wire electrode at three different power levels (compared by the method of initial temperature change) at 800 kHz frequency insonated from a bath, all other factors remaining constant. A steady increase in limiting current is observed with increasing power, within the range studied.

This is supported by results at lower frequency from the ferrocene/acetonitrile system at platinum macroelectrodes directly insonated by a 20 kHz horn, at variable ultrasonic power levels. The limiting currents were used to infer a mean diffusion layer thickness, z^*, from the following equation:

$$I = D\pi r_e^2 F[Cp_2Fe]_{bulk}/z^*$$

where D is the diffusion coefficient of ferrocene, r_e the electrode radius and F is the faradaic constant. Figure 9 shows the inferred relationship between z^* and the incident power (p). It can be seen that, as would be anticipated, greater power causes increased mass transport due to enhanced cavitation leading to a greater thinning of the diffusion layer and thus a reduced value of z^*. It was estimated that the diffusion layer thickness correlated empirically with $p^{-0.6}$. A more extensive account of this derivation is in hand [23].

3.3. *Effect of system geometry and ultrasonic source characteristics upon voltammetry of solution-phase electroactive species*

Some difficulty has been mentioned above in the obtaining of noise-free steady limiting currents, and hence meaningful potential data from sonicated voltammetry of solution-phase systems. This makes comparison difficult between data from different ultrasonic sources and different cell and electrode geometries. Of particular importance is the need for comparable powers since this parameter markedly

affects the limiting current. This is not straightforward since the power received in the electrode region may not reflect the rated power output of the sonic source. Quantification of actual power delivered to a reaction site remains a persistent problem in all sonochemical studies. Simplistically, using an ultrasonic bath as source, and noting the transducer geometry, which usually but not always is in the base pointing upwards, other factors will modulate the power reaching the electrolysis cell. For example, cell shape, position in the bath, thickness and density of construction material are all important, as are damping characteristics in cell and electrode support system.

This phenomenon is demonstrated in Fig. 10, which shows voltammetry of ferrocyanide in dilute aqueous hydrochloric acid at platinized platinum. The cell is a beaker, ultrasound is provided by a Julabo sonic bath and here the reference electrode was a normal hydrogen electrode separated from the cell by a salt bridge in a plastic tube to minimize vibrational transmission. Despite these precautions it proved impossible to obtain a meaningful limiting current, and the sonicated trace resembled the trace obtained under simple stirring by rapid bubbling of nitrogen through the cell, also shown. As a rule of thumb, if nitrogen bubbling gives a similar current increase as does insonation, then the experimental setup is not producing effective coupling of ultrasonic power. True sonoelectrochemical enhancement provides considerably higher limiting currents (cf. Figs 1, 5 and 6).

It may be that too much ultrasonic power causes a problem, since the results at different powers given in Fig. 8 all involve backing-off the 800 kHz source from its maximum power to lower levels, where it would seem that more effective coupling of ultrasound occurs. It may also be that the setup employed for Fig. 10 has inappropriate cell geometry as it is evident that a number of factors can influence any particular system. This is known to sonochemists but should
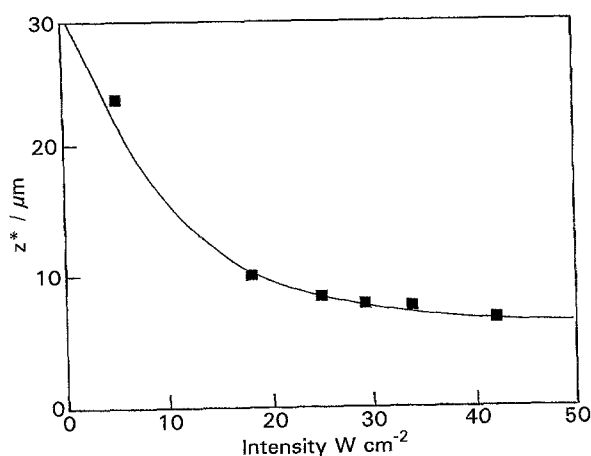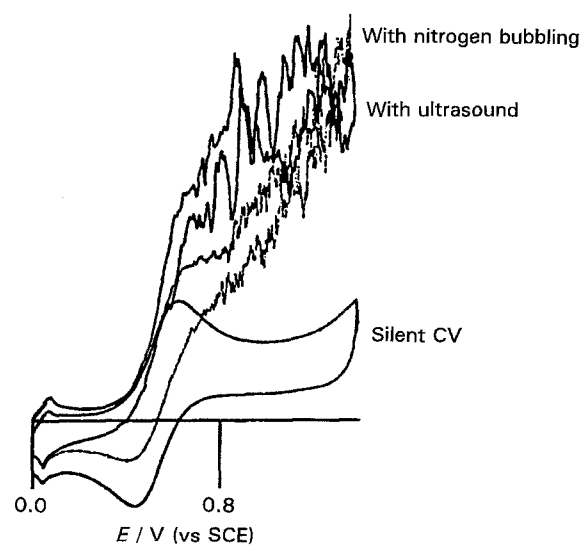

Fig. 9. The variation of the diffusion layer thickness with the intensity of the incident ultrasonic power at macroelectrodes of radius of 0.39 cm, as inferred from the voltammetry of Cp_2Fe.

Fig. 10. Voltammetry of ferricyanide (30 mM in 0.1 M HCl) at platinum wire (0.3 mm × 1.0 cm) at a scan rate of 50 mV s^{-1}. Comparison of silent system, the stirring of solution by bubbling nitrogen, and under insonation from 38 kHz bath.

also be noted by sonoelectrochemists, particularly when making comparisons between results obtained using different ultrasonic sources.

3.4. Effect of ultrasound upon surface electrochemistry at platinized platinum

The above results all demonstrate the marked effect that even lower powers of ultrasound have upon transport controlled voltammetry. We have also examined the effect of sonication upon the relatively-complex redox events at platinized platinum in aqueous acidic medium. The results are given in Fig. 11. Here there is very little difference between the silent and the sonicated traces, despite use of a powerful ultrasonic bath and alteration of cell geometry and position relative to the sonic source, in order to maximize power uptake.

In the hydrogen adsorption region the electrochemistry is dominated by surface effects predicated upon the strong adsorption of hydrogen atoms on platinum [24]. Here enhanced mass transport in solution will not affect rate-determining processes.

Arguably the most notable difference under ultrasound concerns the small peak at +200 mV in the oxidation scan in the hydrogen adsorption region (Fig. 11). There is some discussion about the significance of this feature in the literature of silent platinum voltammetry [25], and the effect of ultrasound here may help to clarify matters.

It is also noticeable that the current in the double-layer region (from +400 to +700 mV during oxida-

tion) appears lower under ultrasound, and there is a small but perceptible current increase at +600 mV. This region is thought to have implications for electro-catalysis at platinum [26].

The situation is further complicated by the formation of surface monolayer oxides (via hydroxy radicals or other adsorbed oxo-species) during the oxidation scan [24]. However, it would seem that ultrasound does not sufficiently perturb the system to produce a significant effect, even though too high ultrasonic power in appropriate conditions may physically abrade away the platinum surface. We intend to support this study by examining sonicated platinum electrode surfaces by atomic force microscopy and other appropriate techniques to identify possible surface modifications [27].

4. Conclusions

Even quite low power levels of ultrasound in the 20–800 kHz frequency range markedly affect the voltammetry of a solution-phase redox species, here exemplified by the ferrocyanide/ferricyanide couple in dilute aqueous acid medium and ferrocene in acetonitrile both at platinum. The result is a character-istic 'step'-shaped voltammogram leading to an enhanced limiting current at both macro and micro-electrodes. This limiting current increases with increas-ing ultrasonic power at fixed frequency; but does not significantly alter with frequency at fixed power, at least over the frequency range from 25 to 800 kHz.

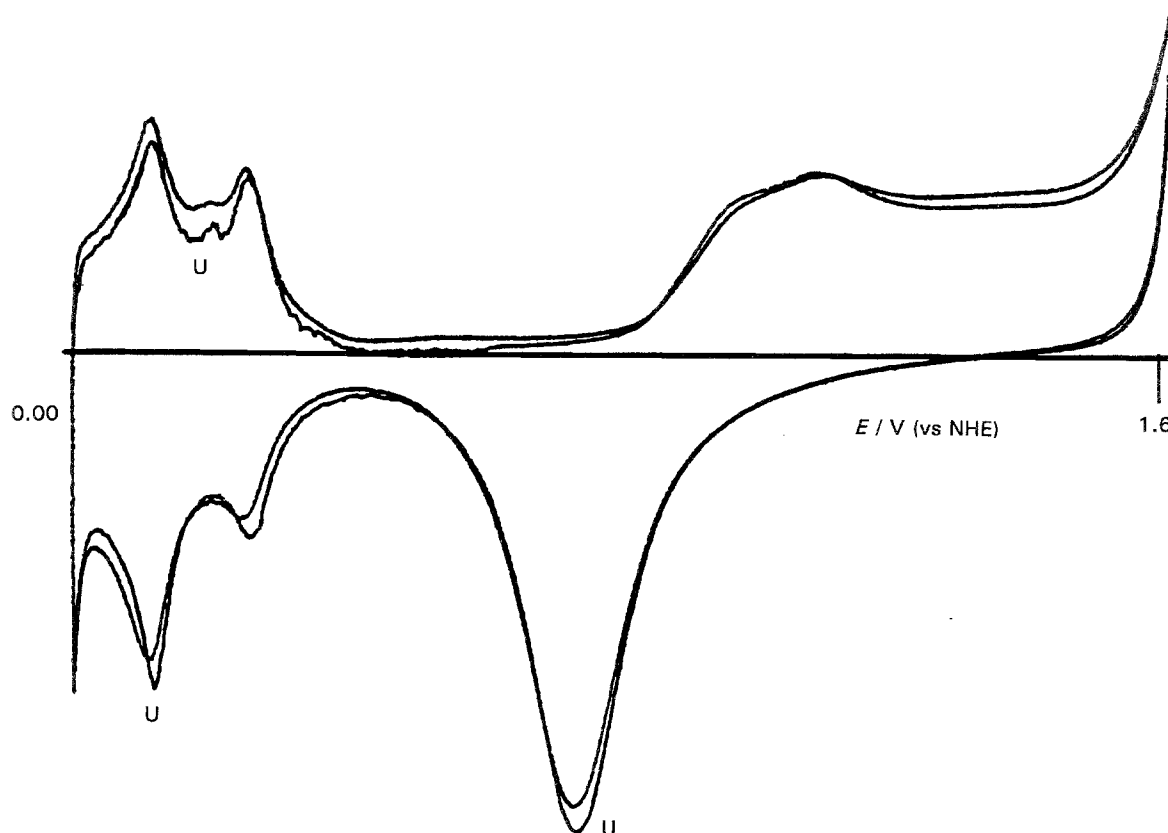The geometry and configuration of the ultrasonic

Fig. 11. Cyclic voltammetry of platinised platinum in 1.0 M H_2SO_4, in presence (U) and absence of ultrasound from 38 kHz bath. Scan rate: 50 mV s^{-1}.

system and of the electrochemical system both affect the voltammetry and careful control of all parameters is necessary if comparison between results is to be made. The superposition of a pulsed duty-cycle upon the ultrasonic source can help to clarify the limiting current value, and helps to avoid the buildup of microscopic temperature differentials within the cell during slow scans.

Within the limits of experimentation in this report there appears to be an observed shift in potential with ultrasonic frequency between 25 and 800 kHz for ferrocyanide oxidation in acidic medium at a platinum wire undergoing sonication.

In contrast, the voltammetry of surface-immobilized species is much less affected by ultrasound. The complex voltammetry of platinized platinum in aqueous acid throughout the normal potential range is little altered by sonication at 38 kHz, but such changes as are observed may prove meaningful in platinum electrochemistry.

A consequence of this work is that it is now possible to differentiate between the peaks in a complex voltammogram that are diffusion controlled from those that involve surface phenomena, simply by contrasting silent and sonicated scans.

Acknowledgements

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