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# INFLUENCE OF ULTRASOUNDS IN ELECTROCHEMICAL PROCESSES

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***ABSTRACT.*** Sonoelectrochemistry is an emergent and interdisciplinary field of research which couples the power of ultrasound to electrochemical systems in order to both achieve and develop new process and allow their measurement and quantification in combination with ultrasound associated reaction kinetics. The present review focuses on the influences of ultrasounds on mass transport at the electrode, induced surface electrode effects and electrode processes. Based on the tools and methods now available it is hoped that the application of ultrasound in areas as diverse as electroanalytical and synthetic electrochemistry will be beneficial and new innovative approaches employing the various mechanical and chemical effects of ultrasound will result.

## Introduction

Ultrasound is defined as sound of a frequency beyond that to which the human ear can respond. The normal range of hearing is between 16 Hz and about 18 kHz and ultrasound is generally considered to lie between 20 kHZ to beyond 100 MHz. Sonochemistry uses frequencies between 20 KHz and 2 MHz.

Like all sound energy, ultrasound is propagated *via* a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. At sufficiently high power the rarefaction cycle may exceed the attractive forces of the molecules of the liquid and cavitation bubbles will form. These bubbles will grow over a few cycles taking in some vapour or gas from the medium to an equilibrium size which matches the frequency of bubble resonance to that of the sound frequency applied. The acoustic field experienced by the bubble is not stable because of the interference of other bubbles forming and resonating around it. As a result some bubbles suffer sudden expansion to an unstable size and collapse violently. It is the fate of these cavities when they collapse which

generates the energy for chemical and mechanical effects. Each cavitation bubble acts as a localised microreactor which, in aqueous system, generates temperature of several thousand degrees and pressures in excess of one thousand atmospheres.

In addition to the generation of extreme conditions within the bubble there are also major mechanical effects produced as a result of its rapid collapse.

An empirical classification of sonochemical reactions based upon purely chemical effects induced by cavitation was proposed by J.-L. Luche [1]:

- Homogeneous systems which proceed *via* radical or radical-ion intermediates. This implies that sonication is able to affect reactions proceeding through radicals and further that it is unlikely to affect ionic reactions [2-5].
- Heterogeneous systems proceeding *via* ionic intermediates. Here the reaction is influenced primarily through the mechanical effects of cavitation such as surface cleaning, particle size reduction and improved mass transfer [6,7].
- Heterogeneous reactions which include radical pathway or a mixed mechanism *i.e.* radical and ionic. Radical reactions will be chemically enhanced by sonication but the general mechanical effect referred to above may well still apply. If the radical and ionic mechanisms lead to different products, ultrasound should favour the radical pathway and this could lead to a switch in the nature of the reaction products [2,8-10].

It was observed that if cavitation bubbles are formed at or near to any large solid surface (heterogeneous systems), the bubble collapse will no longer be symmetrical. The large solid surface hinders liquid movement from that side and so the major liquid flow into the collapsing bubble will be from the other side of the bubble. As a result of this a liquid jet will be formed which is targeted at the surface with speeds in excess of 100m $s^{-1}$. Depending upon the conditions used this powerful jet can activate surface catalysis, force the impregnation of catalytic material into porous supports and generally increase mass and heat transfer to the surface by disruption of interfacial boundary layers [11].

Coupling of power ultrasound to electrochemical systems leads to an emergent and interdisciplinary field of research *sonoelectrochemistry.* Sonoelectrochemistry may be compared to other synergistic approaches in which two independent sources of energy or activation are coupled. The result is a new powerful metodology for the study of each source of activation on its own but furthermore capable of the detection of new processes induced by dual activation [12]. The particular advantages of the sonoelectrochemistry include:

*(a)* degassing at the electrode surface,

*(b)* disruption of the diffusion layer which reduces depletion of electroactive species,
*(c)* improved mass transport of ions across the double layer and
*(d)* continuous cleaning and activation of the electrode surfaces.

All of these effects combine to provide enhanced yield and improved electrical efficiency.

## 2. The Influence of Ultrasound on Mass Transport at the Electrode

As stated in the introduction, the application of ultrasound to a solution may drastically increase the rate of mass transport of material to a solid surface. Mass transport is a very important aspect of electrochemical processes as well as heterogeneous processes in general. Many heterogeneous reactions proceed under mass transport control and the variation of the flux of material transported to and from an interface has been reported to cause in some cases a “switching” to a different reaction pathway [8, 13]. The corresponding parameter describing the mass transport in electrochemistry is the diffusion layer thickness, $\delta$, which can be used intentionally to control the nature of a chemical process [14].

The use of the diffusion layer thickness is based on the diffusion layer model [15] which allows an approximate description of the mass transport at the electrode-solution boundary by assuming a laminar sublayer close to the surface and an approximately linear concentration gradient across a thin layer adjacent to the electrode. Using this simple concept, the mass transport to the electrode is described by the equation (1):

$$I_{lim} = nFDA\,(c_{bulk} - c_{surface})/\delta \qquad (1)$$

where: n = the number of transferred electrons, F = the Faraday constant, D = the diffusion coefficient, A = the electrode area, c = the concentration, $\delta$ = the diffusion layer thickness.

Figure 1 shows two voltammograms of which the first was obtained in the absence (a) and the second in the presence (b) of ultrasound at Pt disk electrode for the oxidation of $Cp_2Fe$ ( $Cp = \eta\text{-}C_5H_5$ ) in acetonitrile [16].

The transport limited current is significantly enhanced as compared to the silent case, and the form of voltammogram 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 an, in average, steady current. The magnitude of the current is considerably greater than that of the peak current seen under silent conditions.

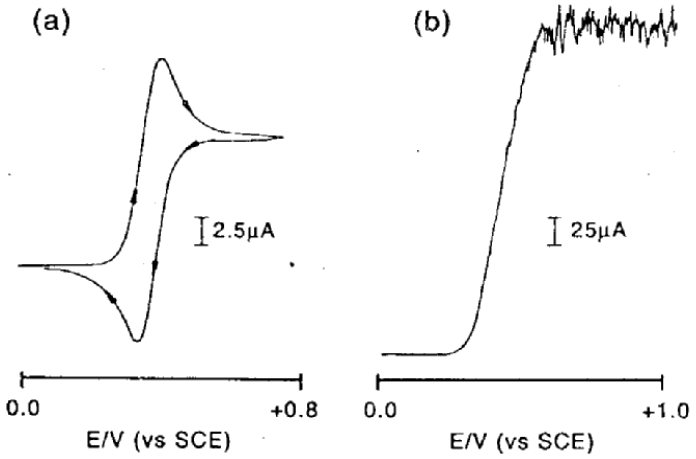



Figure 1. a) Cyclic voltammogram and b) sonovoltamogram (20 kHz, power 50 W $cm^{-2}$, distance 40 mm) for the oxidation of 2 mM ferrocene in acetonitrile (0,1 M $NBu_4ClO_4$), at Pt-disk electrode (2mm diameter); v = 20 mV $s^{-1}$ [24].

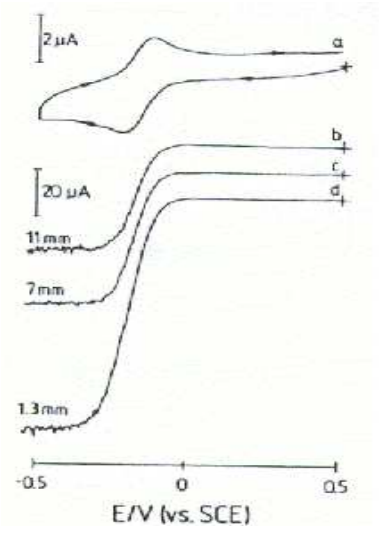



Figure 2. Voltammograms for the reduction of 0,23 mM $Ru(NH_3)_6^{3+}$ in aqueous 0,1 M KCl obtained at $22^0$ C using a 2mm diameter Pt electrode under (a) silent condition (scan rate 50 mV $s^{-1}$), and in the presence of ultrasound (scan rate 20 $mVs^{-1}$, ultrasonic power 30 $Wcm^{-2}$), (b) 11, (c) 7, (d) 1,3 mm electrode-horn separation [17].

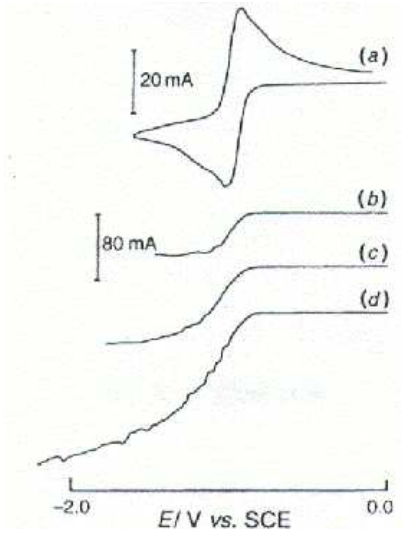



Figure 3. Voltammograms for the reduction of 5 mM $CoCp_2(PF_6)$ at a 23,8 $mm^2$ area glassy carbon plate electrode in acetonitrile (0,1M $NBu_4PF_6$) at $25^0C$; (a) silent condition (scan rate 100mV $s^{-1}$),and in the presence of ultrasound (scan rate 100 $mVs^{-1}$, ultrasonic frequency 20 kHz), (b) 6, (c) 18, (d) 30 W $cm^{-2}$ ultrasonic power [18].

The sonocurrent is found to increase as the electrode-horn tip separation is reduced (fig. 2) and the magnitude of the ultrasonic intensity applied to the system is increased (fig. 3). “Steady state” sonovoltammograms shown in figs. 2(b)-(d) exhibit slopes of 60 mV in mass-transport-corrected Tafel plots (plot of $\log[1/I - 1/I_{lim}]$ versus E [19]), in agreement with fast electron transfer. From the limiting current, $I_{lim}$, the diffusion layer thickness, $\delta$, for this reaction may be determinate [20] using Eq. (2):

$$\delta = nFc_bDA/I_{lim} \quad (2)$$

where $D = 9{,}1 \cdot 10^{-6}$ $cm^2\,s^{-1}$ , was independently determined by rotating disk voltammetry.

The fact that no irreversible signal occurs even at average diffusion layer thicknesses down to 0,65 μm (corresponding to an electrode horn distance of 1,3 mm) allows a lower limit for the apparent standard rate constant for heterogeneous electron transfer, $k_0$ to be estimated (using $k_0 > D/\delta$) as $k_0 > 0{,}14$ cm $s^{-1}$.

Commonly, the electrode material, the electrode pre-treatment and the solution environment strongly influence the rate of heterogeneous electron transfer [21-23].

The enhancement of the mass transport is very dependent upon the geometry of the ultrasonic horn relative to the electrode surface. It have been studied three alternative geometries (fig. 4) [24]:

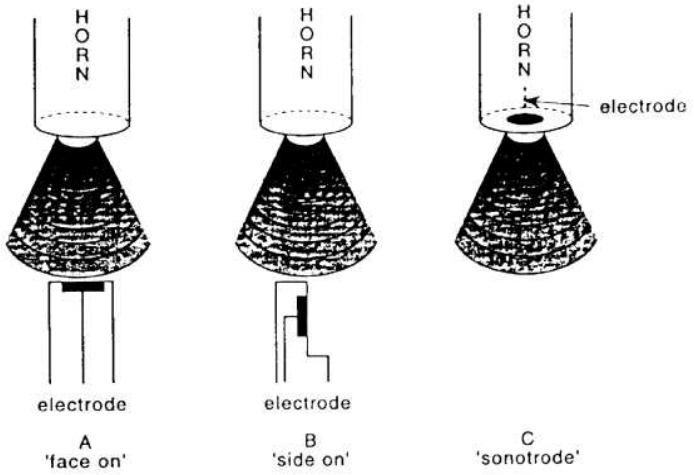



Figure 4. Types of electrode geometries used in sonovoltammetric experiments

- the conventional or “face-on” geometry,
- the “side-on” electrode geometry with the electrode placed perpendicular to the tip of the ultrasonic horn with the centre of the electrode at the

same separation from the tip as the surface of the electrode in the "face-on" geometry,

- "sonotrode" - the actual tip of the ultrasonic horn may be used as the working electrode directly or after insertion of an isolated metal disk.

In the "side-on" case, the mass transport of material to the electrode could be crudely modelled as the flow of material over a metal plate embedded in a nonconducting surface, a problem which has been treated by Levich [25]. In this case, the diffusion layer is nonuniform, its thickness being proportional to the square root of the distance along the electrode. The fact that a model using an intensity dependent flow over the electrode surface could be used successfully implies that acoustic streaming, a process induced by intense sound waves in which a macroscopic jet of liquid originating from the sound source is formed, is governing the mass transport properties in this experimental arrangement [26, 27]. In these cases, the diffusion layer thickness was empirically found to be dependent on the diffusion coefficient following a $\delta \propto D^{1/3}$ law. This result is in marked contrast to the dependence observed in acetonitrile solutions in which the diffusion layer thickness was found to be independent of the diffusion coefficient. The empirically observed non linear dependence is in agreement with a whole range of other "classical" hydrodynamic techniques [28], as well as with turbulent voltammetry [29] and the behaviour predicted by Perusich [30] all of which rely on a convective flow of liquid past on electrode surface. The individual contribution of the macroscopic jet and, on the other hand, of the microjets induced by cavitation may depend on the experimental conditions, but the use of an immersion horn appears to strongly favour the contribution from macroscopic turbulent streaming.

In the third and last case of alternative electrode geometries, the titanium alloy tip surface of the ultrasonic horn can be used directly, as described by Reisse et al. [31] for the case of an immersion horn with tip being connected to the potentiostat. In general it was found that this "sonotrode" design vastly improved the yield and current efficiency for the reduction of $Cu^{2+}$ to Cu, however in the case of the titanium immersion horn [31] details of the nature of the electrode process are not clear and background processes as hydrogen evolution may occur. The work conducted on a similar system by Compton et al. [32] suggested that the "sonotrode" surface consisted of a $TiO_2$ containing layer with the characteristic properties of an n-type semiconductor. The voltammograms observed for the reduction of $Cu^{2+}$ were only slightly effected by insonation and it was suggested that under these conditions the observed electrode current was not mass transport limited. Further, in the electrochemistry of a number of simple electron transfer systems (i.e., the reduction of ferricyanide, the oxidation of 1,4-N,N,N',N'-tetramethyl-phenylenediamine) was found a change in the reversibility of the simple reductive electron transfers and no voltammetry was observed for the oxidative systems in accord with the electrode surface behaving like an n-type

semiconductor. Using a modified sonotrode - a Pt electrode inserted into the tip of ultrasonic horn - it was found that even for low powers this system was restricted to huge enhancements in the rate of mass transport of the electroactive material to the Pt electrode surface for the oxidation of ferrocene (in acetonitrile) and the reduction of benzoquinone (in water) [24].

In summary it can be stated that ultrasound enhances the mass transport of electroactive material to an electrode surface. This enhanced mass transport can, for the case of the "face-on" geometry, simply be described by a thinning of the diffusion layer. The enhancement of the mass transport is very dependent upon the geometry of the ultrasonic horn relative to the electrode surface. A good approximation of the effect of ultrasound on the mass transport at the electrode surface, is possible by considering only the effect of "acoustic streaming" and by treating the system similar to related cases in hydrodynamic voltammetry [33, 34].

## 3. Ultrasound Induced Surface Effects

Effects of ultrasounds on heterogeneous processes include most notably erosion at solid surfaces induced by asymmetric cavitation close to a solid-solution interface [35, 36]. This process is thought to be responsible for the damage to the surface as well as for cleaning the surface of particles and adherent films.

There is a wide range of ex-situ and in-situ methods available for the investigation of surface properties. First of all microscopy allows the detailed study of changes in the surface morphology caused by ultrasound [37, 38]. Electrochemical AC impedance methods are well suited for in-situ monitoring of changes in surface roughness and capacitance [38].

Different types of damages were observed for glassy carbon and gold electrodes after a period of ultrasound treatment in 0,1 M NaOH [37, 38]. After 30 min. of ultrasound (20 kHz, 60 $Wcm^{-2}$ ) treatment the atomic force microscopy of a gold surface shows a roughening in the 10 μm scale, as well as in a smaller scale with little (ca. 0,1 μm) sized pits. Under similar conditions, the glassy carbon electrode surface shows cracks caused by high amplitude vibrations. This kind of severe damage occurs only after a prolonged treatment with high intensity ultrasound at a close distance between electrode and immersion horn. Voltammetric experiments, however, require shorter periods of time and usually a lower sound intensity with much more subtle changes in the surface properties.

The study of a platinum electrode surface in acetonitrile solutions and of aluminium and nickel electrodes in aqueous environments [37] also demonstrated the destructive effect of sonication which is possibly in most cases attributable to cavitational collapse of bubbles close to the surface. In figure 5 cyclic voltammograms for the oxidation of a nickel electrode immersed in aqueous 1M KOH are shown. In the presence of ultrasound,

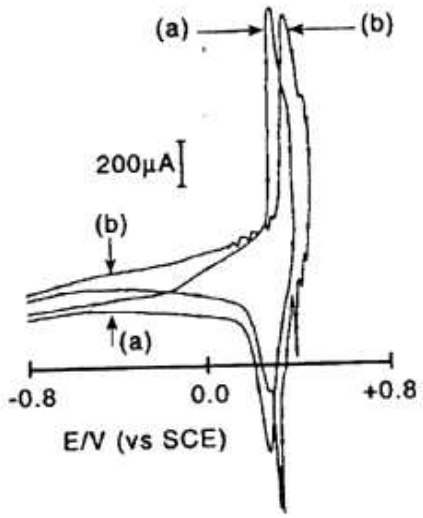



Figure 5. Cyclic voltammograms for the oxidation of a nickel electrode in 1M aqueous KOH solution a) in the absence and b) in the presence of ultrasound (20 kHz, 60 $Wcm^{-2}$, scan rate 100 $mVs^{-1}$)

the magnitude of the observed current and the overall shape of the signal apart from added current fluctuations remains unchanged, consistent with surface confined processes independent of mass transport in the solution phase. The potential shift, up to 60 mV, towards more anodic potentials - depending on the applied ultrasound intensity - may be attributed to ultrasound causing an effect, such as surface cleaning, which could compete with the film growth. Alternatively, a local change of the temperature may also be considered due to direct cavitation on the surface of the electrode.

An other example for ultrasound affecting electrode properties and surface confined electrode processes is presented in figure 6 [24]. In the presence of ultrasound the oxidation process proceeds with a higher current whereas the reduction process is split into two signals. Further, in the presence of ultrasound at elevated temperature ($50^0C$) a massive change occurs with high anodic currents being detected even on the reverse scan. In figure 6f, the presence of a cathodic process can only be assumed from the presence of a small peak superimposed onto the oxidation response which is caused by a ultrasonically enhanced gold depassivation process. Three potential regions may be identified corresponding to the processes at the gold electrode with an inert region at lower potential, a corrosion region in which gold dissolution is possible, and a passivation region at very positive potentials.

Further examples for the cleaning effect of ultrasound have been given for the electrode poisoning by $Cr(CO)_6$ by Compton et al. [37] and for the case of the formation of a polymer film [39-42].

Coury has shown that sonication of an insulating polymer film prepared by electropolymerisation of o-phenylendiamine results in the formation of a microarray electrode [39]. This effect is explained on the

basis of microjetting, i.e. the microjets of solution are pitting microscopic holes through the insulating film. Another example of the formation of a microarray electrode by sonication of the electrode covered by a passivating film is presented by Klima [42]. Their study of sonassisted electroxidative polymerisation of salicylic acid shows that whereas all the acoustic streaming, turbulence of solution and microjetting, can accelerate electrochemical processes by mass transfer enhancement, only the last one, i.e. microjetting, can reactivate the electrode covered by passivating polymeric film. Consequently, as the microjets are connected with transient collapses, the electrode reactivation can be observed only in the points in the cell with high acoustic intensity where transient cavitation takes place, whereas the acoustically induced increase of electrochemical current can be observed even at an electrode in areas in the cell with lower acoustic intensity where no transient cavitation is present.

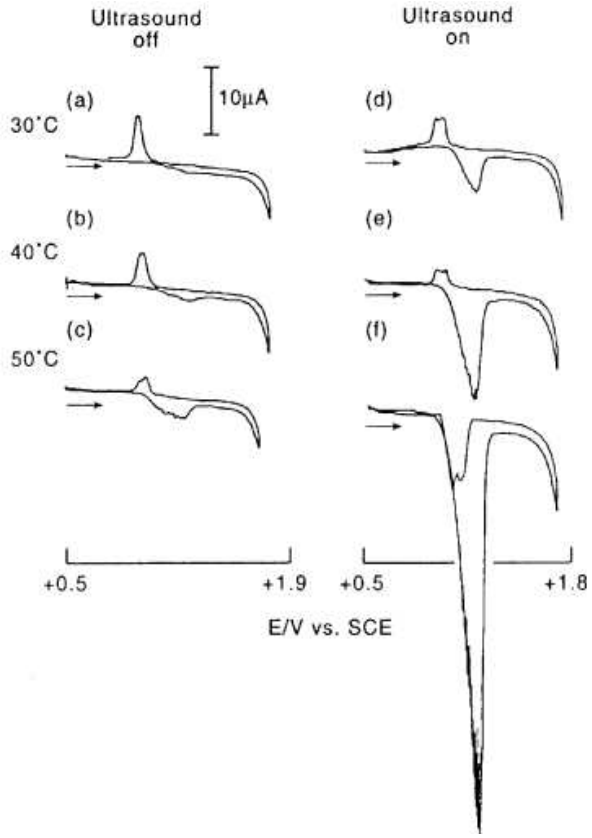



Figure 6. Cyclic voltammograms for the oxidation of a 1mm diameter gold electrode in aqueous 1M $HClO_4$ at temperatures of 30, 40 and $50^0$ C under silent conditions (a-c) and in the presence of ultrasound (d-f) (20 kHz, 40 W $cm^{-2}$, scan rate 100 $mVs^{-1}$).

### 3. The Influence of Ultrasound on Electrode Processes

The potential of ultrasound to enhance the rate or to alter the pathway of heterogeneous chemical reactions has been exploited by workers in organic and inorganic electrochemistry for many years [43-45]. The nature of the processes involved varies from the surface activation of solid reactants to the generation of active radical species and to great changes in the transport leading to new dominant reaction pathways and is in many cases not fully known.

The electrode reactions may be grouped into two categories:

- the surface confined reactions, such as the heterogeneous electron transfer and surface catalytic or adsorption steps,
- the large group of homogeneous reactions which may be coupled to the electrode process by mass transport.

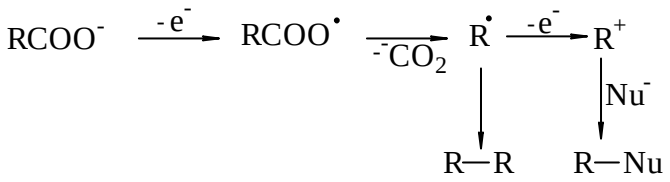
Ultrasound may affect chemical reaction which occur in a simple liquid phase mainly via four possible routes:

⇒ enhanced mass transport;
⇒ thermal fluctuation caused by cavitation or “hot spots”;
⇒ the formation of highly reactive intermediates, e.g., radical species in the solution near a “hot spots”;
⇒ strong shear forces which can effect large molecules, particles or surfaces.

The sonication of systems comprising simple one-electron transfer reactions, in aqueous solutions, e.g. $Ru(NH_3)_6^{3+/2+}$, $Eu^{3+/2+}$ [17] and $Fe^{3+/2+}$ [46, 47] showed that even with high intensity ultrasound the deviation of the measured rate constants for heterogeneous electron transfer at the electrode-solution interface remain within the experimental error unaffected. Data on other important and more complex reaction, such as the $H_2$ and the $O_2$ evolution processes would be interesting for comparison. Gas evolution processes in the presence of ultrasound were studied very early in the history of sonoelectrochemistry [48-51] and a significant depolarisation effect has been reported. In the presence of ultrasound, gases appear to be very effectively removed from the electrode surfaces.

Until recently there have been relatively few studies on the effect of ultrasound on electrode reaction mechanisms involving homogeneous as well as heterogeneous chemical steps. The Kolbe reaction [52, 53] and an electrochemically induced aromatic substitution reaction [54] were found to benefit from or be affected by the application of ultrasound, and in the case of the Kolbe reaction a significant change in the reaction pathway in the presence of ultrasound was reported. Different reaction pathways exist under different kinetic regimes, and adsorption and other electrode phenomena are known to be important, all of which might be influenced to differing extents by ultrasound. Scheme 1 gives the usual and plausible scheme to account for the range of products obtained from electrooxidation of a typical carboxylate anion. The general mechanisms break down into a

pathway involving one electron per molecule of starting material, giving products from the radical intermediate, and a two electron pathway per starting molecule, giving products from an intermediate cation.




**Scheme 1.**

The Coventry group chose to examine a system almost at balance where both pathways operate [55] in order to best identify any sonoelectrochemical effect on mechanism [52]. Table 1 shows product ratios (by GLC) from the electrooxidation of partially neutralised cyclohexanecarboxylate in

**Table 1.**

Electrooxidation of cyclohexane carboxylate[a,b]

| **Product** | **Amount [%]** | |
|---|---|---|
| | without ultrasound | with ultrasound |
| Bicyclohexyl | 49.0 | 7.7 |
| Cyclohexane | 1.5 | 2.6 |
| Cyclohexene | 4.5 | 32.4 |
| Methoxy-cyclohexane | 24.9 | 34.3 |
| Methyl-cyclohexanoate | 17.0 | 2.5 |
| Cyclohexanol | 2.1 | 6.8 |

[a] - relative product ratios after the passage of 2,2 F· $mol^{-1}$

[b] - average cell potential to maintain current density of 200 mA $cm^{-2}$ is 8,3 V in the absence and 7,3 V in the presence of ultrasound

methanol at Pt electrode, at a current density of 200 mA·$cm^{-2}$ . The column 2 (tab. 1) shows the effect on product ratio of ultrasonic irradiation from a Kerry Pulsatron cleaning bath (35 kHz, 50 W) during electrolysis. The preponderance of cyclohexene over cyclohexane shows its formation by proton loss from the carbocation intermediate, since free-radical routes to cyclohexane also produce cyclohexane in equal if not greater amounts [55, 56]. It is also noted in column 2 that the parasitic formation of methyl cyclohexanoate ester is lessened under ultrasound, perhaps suggesting enhanced adsorption of carboxylate with concomitant suppression of solvent discharge. This has precedent since ultrasound is thought to enhance adsorption phenomena in dissolving-metal chemical reactions [57].

Other procedural benefits in the electrooxidation of cyclohexane carboxylate under ultrasound include a drop in overall cell voltage from 8.3 to 7.3 V needed to maintain the same cd for the galvanostatic system. The reaction approached completion in a shorter time-span despite the apparent switch to the two-electron process, suggesting diminution of parasitic processes.

Overall, ultrasound appears to favour the two-electron mechanism, but the greatest effect of sonication upon product distribution was the substantial enhancement of alkene formation.

Table 2 shows relative product ratios for electrooxidation of phenylacetate, where is no proton-loss pathway from the intermediate carbocation, in similar conditions to those used for cyclohexane carboxylate but employing 100 $mA \cdot cm^{-2}$ [58].

**Table 2.**

Electrooxidation of Phenylacetate[a,b]

| **Product** | **Amount [%]** | | | |
|---|---|---|---|---|
| | without ultrasound | | with ultrasound | |
| | no pyridine | 13% pyridine | no pyridine[c] | 13% pyridine |
| Bibenzyl | 0 | 59.8 | 52.7 | 51.3 |
| Toluene | 0 | 0.4 | 3.1 | 1.5 |
| Benzyl methyl ether | 0 | 21.1 | 32.3 | 27.8 |
| Methyl phenylethanoate | 0 | 10.2 | 6.2 | 4.2 |

[a] - relative product ratios after the passage of 1.1 $F \cdot mol^{-1}$

[b] - average cell potential to maintain current density of 100 mA $cm^{-2}$ is 7.9 V in the absence and 6.6 V in the presence of ultrasound

[c] - a fine white powder precipitate was formed in these conditions

Because the simple electrolysis of the partially neutralised salt in methanol causes a very rapid increase in applied cell voltage, due to the coating of the anode with a pale-coloured material that causes the reaction to cease, is necessary to add pyridine (up to 50% v/v) to keep the electrode clean, presumably by simply solubilizing the inhibiting layer. A major component of the remaining (8%) material is benzaldehyde, a persistent by-product of arylacetate electrooxidations whose exact mechanistic origin remains uncertain.

The column 3 (table 2) shows the effect of ultrasound upon the product ratio from methanol / pyridine; the results suggest only a slight shift towards the two-electron products, but with an overall diminution of solvent discharge and side reactions. Phenylacetate electrooxidation, however, is known to favour the one-electron route to bibenzyl in a wide range of conditions [59], and to be much less sensitive to mechanistic switches by

manipulation of parameter than is cyclohexane carboxylate electrooxidation [56]. This trend remains even under ultrasound.

The column 4 (table 2) shows the product ratios under ultrasound in the absence of pyridine; there is the same trend with the electrolyse without sonication in the presence of 13% pyridine, namely a slight shift from one-electron towards two-electron pathway, although here there seems to be a higher yield of benzaldehyde-derived by-products.

The most significant factor is that there is no evidence of electrode fouling, and the reaction maintains cd at a steady and lower voltage. In addition, a fine white powder (a polymer containing aromatic rings as well as two types of methylene groups and an aliphatic ester carbonyl) was formed during the electrolysis, which was isolated by filtration (14%). It may be supposed that enhanced mass transport under ultrasound and the abrasion effect near the electrode surface has swept the inhibiting species into solution, thus keeping the electrode clean. There is much less of this powder under ultrasound in the presence of pyridine, suggesting that it is indeed solubility factors that demand the use of the cosolvent in silent conditions.

The obviation of pyridine under ultrasound represents a significant procedural enhancement since its presence considerably hampers work-up, and also has environmental implications. A further feature is again the lowering of the applied cell voltage from 7.9 to 6.6 V under ultrasound, representing an energy saving.

The same conclusions were obtained by Japanese workers [60] who employed crossed Kolbe electrolyses of phenylacetates, succinates, variously deuterated and palmitates.

The Coventry group has also examined the behaviour of p-chlorophenyl acetate electrooxidation under ultrasound [58]. This substrate is known to markedly favour the two-electron mechanism [56], showing that the choice of reaction pathway is more dependent on substrate nature than upon manipulation of electrolysis parameters. A further feature of this system is the appreciable yield of p-chlorobenzaldehyde-derived products. The sonication produces little change in relative product ratio. An unexpected advantage of sonication was found here. There was no formation of polymeric coating on the anode, tending to confirm that the free para-position of unsubstituted phenylacetate is necessary for production of the inhibitory species; instead the cathode became coated in a black deposit as the electrolysis proceeded. It is possible to envisage a reductive cleavage process occurring on the protonated acid molecule with loss of chloride ion to yield species that could polymerise on the cathode.

The origin of ultrasonic effect upon carboxilate electrooxidation is not straightforward to establish in view of complex mechanism of the reaction with different kinetic regimes, the loss of carbon dioxide, and also the role of

adsorption and other electrode phenomena. It has also been suggested that the second electron transfer to give the carbocation need not occur in bulk solution, although this requires methoxyradicals from solvent discharge or other species to act as redox mediators in the solution phase [61].

The Coventry group also examined the use of higher ultrasonic frequencies (500 and 800kHz) [5]. It would seem that higher frequencies are more suitable for the insonation of these reaction systems, although this is not straightforward to explain since cavitation phenomena, effects of acoustic impedance, cell geometry implications and other factors all change with frequencies.

Cavitation is substantially more difficult to induce at higher frequencies and since these experiments were performed at the same ultrasonic power, suggests that the observed sonoelectrochemical benefits are not cavitational in origin. However, it may be simply an effect of the shorter wavelength at higher frequency. Thus in the 20 - 60 kHz frequency region, the half-wavelength is of the order of centimetres so that only a limited number of nodes and antinodes span the dimensions of the electrolysis cell used; in the 500 -800 kHz region, however, the distance between nodes and antinodes is only in the order of millimetres. If, as seems likely from electroanalytical studies, certain sonoelectrochemical benefits originate from nodes or positive regions of the wave, but antinodes or negative regions of wave do not interfere, then simplistically an increase in the number of nodes within the active region of the cell will produce more uniform and effective sonoelectrochemical phenomena.

One of potentially most useful preparative-scale electroreduction reactions involves the transformation of aryl nitrocompounds to amino derivatives 62-67], but in practice this is a complicated system in which there are a number of competing reactions including, for example hydrodimerization to hydrazo compounds [14a, 68].

A schematic description of the electrochemical reduction of nitrobenzene, a model voltammetric system, as proposed by Laviron et al. [69] is given in scheme 2. At pH 13, in aqueous media, the first reduction is followed by a protonation step. The second reduction then leads, after loss of $OH^-$, to nitrosobenzen as an intermediate. After further transfer of two electrons and uptake of two protons, the product phenylhydroxyamine is generated.

Side products due to a condensation reaction may also be observed under certain conditions [70].

Despite the multipathway nature of nitroelectroreductions, there appears to be no further reports of sonoelectrochemical studies on this type of reaction.

The nitrobenzene radical-anion is known to be only metastable in alkaline solution due to slow disproportionation [71]. This and the fact that certain electrode materials appear to allow catalysis [72,73] of the decay of

the nitrobenzene radical-anion allow several aspects of the effect of ultrasound to be studied.

Scheme 2. Reaction pathway for the electrochemical reduction of nitrobenzene in aqueous media at pH 13

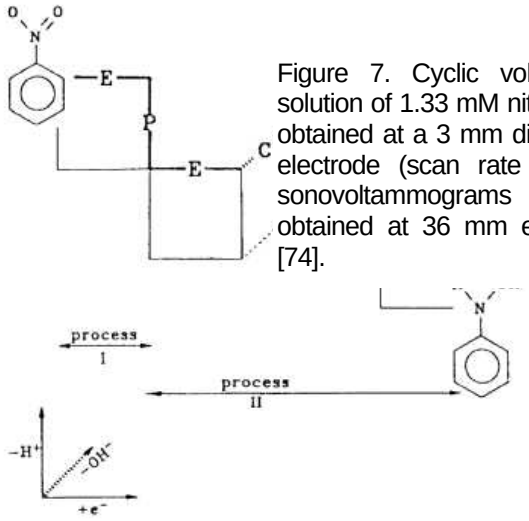
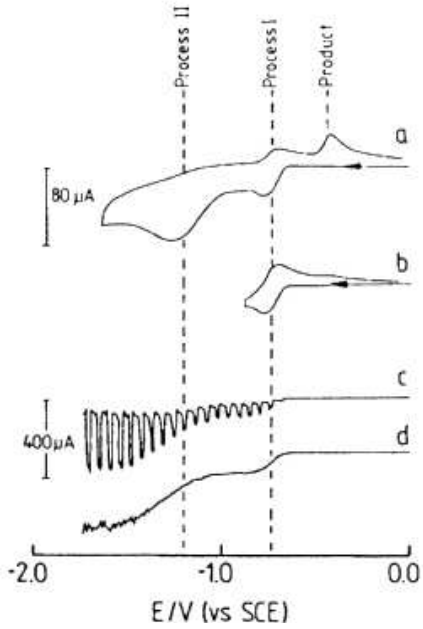



Figure 7. Cyclic voltammograms (a,b) of a solution of 1.33 mM nitrobenzene in 0.1 M NaOH obtained at a 3 mm diameter glassy carbon disk electrode (scan rate 50 $mVs^{-1}$, $T=25^0C$) and sonovoltammograms (c,d) ($20mVs^{-1}$, $25Wcm^{-2}$) obtained at 36 mm electrode to horn distance [74].

In voltammetric studies in 0.1 M NaOH, glassy carbon electrodes



allow well-defined voltammograms to be recorded both under silent conditions and under sonication and over a wide potential range [74]. In fig. 7 it may be observed a reversible one-electron reduction (process I) at $E_{1/2}$ = - 0.73 V/SCE followed by an overall three-electron reduction (process II) with a peak potential $E_p$ = -1.25 V/SCE. A product signal at $E_p$ = -0.43 V/SCE can be identified as a two-electron / two proton oxidation process from phenylhydroxylamine to nitrosobenzene [73]. The sonovoltammograms (fig. 7 c,d) using pulsed (providing important additional information, e.g. on back-ground processes [75, 76]) and continuous ultrasound are in agreement both with the one- and the three-electron nature of the reduction process. The variation of the distance between horn and electrode allowed almost linear variation of the average diffusion layer thickness $\delta$ from 1.3 to 5.8 μm. The number *n* of electron transferred, calculated using the limiting currents for the reduction of nitrobenzene, remains in good approximation, constant at one (process I) and three (process II) without any obvious effect of the soundfield.The reduction of nitrobenzene on gold electrodes occurs with a mechanism of considerably high complexity. Voltammetric studies on mercury and on gold electrodes with a single four- electron reduction process for nitrobenzene in aqueous alkaline media have been reported [77,78], and a surface catalytic process was suggested involving the protonation of the adsorbed nitrobenzene radical anion [79].

Figure 8 (a) shows that upon continuos cycling, a complex change occur: a dramatic increase in current for process I accompanied by a shift of the peak potential for process II towards more positive potentials. After only 5 cycles one reduction process (of the four electron) is observed, followed by a new and uncharacterised reduction peak at $E_p$ =1.29 V / SCE. Figure 8 (b,c) demonstrates the change in mechanism using gold rotating disk voltammetry. The negative scan direction consists of the anticipated $1e^-$ and $3e^-$ processes, but the positive scan direction exhibits only one $4e^-$ wave. This phenomenon has been described [80] and attributed to a change of the gold surface properties. The sonovoltammograms (fig.8 d-f) exhibit similar behaviour, although at decreasing diffusion layer thickness the effect of the electrocatalyst diminishes. There are two possible mechanisms likely responsible for this effect. On the one hand the loss of catalyst from the electrode surface due to ultrasonic cleaning or, alternatively, a purely kinetic effect due to high mass flux. In the presence of intense ultrasound (or a high rate of mass transport), the homogenous reaction pathway (one-reduction) could out-run the rate of the heterogeneous reaction pathway (chemical step such as protonation) hence, a different mechanistic pathway would dominate the overall reaction. Marken et al. [74] proposed a simplified reaction scheme which supposes that the nitrobenzene radical-anion, formed by one-electron reduction of nitrobenzene at the gold surface electrode, than diffuse away, or

after surface catalytic protonation, takes up three more electron before diffusing into the bulk solution. Their kinetic results, obtained for the reduction of nitrobenzene in aqueous NaOH, suggests that sonovoltammetry may be applied in mechanistic studies using the concepts which apply to rotating disk voltammetry, such as an average uniform diffusion layer and the reaction layer concept.

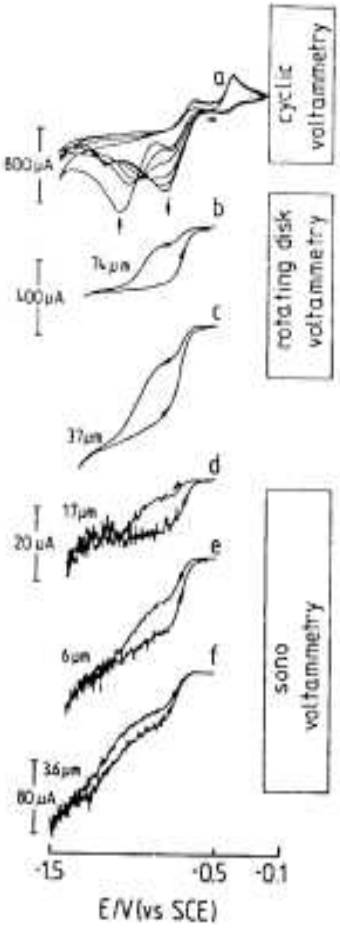
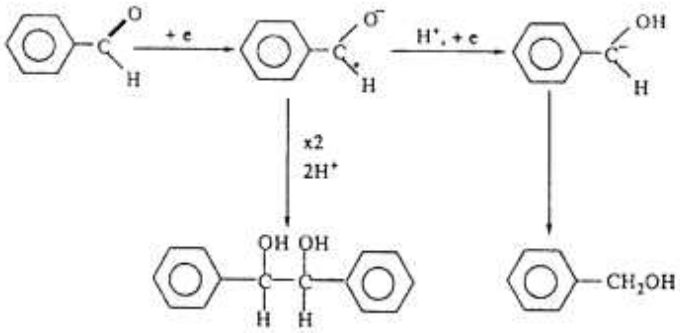



Figure 8. Cyclic voltammograms (a) of a solution of 10 mM nitrobenzene in 0.1 M NaOH obtained at a 7 mm diameter gold electrode (scan rate 100 $mVs^{-1}$ , $T=25^0C$). Rotating disk voltammograms (b,c) and sonovoltammograms (d-f) of 1 mM nitrobenzene in 0.1 M NaOH obtained at a 7 mm (b,c) and 1mm (d,f) diameter gold electrode (scan rate 20 $mVs^{-1}$) with (d,e) 37mm and (f) 4mm electrode to horn separation and (d) 15 W $cm^{-2}$ , (e,f) 30 $Wcm^{-2}$. The average diffusion layer thickness obtained are indicated [74].

Recent works from the group at the Tokyo Institute of Technology have been specifically directed at ultrasonic control of product selectivity in electroreductions. Thus the electroreduction of benzaldehydes [81-83] can lead to either the hydrodimer in a one-electron per substrate molecule process, or to the benzyl alcohol in a two-electron process, as indicated in scheme 3.




Scheme 3.

Using a lead cathode in dilute methanolic sulphuric acid at constant current of 20 mA $cm^{-2}$, the benzyl alcohol was the major product from unstirred solution, while mechanical stirring reversed the position to favour the hydrodimer. However, ultrasonic irradiation from a cleaning bath (100 W, 36 kHz) so strongly favoured the hydrodimer that the alcohol was barely evident. The current efficiency for reduction and product selectivity for the corresponding hydrodimeric products were increased with increasing ultrasound oscillating power in different manners on the cathode. The lateral cathodes could exhibit the effect at relatively low ultrasonic powers compared with the sectional one (see fig. 9).

In addition, higher efficiency and selectivity were obtained at the lateral loop cathode than at the node one (see tab.3). Interfacial layers of the lateral electrodes (LN and LL cathodes) are reciprocally sheared by the parallel vibration, while those of the TSL cathode are cyclically compressed and expanded. In a sense, the vibrating lateral electrode may affect an electrochemical reaction in a way a little similar to a rotating cylindrical electrode. It is suggested that a reciprocal shearing phenomenon in the ultrasonically vibrating lateral cathode interfaces causes the clear increase in efficiency and selectivity as well as the cyclic compression/ expansion phenomenon in the ultrasound irradiated and oscillating sectional cathode interfaces. On another basis, the ultrasonic effects observed on the lateral electrodes may be caused by a peculiar interaction of stationary surface waves occurring on the electrode (solid) with the solution (liquid), though the physical mechanism has not been verified at present.

The reduction of benzoic acid at a lead cathode in an aqueous 0.05M $H_2SO_4$/0.2 M citric acid solution gives not the corresponding hydrodimeric product but hydro-monomeric 2- and 4- electroreduction products such as benzaldehyde and benzyl alcohol. Here ultrasound produces some switch towards the two-electron product; thus in all studied

cases the authors found that ultrasound favoured the process involving the smaller number of electrons per molecule [82]. This is opposite to the sonoelectro-chemical effect seen in carboxylate electrooxidation [52,58] where the process involving the greater of electrons was favoured by ultrasound, and shows that in the present state-of-the-art generalisations are inappropriate. The nature of the electrochemical system is an important consideration in the establishment of sonoelectrochemical phenomena.

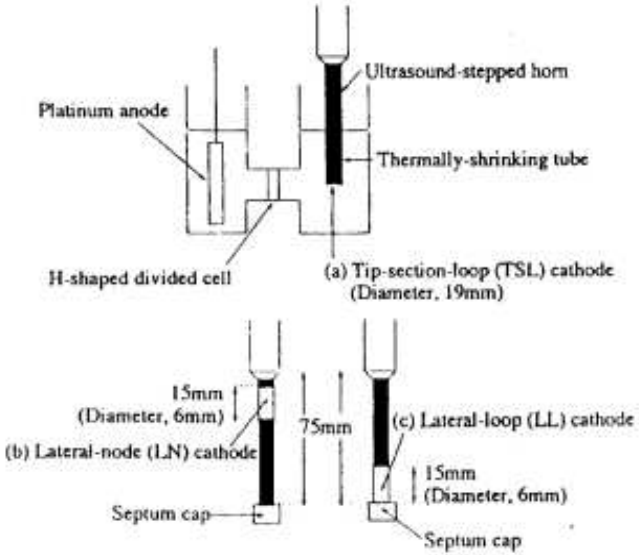



Figure 9. Ultrasound vibrating electrodes [83]

**Table 3.**

Electroreduction of 40 mM benzaldehyde in 0.25 M $H_2SO_4$-50% $CH_3OH$ catholyte on the tip-section loop cathode an ultrasound stepped horn [83].

| Ultrasound power [W] | Current density [mA $cm^{-2}$] | Current efficiency [%] | Selectivity for hydrodimer [%] |
|---|---|---|---|
| 0 | 20 | 5 | 29 |
| 50 | 20 | 26 | 36 |
| 0 | 40 | 3 | 39 |
| 80 | 40 | 25 | 47 |
| 0 | 80 | 4 | 46 |
| 50 | 80 | 18 | 61 |

The group at Tokyo Institute of Technology have also examined the electro-reduction of methyl and benzyl halides at a reactive tin and respectively, lead cathodes [5,82]. The first example is a different type of electrochemical system in which the cathode is a reactive metal. For

reduction of $CH_3I$ in DMF/$Bu_4NClO_4$ at room temperature and 10 mA $cm^{-2}$, an unstirred reaction gave 1:10 ratio distannane to stannane, while ultrasound, from a 20 kHz probe, increased the dimmer to give 1:5 ratio.

## CONCLUSIONS

Ultrasonic irradiation produces a number of significant benefits in a wide range of electrochemical systems. Insonation of an electrosynthetic reaction can produce altered product ratios, greater efficiencies, lessened cell power requirements and a diminution of detrimental electrode fouling. The technique also provide a probe into fundamental physico-chemical principles of electrolyte solutions, electrode phenomena, and associated processes.

The best established effect of ultrasound in electrochemistry is the diminution of the diffusion layer and the enhanced limiting currents so produced. This is of benefit towards sensitivity improvement in electrochemical sensors, and is also the origin of many sonoelectrochemical phenomena. Ultrasound also affects electrode surfaces and has a beneficial effect during electrolysis.

It is hoped that applied as well as fundamental aspects of sonoelectrochemistry will develop over the next decade or so similar to the development in sonochemistry, in general.

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