DOES POWER ULTRASOUND AFFECT HETEROGENEOUS ELECTRON TRANSFER KINETICS?

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ABSTRACT

Most of the observations seen in the application of power ultrasound in electrochemistry or also known as *sonoelectrochemistry* are due to enhanced mass-transport of electroactive species from the bulk solution to the electrode surface caused by efficient stirring, acoustic streaming and cavitation. However, fundamental studies on the effect of ultrasound on electrode kinetics i.e. on the electron-transfer are scarce. The main question still remains to be answered:

Does power ultrasound affect heterogeneous electron transfer kinetics?

This opinion paper discusses the effect of ultrasonic frequency and intensity upon the electrode kinetic parameters such as the half-wave potential ($E_{1/2}$) and the apparent heterogeneous rate constant (k_o). A few sonoelectrochemical studies have highlighted changes in half-wave potential and in apparent heterogeneous rate constant for both quasi-reversible and irreversible systems when the data were compared to *silent* conditions. These observations are thought to be due to the contribution of mass-transport and macroscopic temperature effects, as well as the continuous cleaning of the electrode surface caused by the collapse of high-energy cavitation bubbles and the production of high velocity jets of liquid. However, there still remains mechanistic controversy in assigning whether these findings could also be due to localised temperature increases, the contribution of sonolysis products or solely due to enhanced mass-transport at the electrode surface. Thus, the effect of stirring, macroscopic temperature and sonication time upon these electrode kinetic parameters is also shown to be important factors in comparing the validity of any sonoelectrochemical effects.

Key words: Sonoelectrochemistry; Power Ultrasound; Electrode Kinetics; Quasi-Reversible/Irreversible Systems

Sonoelectrochemistry is a special and niche field in electrochemistry and electrochemical engineering that has gained a special growth at the beginning of the 1990´s due to its extraordinary effects [1]. With the growing pressure to lower energy consumption and dramatically reduce environmental impact in the industry, recently the use of new process intensification methods in industrial electrochemical processes has appeared as a necessity to improve environmental impact, process efficiency and cost. The use of ultrasound, a process intensification technique, has been proposed and applied to many electrochemical systems, processes and areas of electrochemistry, to name but a few: electroplating, electrodeposition, electropolymerisation, electrocoagulation, organic electrosynthesis, materials electrochemistry, environmental electrochemistry, electroanalytical chemistry, and more recently in hydrogen energy and fuel cell technologies [1]. However, the use of ultrasound in industrial electrochemical processes have only been presented in the literature from the chemistry and chemical engineering point of view with few further sonoelectrochemical explanations.

It is well-known in the field of sonochemistry that sonoelectrochemistry offers many advantages, e.g. a) enhanced electrochemical diffusion processes, b) increase in electrochemical rates and yields, c) increase in process efficiencies (electrode and current efficiencies), d) decrease in cell voltages and electrode overpotentials, e) suppression of electrode fouling (and degassing at the electrode surface), f) improved electroplated and electrodeposited materials (in terms of quality, hardness, porosity and thickness), and g) improved electrode surface activation. Most of the observations are attributed to: a) electrode surface cleanliness, b) metal depassivation and gas bubble removal at the electrode surface, induced by acoustic cavitation and acoustic streaming, and c) enhanced mass-transport of electroactive species to the electrode surface (a thinning of the diffusion layer thickness, δ) [1-3].

For example, several workers have observed sigmoidal shape voltammograms and named these new shapes ‘sonovoltammograms’ for quasi-reversible systems (Figure 1) [1]. The figure shows a series of linear sweep voltammograms (LSV) in the potential range [0 – 0.40 V *vs.* SCE] i.e. a ‘sonovoltammogram’ (US) and rotating disc electrode (RDE) voltammograms of a typical quasi-reversible system ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple) at 298 K on Pt and at various rotation speeds (*silent*: 200, 550 and 950 rpm) and at 20 kHz, recorded at a scan rate of 2 mV/s. They concluded that sonovoltammetry is closely related to hydrodynamics methods e.g. polarography, dropping mercury electrode (DPE), rotating disc electrode (RDE), wall-jet electrode (WJE), etc and showed that Equation 1, which relates the limiting current (I_{lim}) to the diffusion layer thickness (δ), still applies in the presence of ultrasound.

$$I_{\text{lim}} = nFAD_oC^* / \delta \qquad (1)$$

where I_{lim} is the limiting current, n is the number of electrons transferred during the electrochemical process, F is the Faraday constant, A is the electrode area, D_o is the diffusion coefficient of the electroactive species, C^* is the bulk concentration of the electroactive species and δ is the diffusion layer thickness [1,2].

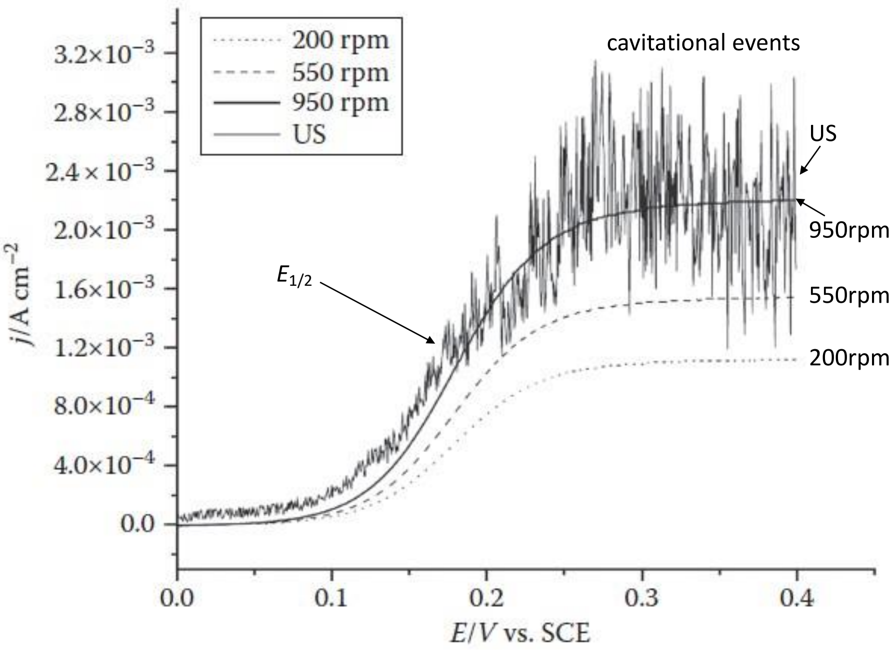

Figure 1 - A ‘sonovoltammogram’ (US) and rotating disc electrode (RDE) voltammograms of a typical quasi-reversible system ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple) at 298 K on Pt and at various rotation speeds (*silent*: 200, 550 and 950 rpm) and at 20 kHz, recorded at a scan rate of 2 mV/s [4]. For the sonovoltammogram, the

current spikes are not due to noise but to cavitational events occurring at the electrode surface as demonstrated by Birkin *et al.* [5] in the 1990's.

The effect of ultrasound on heterogeneous systems has been studied and discussed in the last 30 years, although there is little information on the effect of ultrasound on homogeneous systems. For example, in 1994 Jean-Louis Luche [6] published a review paper in *Ultrasonic Sonochemistry* highlighting some examples of sonochemical reactions occurring under heterogeneous conditions with respect to their mechanism. In his paper, Luche also emphasized that homogeneous systems should not be affected by sonication.

The effects of ultrasound on many electrochemical processes can be found in the literature [1] but fundamental studies on the effect of ultrasound on electrode kinetics have hitherto been few. For example, there are only a few reports where ultrasound has been shown to enhance the rate of certain chemical reactions e.g. the *Kolbé reaction* or to affect the homogeneous electron-transfer reactions [3,6,7]. In the particular case, it has been shown that ultrasound switches the reaction from a one electron to a two electron-transfer leading to higher product yields. However, there still remains mechanistic controversy in assigning whether this result is due to localised temperature increases, the contribution of sonolysis products or solely due to enhanced mass-transport at the electrode surface. Moreover, it is well-known in the field that the use of power ultrasound on electrolytic systems leads to a decrease in cell voltages and, affects anodic and cathodic overpotentials [1], an area which has not been fully explained yet.

Electrochemical Reversibility

To understand electrochemical reversibility, the *Butler-Volmer* kinetic equations (BVE) should be mentioned herein [8]. Let's consider the following redox reaction:

$$Ox + n\mathrm{e}^- \leftrightarrow Red$$

where *Ox* and *Red* are the oxidized and reduced species respectively and *n* is the number of electrons transferred during the redox reaction.

BVE must be regarded as the fundamental equation of electrode kinetics and it shows how the net current density (j_{net}) varies with the exchange current density (j_{o}), the overpotential (η) and the electron-transfer coefficient (α).

$$j_{\mathrm{net}} = j_{\mathrm{o}}\{\exp[((1-\alpha)nF/RT)\eta] - \exp[(-\alpha nF/RT)\eta]\} \qquad (2)$$

with

$$j_{\mathrm{o}} = nFk_{\mathrm{o}}(C_{\mathrm{R}}^{*})^{\alpha}(C_{\mathrm{O}}^{*})^{1-\alpha} \qquad (3)$$

where:

j_{net} is the net current density of the redox reaction in A/m^2.

j_{o} is the exchange current density in A/m^2.

α is the transfer coefficient.

n is the number of electrons transferred per ion or molecule.

F is the Faraday constant in C/mol (F = 96,484.6 C/mol).

R is the gas constant in J/K/mol (R = 8.3184 J/K/mol at 298 K).

T is the temperature in K.

η is the net overpotential in V.

C_{O}^{*} is the electroactive species O bulk concentration in mol/m^3.

C_{R}^{*} is the electroactive species R bulk concentration in mol/m^3.

k_{o} is the heteregeneous rate constant in m^2/s.

For clarification, herein, the electrochemical reversibility is defined as the ratio of charge-transfer to mass-transfer, and the mass-transfer is dependent upon the scan rate; and an electrochemical quasi-reversible system involves charge-transfer which is relatively fast relative to mass-transfer. Electrochemical reversibility revolves around three important concepts: a) “electrochemical facility” defined by the magnitude of the exchange current density (j_{o}) and the heterogenous rate constant (k_{o}), b) “electrochemical reversibility” defined by the ratio of charge-transfer to mass-transfer, and c) “electrochemical asymmetry” defined by the variations of α from 0.50.

"Filling the gaps"

The objective of this opinion paper is to stimulate the area in views of "filling the gaps" in knowledge and understanding that explain the effects of ultrasound on heterogeneous electron transfer kinetics (electrode surface – redox couple in solution) with a particular focus on the electrode kinetic behaviour of, for example, (i) well-known quasi-reversible redox systems and (ii) the hydrogen evolution reaction (HER) at platinum electrodes, by undertaking an in-depth and systematic scientific approach.

Research Questions and Hypotheses

Research Questions

This opinion paper is aiming at highlighting the main problems, unknowns and missing knowledge requiring to be addressed. Thus, from the author's point of view, there are three main research questions (RQ) remaining to be answered in this specific area of sonoelectrochemistry:

RQ1. Is the heterogeneous electron transfer kinetic of quasi-reversible and irreversible redox couples on platinum electrodes affected by power ultrasound and if so, to what extent?

RQ2. Is the hydrogen evolution reaction (HER) on platinum electrodes in acidic and alkaline conditions affected by power ultrasound and if so, to what extent?

RQ3. What are the contributors for the observed decrease in electrolysis cell voltage, anodic and cathodic overpotentials on platinum for water electrolysis observed in the presence of ultrasound?

Hypotheses

The overall hypotheses (OH) could be as follows:

OH1. The electrode kinetic parameters such as the half-wave potential ($E_{1/2}$) and the apparent heterogeneous rate constant (k_0) for well-known and well-characterised quasi-reversible redox couples on Pt electrodes are affected by sonication and depends upon the ultrasonic frequency, intensity and irradiation duration.

OH2. The hydrogen adsorption and desorption mechanisms at polycrystalline and single crystal Pt electrodes are affected by power ultrasound and depends upon the ultrasonic frequency, intensity and irradiation duration.

Heterogeneous Electron Transfer Kinetics

Half-wave Potential ($E_{1/2}$)

The determination of half-wave potential in electrochemistry is important as it provides qualitative information about the redox reaction. Because the measured half-wave potential is affected by diffusion (a non-thermodynamic effect), it is related to the *formal* potential (for a reversible/quasi-reversible system) by [8]:

$$E_{1/2} = E^{\varnothing}_{O/R} + RT/nF \ln (D_O/D_R) \qquad (4)$$

where

$E^{\varnothing}_{O/R}$ is the *formal* potential of the redox couple in V.
R is the gas constant in J/K/mol (R = 8.3184 J/K/mol at 298 K).
T is the temperature in K.
n is the number of electrons transferred per ion or molecule.
F is the Faraday constant in C/mol (F = 96,484.6 C/mol).
D_O is the diffusion coefficient of the *Ox* species in m^2/s.
D_R is the diffusion coefficient of the *Red* species in m^2/s.

When the diffusion coefficients of the oxidized and reduced species are similar, the half-wave potential provides a good approximation to the formal potential is related to the formal potential.

Under *silent* conditions and for quasi-reversible systems, the most common methods to determine the $E_{1/2}$ are by cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

CV method: CVs are recorded and the $E_{1/2}$ are obtained by determining the anodic and cathodic peak potential E_{pa} and E_{pc} values respectively from the cyclic voltammograms and using the following equation [8].

$$E_{1/2} = (E_{pa} + E_{pc}) / 2 \qquad (5)$$

LSV method: *S*-shaped voltammograms are recorded using a rotating disc electrode (RDE). The half-wave potentials are determined by plotting the *Mass-Transport Corrected Tafel* (MTCT) plots [8] from the LCVs i.e. log $[(j)/(j_{\mathrm{lim}} - j)]$ against E and recording the intercept value with the x-axis.

Compton *et al.* [9] and Pollet *et al.* [10,11] both observed a shift of half-wave potential under sonication at 20 kHz and 800 kHz. Compton *et al.* [9] showed an anodic shift in $E_{1/2}$ (for the ferri/ferrocyanide redox couple) under sonication and ascribed this anodic shift to ultrasonically-generated reactive species, e.g. hydroxyl radicals (•OH), which induced chemical irreversibility in a system which was reversible under *silent* conditions. In other words, they demonstrated that the anodic shift in $E_{1/2}$ was mainly attributed to the existence of a homogeneous chemical step (*C*) following the electroreduction of ferricyanide (*E*) - an *EC* process, as opposed to a purely *E* process under *silent* conditions. They found that high frequency ultrasonic sources were thought to produce more hydroxyl radicals in aqueous media than low frequency sources at similar powers, suggesting the involvement of such species might indeed be a contributory factor to the shifting in $E_{1/2}$. Contrarily to the observations of Compton *et al.* [9], Pollet *et al.* [10,11] showed a cathodic shift in $E_{1/2}$ (Figure 2) and attributed this shift to the continuous electrode surface cleaning induced by sonication.

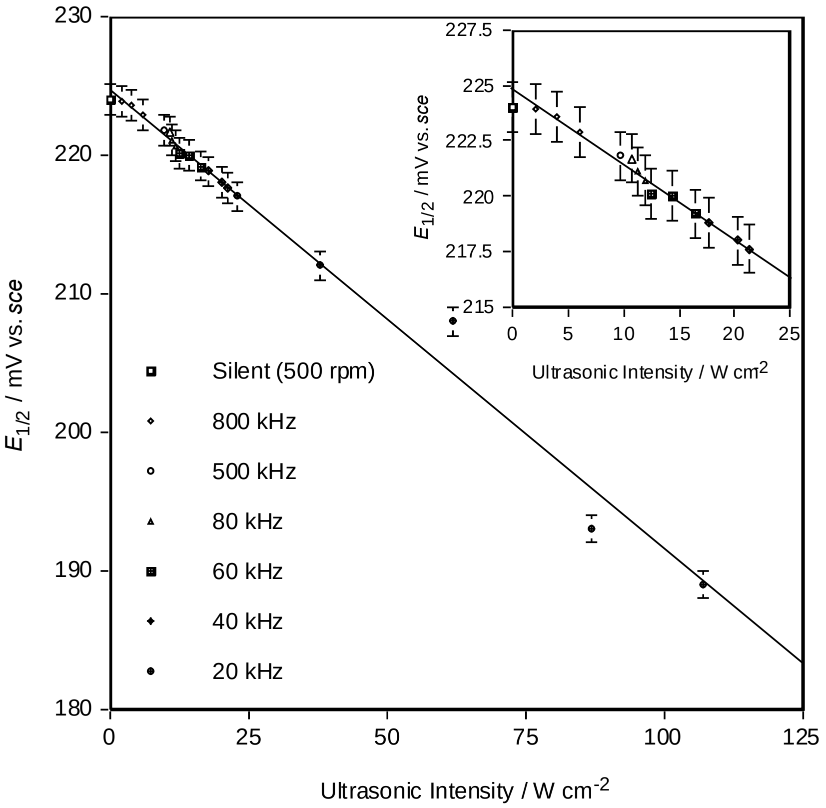

Figure 2 - Half-wave potentials ($E_{1/2}$) plotted against various ultrasonic intensities (up to 107 W/cm^2) at six ultrasonic frequencies (20, 40, 60, 80, 500 and 800 kHz) and at (298 ± 1) K. The half-wave potentials were obtained from sonovoltammograms of 1.0 mmol/dm^3 ferricyanide in 1.0 mol/dm^3 KCl on a polished platinum rotating disc electrode at 100 mV/s and at (298 ± 1) K. The distance between the base of the cell or the ultrasonic horn and the working electrode was d = 2 mm. The inset figure shows the linear relationship of the half-wave potentials *vs.* the ultrasonic intensity for ultrasonic intensities in the range [0 – 25 W/cm^2]. All half-wave potentials were determined by plotting the mass-transport corrected Tafel (MTCT) plots i.e. log $[(I - I_{\mathrm{lim,c}}) / (I_{\mathrm{lim,a}} - I)]$ *vs. E* and recording the intercept value with the *x*-axis [8]. Here the ultrasonic intensities (ψ) were calculated by dividing the ultrasonic power (P_d, determined calorimetrically) by either the ultrasonic probe tip area (A) or the electrochemical cell base area (A') when using ultrasonic baths.

Pollet also showed that the ultrasonic frequency is not an important factor in the shift in half-wave potential compared to ultrasonic intensity [10,11], and postulated that the observed cathodic shift may be due to other several possible contributions:

(i) It is well known that the application of ultrasound leads to an increase in temperature.

Thus, it is necessary to establish whether a decrease in $E_{1/2}$ in the presence of ultrasound is due to the influence of temperature. If linearity between $E_{1/2}$ and T (Figure 3) is assumed, it is possible to deduce an 'apparent' bulk temperature in the presence of ultrasound i.e. the bulk temperature which would be necessary to produce the same effect under purely thermal conditions as was obtained under ultrasonic conditions. In the author´s conditions, this temperature was deduced to be 325 K for an ultrasonic intensity of 107 W/cm^2 (20 kHz). Since the bulk experimental temperature of the electrolyte never rose above (298 ± 1) K during the ultrasonic runs the effect was not solely due to macroscopic temperature.

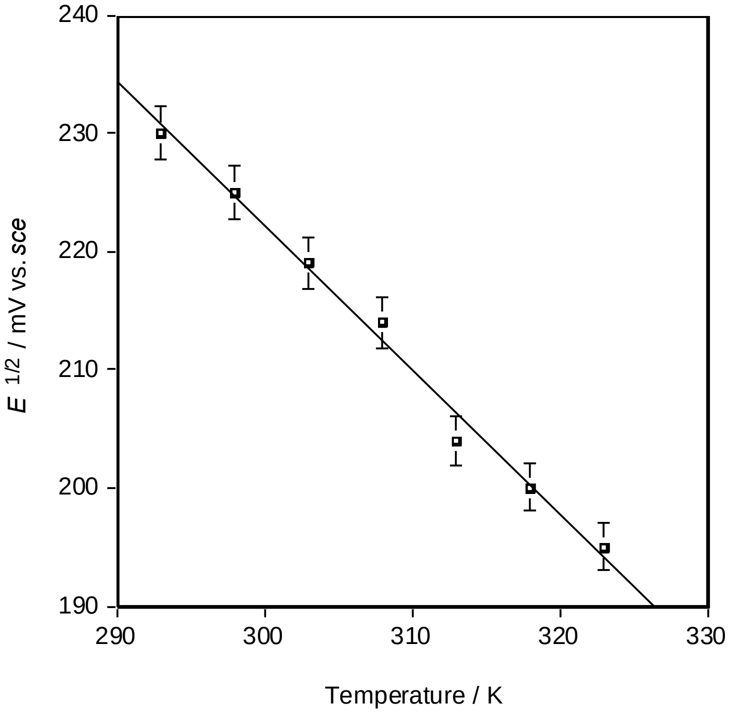

Figure 3 - Dependency of the half-wave potential ($E_{1/2}$) with temperature for the reduction of 2.0 mmol/dm^3 ferricyanide on a stationary Pt electrode at 100 mV/s.

(ii) Decrease in overpotential is also known to be responsible for a decrease in potential. It was shown by Pollet *et al.* [12] that sonication affects overpotentials mainly due to the degassing effect of ultrasound at the electrode surface, i.e. this so-called "bubble" overpotential (η_{bubble}) was reduced under sonication.

(iii) It was also known that ultrasound decreases concentration overpotential ($\eta_{\text{concentration}}$) by favouring the passage of the electroactive ions across the diffusion layer and their discharge due to high mass-transport. However, this suggestion may be dismissed for the following reason. In the author´s conditions, assuming linearity between $E_{1/2}$ and ω (see [10]) and assuming that using a 20 kHz probe at its maximum power (107 W/cm^2) can yield an 'effective rotation speed' of 100,000 rpm [11], it is possible to deduce an 'apparent' half-wave potential at 100,000 rpm. The 'deduced' half-wave potential was found to be +201 mV vs. *sce*. Since the experimental value of the half-wave potential obtained at 20 kHz and at 107 W/cm^2 was much lower (+189 mV vs. *sce*) than that obtained 'theoretically', this cathodic shift was not only due to mass-transport effect.

(iv) This shift in potential may also be due to the collapse of microjets onto the electrode surface involving high microscopic temperature or, to the cleaning effect of ultrasound making the electrode surface more active for any electrochemical processes to occur [1].

Apparent heterogeneous rate constant (k_o)

The apparent heterogeneous rate constant (k_o) is an important electrochemical parameter as it provides information and basic understanding on the kinetics of the reaction at the surface of the electrode as electrode processes are considered to occur commonly via a reaction pathway involving specifically adsorbed intermediates.

Under *silent* conditions and for quasi-reversible systems, the most common methods to determine the k_o are by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) (see Nicholson [13,14], and Kochi and Klinger [15]).

CV method: For this method, the potential peak separation (ΔE_p) are obtained by recording the anodic and cathodic peak potential E_{pa} and E_{pc} values respectively from cyclic voltammograms. The coefficient ψ needed for the deduction of k_o is related to ΔE_p for each scan rate (υ) according to the

Nicholson equation (Equation 4) and tables [13,14]:

$$k_o = \psi \, (D_o \upsilon \, nF/RT)^{1/2} \, (D_R / D_O)^{\alpha/2} \qquad (6)$$

where k_o is the apparent heterogeneous rate constant in m/s, ψ is a dimensionless coefficient, D_O and D_R are the diffusion coefficients of the Oxidative and Reductive species respectively in m^2/s, υ is the scan rate in V/s, n is the number of electrons transferred, F is the Faraday constant (96,489.6 C/mol), R is the gas constant (8.314 J/K/mol), T is the temperature in K and α is the transfer coefficient.

Employing Equation 6, for a one-electron transfer, the apparent heterogeneous rate constants are calculated using known experimental (ΔE_p and υ) and literature values at 298 K for all chosen quasi-reversible redox couples. Peak separation values should indicate nearly reversible behaviour (approximately +59 mV/n).

LSV method: The apparent heterogeneous rate constants are evaluated using the tables for quasi-reversible steady-state voltammograms published by *Mirkin-Bard* [16] i.e. the experimental values of $E_{1/2}$ and quartile potentials ($\Delta E_{1/4}$ and $\Delta E_{3/4}$) and the limiting current density (j_{lim}) are extracted from LSVs (RDE voltammograms) and used to evaluate the apparent heterogeneous rate constant (k_o) using the dimensionless rate constant ($\lambda = k_o / m_o$ – here m_o is a mass-transfer coefficient).

In the 1990´s, Zhang and Coury and Madigan *et al.* showed that the electrode kinetics of a quasi-reversible redox system is altered by the presence of alumina particles under sonication (20 kHz) [17,18]. They observed that the ‘apparent’ increases in the rate of electron transfer were due to a local temperature increase at the electrode surface (from 298 K to 410 K) caused by the impact of alumina particles added to the solution and thrown onto the electrode by the cavitation process. However, Marken *et al.* [19] employed steady-state voltammetry to determine the rate of heterogeneous electron transfer in the presence of ultrasound (20 kHz) and found that no obvious direct effect on the rate of electron transfer processes was observed for the systems studied. Furthermore, it was concluded that the dominating ultrasonic effect was the strongly enhanced mass transport. Huck also investigated the effect of ultrasound on electrode kinetics [20] and reported that ultrasound slowed the rate of electron transfer for the $Fe(CN)_6^{3+/4+}$ redox system. Huck attributed this to surface cleaning of the electrode. In 1994, Birkin and Silva-Martinez determined the heterogeneous electron transfer kinetics in the presence of ultrasound (20 kHz) at microelectrodes employing sampled voltammetry [21]. They showed that the presence of ultrasound did not influence measurably the rate of the electron transfer processes for a series of well-known quasi-reversible redox couples on Pt electrodes.

In the 1990´s, Pollet performed ultrasonic experiments at three ultrasonic frequencies 20, 500 and 800 kHz and at (298 ± 1) K using 1.0 mmol ferricyanide in 1.0 mol/dm^3 KCl [10]. For the sonoelectrochemical experiments using ultrasonic probes, the electrode-horn separation was approximately 2 mm. The apparent heterogeneous rate constants were evaluated using the tables for quasi-reversible steady-state voltammograms published by Mirkin and Bard [16] i.e. the experimental values of the half-wave ($E_{1/2}$) and quartile potentials ($\Delta E_{1/4}$ and $\Delta E_{3/4}$), the dimensionless rate constant (λ), the limiting current density (j_{lim}) were used to evaluate the apparent heterogeneous rate constant (k_{o}).

Figure 4 shows the apparent heterogeneous rate constant at the various ultrasonic intensities for the three ultrasonic frequencies and at (298 ± 1) K. The figure shows that as the ultrasonic intensity increases, then the apparent rate constant increases by 1.2-fold. As observed previously for other systems [9], the figure shows that there appears to be “zero” frequency effect within the ultrasonic frequency range employed (20 - 800 kHz). The 1.2-fold increase in k_{o} (Fig. 4) seen at the largest ultrasonic intensities suggests a detectable effect of ultrasound on k_{o} for this quasi-reversible system.

In order to ascertain any sonochemical effect, it is important to remove any thermal effect caused by sonication. Thus, the effect of temperature on the *formal* rate constant was investigated in the absence of rotation. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} and at various bulk temperatures (298, 310.5 and 323 K) using the same experimental conditions as before.

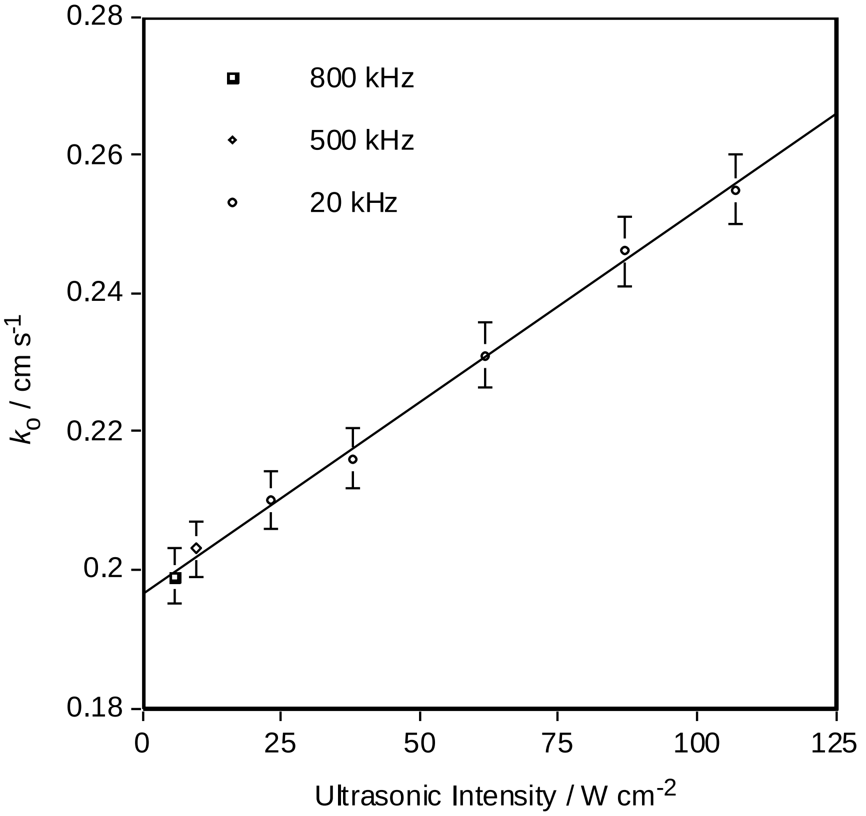

Figure 4 - The apparent heterogeneous rate constant (k_o) plotted against various ultrasonic intensities at three ultrasonic frequencies and at (298 ± 1) K [10]. Here the ultrasonic intensities (ψ) were calculated by dividing the ultrasonic power (P_d) by either the ultrasonic probe tip area (A) or the electrochemical cell base area (A') when using ultrasonic baths. The ultrasonic power (P_d) was determined calorimetrically [1].

Figure 5 shows the variation of the apparent heterogeneous rate constant with temperature for the reduction of ferricyanide on a rotating platinum disc electrode (operating at 500 rpm). The figure shows that the apparent heterogeneous rate constant increases with temperature i.e. an increase of approximately 30 % in the range 298-323 K. According to the *Electrochemical Kinetic Theory* [8], this observation suggests as the temperature is increased, the electron-transfer between the electrode surface and the electrolyte solution becomes more facile. As with chemical reactions, electrode kinetics depends upon the magnitude of the activation energy e.g. the slowness of an electrode reaction is often associated with a large activation energy and may be counteracted by increasing temperature.

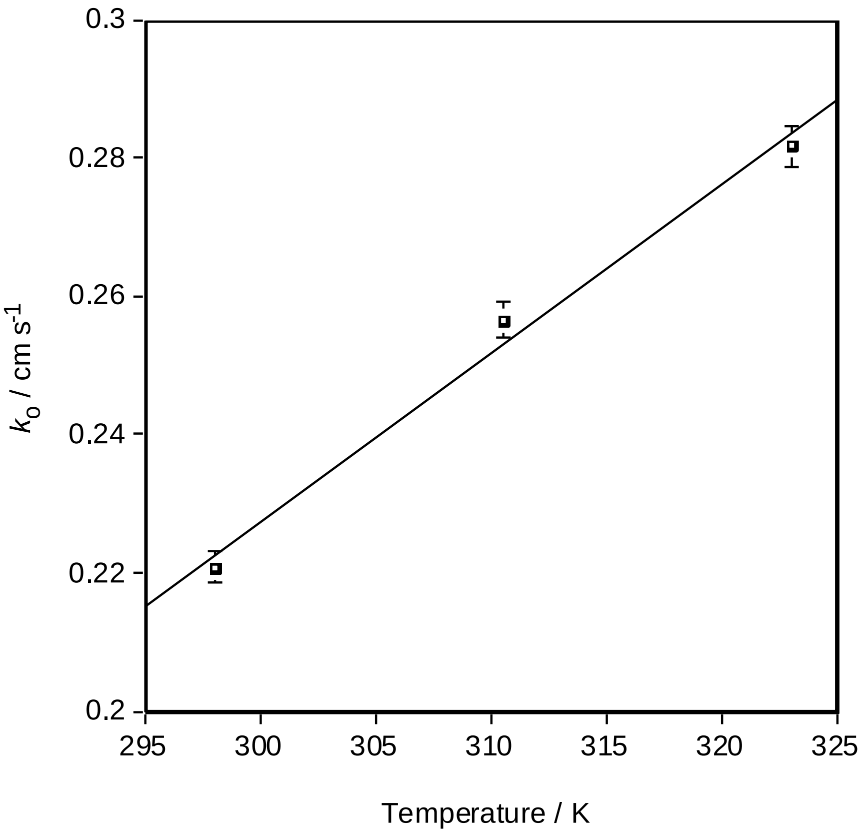

Figure 5 - The effect of temperature on the apparent heterogeneous rate constant (k_o) for the reduction of 1.0 mmol/dm^3 ferricyanide on a platinum (Pt) rotating disc electrode (500 rpm) [data obtained from rotating disc voltammetry at 100 mV/s] [10].

These sonoelectrochemical findings could be due to several possible contributions:

(i) Bulk temperature is an obvious factor in the increase in the apparent heterogeneous rate constant. Assuming linearity between k_o and T (Fig. 5), an 'apparent' bulk temperature in the presence of ultrasound (107 W/cm^2, 20 kHz) was deduced to be 315 K. This result may be dismissed as sonovoltammetric measurements were made within 5 seconds when the potential was scanned between 0 and +500 mV at a scan rate of 100 mV/s. During this time, only 0.2 °C rise was observed in the presence of 107 W/cm^2 ultrasound at 298 K. Thus, as the bulk experimental temperature never rose above 315 K, the increase in apparent heterogeneous rate constant cannot be due solely to a bulk temperature rise.

(v) It is known that the application of ultrasound leads to a change in the electrode surface due to the implosion of microjets. It is now well-accepted in the field that sonication time is an important parameter in the electrode surface modification. Thus, it is possible in this case that the observed increase in the apparent heterogeneous rate constant may be due simply to the ultrasonic exposure time at the electrode surface. However, this suggestion may also be dismissed. Using Figure 6 to deduce a ΔE_p for the time available to complete the sonovoltammetric measurement (i.e. 5 seconds) allows a deduction of the apparent heterogeneous rate constant (from Equation 2) of $k_o = 0.226$ cm/s.

Since the apparent heterogeneous rate constant was found to increase by 1.2-fold in the presence of ultrasound (107 W/cm^2, 20 kHz) compared to *silent* conditions i.e. k_o (0 W cm^{-2}) = 0.222 cm/s (Fig. 5) and k_o (107 W/cm^2, 20 kHz) = 0.255 cm/s (Fig. 4), thus the increase is not solely due to both the sonication time exposure thus to cleaning effect and bulk temperature rise.

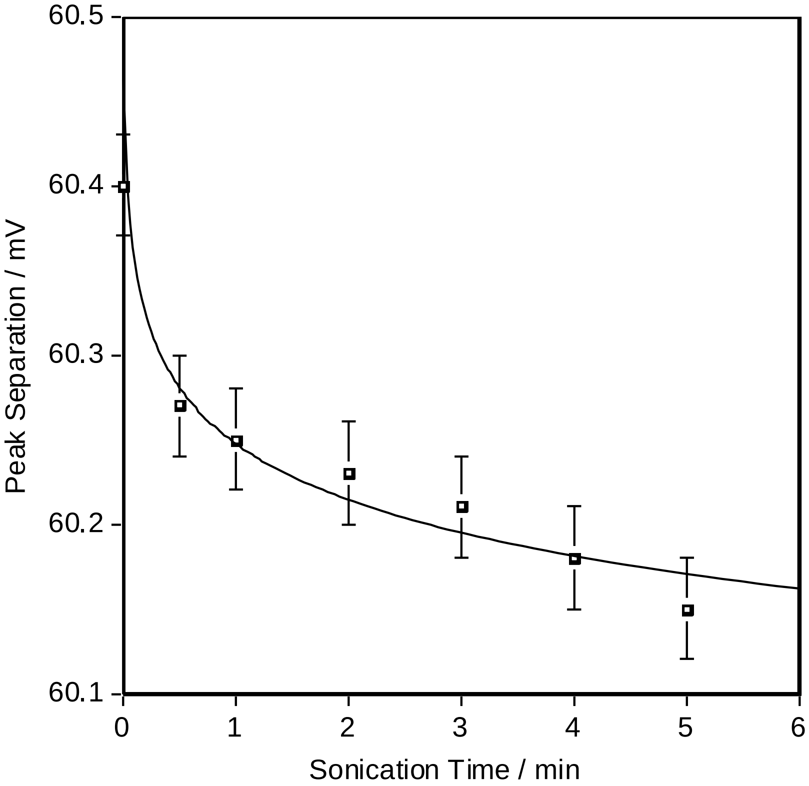

Figure 6 - The effect of sonication time on the peak separation (ΔE_p) for the reduction of 1.0 mmol/dm^3

ferricyanide at 107 W/cm^2 (20 kHz) and at (298 ± 1) K. Apparent heterogeneous rate constant (k_o) can be determined using cyclic voltammetry from quasi-reversible redox couples. Following the method described by *Nicholson* (Eq. 2), the increase in ΔE_p ($E_{pa} - E_{pc}$) may be used to determine the rate of heterogenous electron-transfer by using the published working curves which relate ΔE_p to a kinetic parameter (ψ) [13,14].

(iii) It has been shown in (ii) [above] that the apparent heterogeneous rate constant, k_o, obtained on a macroelectrode in the presence of ultrasound (107 W/cm^2, 20 kHz) was 0.255 cm/s (Fig. 4). This value is similar to that obtained on a microelectrode (k_o = 0.26 ± 0.01 cm/s) [21] and is also in the same order of magnitude to that obtained on radial flow micro-ring electrode (RFMRE) (k_o = 0.36 cm/s) [22] at the same bulk temperature. It has been previously observed [23] that the apparent heterogeneous rate constant values observed with microelectrodes are significantly higher than those observed on a macroelectrode. It is suggested [23] that using 'large' electrodes lead to larger ohmic potential (*IR*) errors compared to 'smaller' electrodes. In other words, this suggests that ultrasound leads to a decrease in ohmic potential. This observation suggests that a macroelectrode under sonication behaves like a microelectrode, which is in excellent agreement with literature results [24]. For example, Compton *et al.* [24] showed that diffusion layer thicknesses obtained on a sonicated macroelectrode were similar to those obtained on a microelectrode.

(iv) Commonly, it is recognised that apparent heterogeneous rate constants are strongly dependent upon the electrode material, the electrode pre-treatment and the solution environment. It has been shown [25] that apparent heterogeneous rate constant values for the $Fe(CN)_6^{3+/4+}$ redox couple observed on a platinum electrode are greatly improved if the electrode is freshly polished in an alumina slurry containing Nanopure water and if the electrolyte contains excess of cyanide ions. It was suggested [23,25] that the low apparent heterogeneous rate constant values were due to chemisorption of $Fe(CN)_6^{3-/4-}$ on the platinum electrode surface. Kawiak *et al.* have shown [26] that cyanide ions (as KCN) prevent the $Fe(CN)_6^{3+/4+}$ chemisorption and the improvement of the electrode performance as CN^- forms a protective layer by occupying chemisorption sites. They also showed that increasing cyanide ion concentration in solution led to an increase in the apparent heterogeneous rate constant values. Since in the author´s conditions, an increase in apparent heterogeneous rate constant values was found with increasing ultrasonic intensity (Fig. 14), it may be speculated that sonication leads to a new electrode surface composition. Following the argument of Compton *et al.* [9,24], it may be possible that hydroxyl radicals formed by the sonolysis act as oxidising agents. It may also be possible that these iron (III) species act as cyanide ions, thus leaving the $Fe(CN)_6^{3-/4-}$ ions free for electron-transfer.

(v) Large apparent heterogeneous rate constant values (around 0.5 cm/s) are also observed when the platinum electrode is being laser activated [27] i.e. being heated around 1,500 K at very short laser pulse (in the order of nanoseconds) and at a power of around 50 MW/cm^2. It was shown [27,28] that the heavily activated surface has a microscopic area of approximately twice that of the initial surface due to rapid surface heating and thus desorbing effect of impurities. By analogy with laser activation, the increase in apparent heterogeneous rate constant values in the presence of ultrasound might indicate that sonication leads to very short high temperature at the electrode surface. It is well-known [1-3] that the collapse of transient cavitation bubbles generates extremely high microscopic temperature (up to 5,000 K) and pressure (up to 2,000 atms).

Hydrogen evolution reaction (HER)

Reactions occurring at gas-evolving electrodes constitute an important area of electrochemical engineering, especially in water electrolysis for hydrogen production, electrowinning of metals and corrosion. In the case of water electrolysis, the cell voltage (V_{cell}) includes a term E_{IR} due to the ohmic drop across the cell, which is increased by gas bubbles adhering to the electrode surface. Usually, the ohmic contribution is minimized with a suitable geometric configuration of the electrodes and the use of highly conducting electrolytes. However, hydrogen (H_2) and oxygen (O_2) gases possess insulating properties, so their presence on the electrode surfaces reduces their effective area and contributes to an increase in E_{IR}. There are also effects of the attached gas bubbles onto the surface and concentration overpotentials, which were discussed by Dukovic and Tobias [29]. As the bubbles escape the electrode surface and enters into the electrolyte, they affect mass transfer. In the electroplating and electrolysis industries, managing gas bubble resistance is an important issue. Thus, one of the main objectives in this research area is to show that ultrasound decreases E_{IR} by removing effectively adhered hydrogen gas bubbles at the Pt surface, as well as quantifying the decrease in the term. Moreover, the effect of power ultrasound on the hydrogen evolution reaction (HER) has not been greatly investigated, there are only just a few reports on the subject, with most of the investigations performed using different experimental setup and solutions, and thus data cannot be compared (or used for industrial applications). Ultrasound can also affect the electrode overpotential of a process and reports by Morigushi [30] and Pollet *et al.* [10,12,31] showed that the overpotential of hydrogen evolution on Pt and SS (stainless-steel) electrodes immersed in aqueous solutions decreases upon sonication. More recently, Li *et al.* [32] showed that ultrasound (60 kHz; 50 W) increased the production of hydrogen for fairly weak electroanalytes, and by lowering the electrolysis cell voltage (V_{cell}), an increase in electrolytic efficiency and a decrease in energy consumption was observed. In previous studies, it was demonstrated that power ultrasound enhances mass-transfer of electroactive species from the bulk solution to the electrode surface, however little information in the literature is given on hydrogen adsorption and desorption mechanisms at micro and single crystal Pt electrodes during and after sonication.

Recommendations

To answer the above research questions and verify the hypotheses, two electrochemical systems, namely quasi-reversible and irreversible systems should be investigated:

(i) A series of quasi-reversible redox couples at polycrystalline and single crystal Pt electrodes. The voltammetric characteristics of well-known quasi-reversible systems on Pt have been extensively studied as they are mostly used as “reference systems” in electrochemistry. Here, electrochemistry software should also be used as simulation/fitting tool to determine the important kinetic parameters.

(ii) The H^+/H_2 redox couple at polycrystalline and single crystal Pt electrodes. The voltammetric characteristics of Pt in acidic and alkaline solutions have been studied in considerable detail over the past 60 years. Despite complications which may arise due to the presence of surface oxides, surface atom rearrangements, and hydrogen adsorption, Pt is the electrode material of choice for sonoelectrochemical experiments.

In order to generate the required data, the following experimental conditions should be considered:

Choice of electrode sizes. First, the use of microelectrodes ($\varnothing = 25\ \mu m$, sometimes referred to as ultramicroelectrodes) in conjunction with ultrasound enables high mass transfer rates to be achieved. Second, any effects of ultrasound should, in theory, be concentrated at the moment of impact with the electrode surface. Ultramicroelectrodes are ideally suited to fast scan rate voltammetry because of their inherently low capacitive current and low *IR* drop.

Choice of quasi-reversible (QR) and irreversible (IRR) redox couples. The electron transfer kinetics of the following redox systems should be studied: (i) *QR* - ferrocene/ferrocenium (Fc/Fc^+ in acetonitrile, 0.1 mol/dm^3 tetraethylammonium tetrafluoroborate, TEATFB), hexaammineruthenium (III/II) chloride ($[Ru(NH_3)_6]Cl_3$, in aqueous 0.1 mol/dm^3 potassium chloride solutions), and hexachloroiridate (III/IV) ($K_3[IrCl_6]/Na_2[IrCl_6]$ in 1.0 mol/dm^3 NaCl and $K_3[IrCl_6]$ in 1 mol/dm^3 KCl). It is believed that all three systems have relatively rapid electrode kinetics under the proposed conditions employed. (ii) *IRR* - 0.1 mol/dm^3 $HClO_4$ could be used to study the H^+/H_2 redox couple.

These particular redox systems are chosen because of the pre-existing knowledge of their heterogeneous electron transfer rates in the literature. This would enable researchers to make a direct comparison of the results with those obtained in experiments by other workers.

Reproducibility and platinum electrode pre-treatment in the absence of ultrasound.

When employing cyclic voltammetry at solid electrodes, the electrode cleaning must be carefully chosen since it has considerable effect on the data obtained. Contaminants left behind after cleaning and/or those not removed by the cleaning technique may cause erroneous data. Commonly used methods for the cleaning of electrodes include acid etching, polishing, pulsing and flaming [6]. The electrode cleaning procedure chosen differs greatly between researchers. In general, experimenters have placed an emphasis on consistency and reproducibility rather than optimisation of current or rate data. An in-depth work effort should be dedicated in ensuring that the Pt electrode surfaces are reproducible prior to any sonoelectrochemical experiments. To test the Pt electrodes, cyclic voltammograms need to be recorded in the relevant redox systems employed in subsequent ultrasound experiments. If classic voltammetry of the redox probe is not observed, the polishing and cleaning process should be repeated until the expected voltammetry is obtained.

Silent conditions.

The effect of stirring, macroscopic (bulk) temperature and sonication time upon these electrode kinetic parameters is also known to be important factors in comparing the validity of any sonoelectrochemical effects. Since ultrasound can lead to increases in mass-transport and bulk temperature, it is important to identify the magnitude of these possible effects using a non-sonicated system. Electrochemical experiments should be conducted on all redox couple systems at fixed electroactive concentration using a stationary Pt ultramicroelectrode and at several temperatures.

In order to demonstrate whether mass-transport has an influence on $E_{1/2}$ and k_o, the effect of stirring the bulk solution, using a rotating Pt disc electrode (RDE) on the voltammetric responses need to be investigated. The electrode kinetic parameters can be determined by using the Mass-Transport

Corrected Tafel method, *Mirkin-Bard* method and other accepted methods in the electrochemical literature.

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