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Stability of mercury film electrodes under the influence of high frequency (500 kHz) ultrasound

J. DAVIS[1], F. JAVIER DEL CAMPO[1], F. MARKEN[1], R.G. COMPTON[1]* and E. CORDEMANS[2]
[1]*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK*
[2]*Undatim Ultrasonics S.A., Zoning Industriel, Rue de l'Industrie 3, B-1400 Nivelles, Belgium*
*(*author for correspondence, fax: +44 1865 27410, e-mail: richard.compton@chemistry.ox.ac.uk)*

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Abstract

The analytical utility of coupling high frequency ultrasound (500 kHz) systems with electrochemical stripping techniques has been investigated. The stability of mercury film electrodes (on either glassy carbon or iridium substrates) under various ultrasound regimes was assessed with cavitational erosion found to occur irrespective of the substrate or position within the cell assembly. Removal of dissolved gas was found to increase the lifetime of the mercury film but only through sacrificing enhancements in mass transport. A second series of experiments investigated the influence of ultrasound frequency (20 and 500 kHz) on the stripping voltammetric determination of lead and cadmium at bare glassy carbon electrodes. The results were compared with silent conditions with the high frequency system shown to significantly enhance the accumulation of the target analyte.

1. Introduction

The fusion of ultrasound with conventional electrochemical technologies has proven to be extremely beneficial for both electrosynthetic and electroanalytical applications [1–4]. Enhanced transport of material to the electrode has been found to accrue directly from ultrasonically induced acoustic streaming and cavitational micromixing with the asymmetric collapse of bubbles at the electrode–solution interface maintaining the activation of the electrode [1]. This is primarily attributed to the continual removal of material from the surface of the electrode whose cumulative adsorption would otherwise serve to passivate it. While the aggressive imposition of sonic irradiation can be extremely advantageous in highly fouling media [5–7] there are, however, a number of instances in which extensive cavitation can be less than desirable. It is possible to envisage situations in which the erosive capacity of the applied ultrasound could lead to the degradation of the electrode substrate [8, 9] especially under prolonged sonication times. This problem is particularly relevant when considering the use of mercury film (MF) electrodes.

The large cathodic range available to mercury film electrodes has proven invaluable to a large number of applications and forms the bedrock upon which electroanalytical ASV methodologies and many electroreductions are based. The toxicity of mercury has however provoked a great deal of concern such that the search for viable alternatives has intensified. The wide potential window that is open to boron doped diamond electrodes holds substantial promise [5] but the majority of these systems have yet to attain sufficient maturity or availability. As such, the development of strategies for minimizing the amount of mercury applied to the base electrode while maximizing electrode lifetime retains a high priority. This poses a considerable problem for systems operating under hydrodynamic conditions, and especially those employing ultrasound, where erosion of the mercury film can occur through the sustained perturbation of the solution–film interface.

Minimizing the loss of mercury under such regimes while retaining both enhanced mass transport and continual electrode activation is a significant challenge. This has been countered to some extent through the use of polymer coatings through which the mercury is deposited. The overlying polymer film (Nafion® [10–12], polypyrrole derivatives [13]) provides a physical framework that can provide a degree of mechanical resistance to the effects of the applied ultrasound. This protocol is however more technically complex and the transport of reagents to the film can be restricted by the polymeric barrier [12, 13]. An ability to temper the cavitational events without conceding the potential gains in enhanced rates of mass transport through simple manipulation of the instrumentation or indeed choice of sono reactor would be highly attractive.

At present, a significant proportion of sonoelectrochemical systems employ power ultrasound (20 kHz) probes whose insertion within the solvent medium can directly generate a localized high intensity acoustic field (~10–250 W cm^{-2}). The facile manipulation of the ultrasound transducer power output combined with placement of the electrode within this field can be used to modulate the effects experienced at the electrode surface. This contrasts a 500 kHz high frequency ultrasound (HFU) assembly (Undatim Ultrasonics SA, Belgium) in that the transducer output is considerably weaker (~1.4 W cm^{-2}) with a more diffuse cloud of cavitation bubbles produced throughout the solution. The principal aim of the present work was to examine how the weaker focus of the cavitational processes originating from the HFU system would affect the retention of a mercury layer and the transport of material to the electrode surface. The latter was assessed through comparing the deposition and subsequent stripping of lead and cadmium at a bare glassy carbon electrode under silent, HFU, and power ultrasound regimes.

2. Experimental details

All reagents were of the highest grade available and used without further purification. All solutions and subsequent dilutions were prepared using deionised water from an Elgastat (Elga, UK) UHQ grade water system with a resistivity of 18 MΩ cm. Electrochemical measurements were conducted using a μAutolab computer controlled potentiostat (Eco-Chemie, Utrecht, Netherlands) with a standard three electrode configuration. Glassy carbon (3 mm dia., BAS, UK), platinum (1 mm dia. sealed in glass) or iridium (1 mm dia. sealed in PTFE) were used as the working electrode with spiral wound platinum wire as the counter electrode and a saturated calomel (Radiometer, Copenhagen) reference electrode. The electrodes were polished between experiments with 1 μm alumina powder (Buehler Micropolish II, USA) and were thoroughly rinsed and sonicated in an ultrasound bath immediately prior to use.

Sonoelectrochemical measurements were conducted using two different types of system for which the cell assemblies have been well characterized [6–8]. The power ultrasound system was comprised of a 20 kHz transducer (VCX400, Sonics and Materials, USA) equipped with a stepped 3 mm titanium probe placed 10 mm vertically above the working electrode and operated at a power setting of 15% (calorimetrically estimated to be about 120 W cm^{-2} [14]). The horn tip was electrically isolated from the test solutions through the combined use of a PTFE spacer and connecting screw. A stainless steel cooling coil, through which water from a constant temperature bath was circulated, surrounded the electrode/horn assembly and maintained the cell temperature at 20 °C within ±2 °C. The HFU sonochemical system consisted of an air cooled 500 kHz 25 W D-type reactor (Undatim Ultrasonics SA, Belgium) recessed into a PTFE base. The transducer comprised a 3.6 cm diameter stainless steel solution exposed surface that has been previously shown to deliver an ultrasound intensity of 1.4 W cm^{-2} [8]. Solution volumes of 20 cm^3 and 100 cm^3 were used in the power ultrasound and HFU investigations, respectively.

2.1. *Preparation of mercury film electrodes*

Mercury film electrodes were prepared *ex situ* through electrodeposition from a solution containing 1 g l^{-1} Hg^{2+} in 10 mM nitric acid/0.1 M KNO_3. The electrode was poised at −1 V for 15 s under quiescent conditions after which the deposited mercury was electrolytically stripped in the plating medium by sweeping from +0.25 V to +0.8 V at 100 mV s^{-1}. This plating/stripping cycle was repeated until a consistent stripping peak was obtained. Once achieved, a final deposition process was initiated. The resulting MF electrode was then removed from the solution and placed in fresh electrolyte (devoid of any mercuric salts) with as little agitation as possible. The electrode was suspended in the solution for 2 min before being placed in the HFU sonoelectrochemical cell. The reproducible preparation of the MF electrodes are crucial to the interpretation of the effects of the applied ultrasound and the conditioning procedure was found to provide stripping peak heights with a relative standard deviation of less than 4% ($N = 3$) on glassy carbon and 3% ($N = 3$) on iridium.

It must be noted that the amount deposited will be significantly less than that normally applied in electroanalytical determinations with the stripping charge approximating to 12 monolayers (ignoring the likely coalescence of the mercury to form hemispherical droplets). This is in keeping with our desire to minimise the amount of mercury applied to electrode but in more immediate terms allows the effects of the applied ultrasound to be rationalised.

3. Results

The erosive capacity of high frequency ultrasound was assessed by examining the loss of mercury from *ex situ* plated MF electrodes. The amount of mercury lost as a consequence of the applied ultrasound was evaluated by comparing the height of the mercury stripping peak after various periods of insonation. Upon terminating the ultrasound, the potential range −0.25 V to +0.8 V was scanned at 100 mV s^{-1} using linear sweep voltammetry. It was found that increasing the duration of ultrasound led to a reduction in the height of the stripping peak as shown in Figure 1 and is consistent with the cavitational erosion of the mercury film from the glassy carbon surface.

Prolonging the duration of ultrasound was found to degas the solution [4]. This can be observed during the

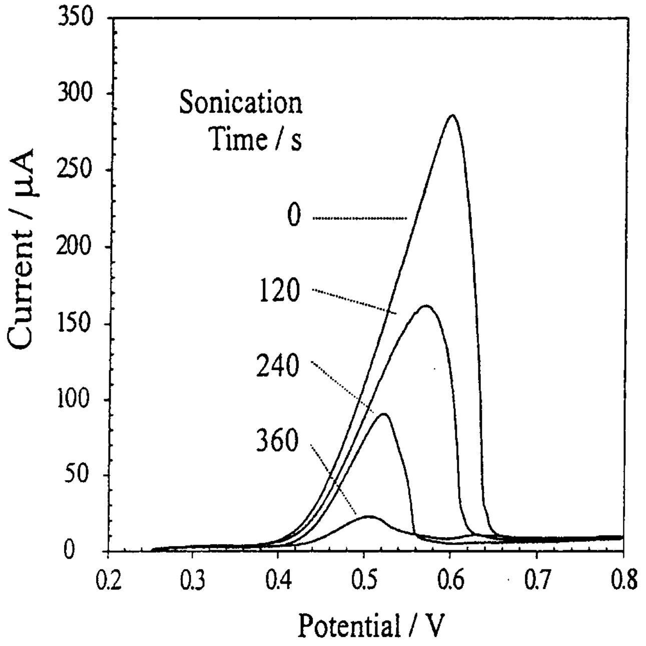

Fig. 1. Linear sweep voltammograms detailing the erosion of mercury from the surface of a glassy carbon electrode after various periods of high frequency irradiation.

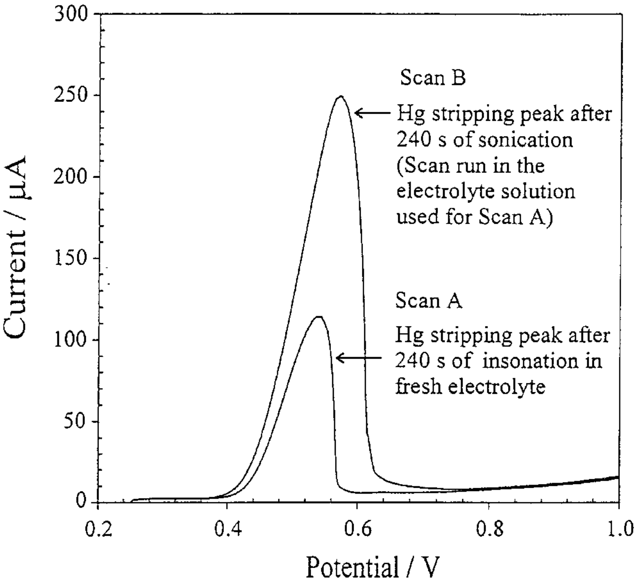

Fig. 2. Stripping voltammograms highlighting the effect of ultrasonically induced degassing on the erosion of mercury from a glassy carbon electrode.

experiments with a significant proportion of the cavitation bubbles seen to travel towards the surface. Although such effects are well established and indeed exploited they can lead to significant problems of reproducibility when employed in electrochemical systems. The removal of gas from the solution will have the effect of increasing the cavitation threshold such that subsequent stripping runs will experience fewer cavitational events and hence retain more mercury. It was found that when the electrolyte used for a stripping experiment was left unchanged and a second, essentially identical, stripping experiment re-run in that media, markedly different results were obtained. This is highlighted in Figure 2 where a mercury coated glassy carbon electrode was prepared and fresh electrolyte introduced into the sonocell. The electrode was subjected to 4 min of ultrasound and the remaining mercury stripped under silent conditions resulting in the voltammetric trace shown as scan A in Figure 2. The electrode was removed, re-plated with mercury and replaced within the cell without exchanging the electrolyte. The electrode was again subjected to 4 min of ultrasound and the stripping process repeated. In this instance the voltammetric profile is shown as scan B in Figure 2 and reveals that very little of the mercury was removed and stands in marked contrast to the results found in scan A. Consistent stripping results were however obtained when fresh electrolyte was introduced prior to each new stripping experiment and highlights the fact that ultrasound can affect not only the electrode but also the media within which it rests.

Corroboration for this was supplied through reducing the amount of dissolved gas present within the electrolyte solution prior to commencing the ultrasound experiments. This was achieved by introducing the electrolyte into a flask modified with a submerged capillary gas inlet. The flask was connected to a vacuum pump system with argon bubbled through the capillary at a pressure of about 10 torr [8]. Sonostripping experiments identical to those described previously were conducted immediately after placing the degassed solution in the sonocell. The results were compared with those obtained at a MF glassy carbon electrode where the electrolyte had been replaced between experiments with the results shown in Figure 3. It can be seen that, barring minor losses, the electrodes placed within degassed solutions were found to be essentially stable to high frequency ultrasound.

An analogous set of experiments were conducted using an iridium rod sealed in PTFE to ascertain if the nature (nonmetallic vs metallic) of the underlying substrate exerted any influence on the removal of mercury. Iridium has emerged as a particularly favourable metallic substrate for mercury deposition, especially in microfabricated systems [15–17]. Unfortunately, removal of the mercury from the substrate under insonated conditions was still observed with little difference between glassy carbon and iridium substrates as shown in Figure 3. Erosion of the mercury films during the application of ultrasound was also found to proceed irrespective of the position of the electrodes within the cell.

The reduction in the extent of cavitation within the degassed solution was confirmed by examining the fixed potential reduction of 1 mM $Ru(NH_3)_6^{3+}$ in unbuffered 0.1 M KCl at a 1 mm diameter platinum macroelectrode. The current–time profiles obtained in solutions saturated with argon under silent and insonated conditions are shown in Figure 4. Cavitational events can be partially resolved at the electrode and manifest

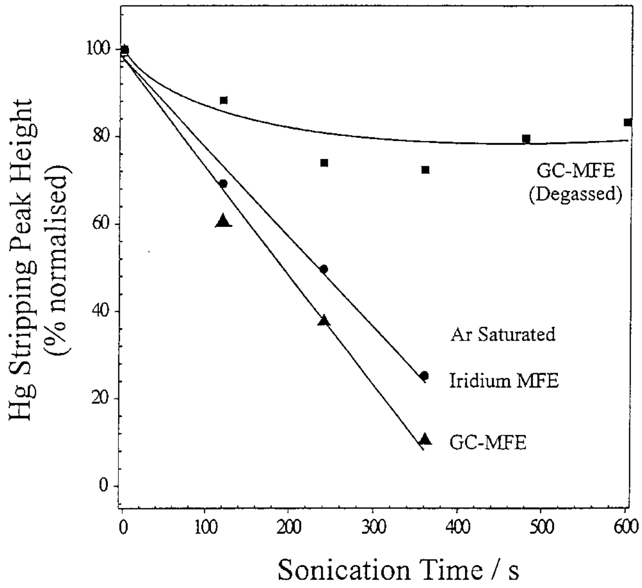

Fig. 3. Influence of substrate and dissolved gas on the ultrasound induced erosion of mercury from the electrode surface.

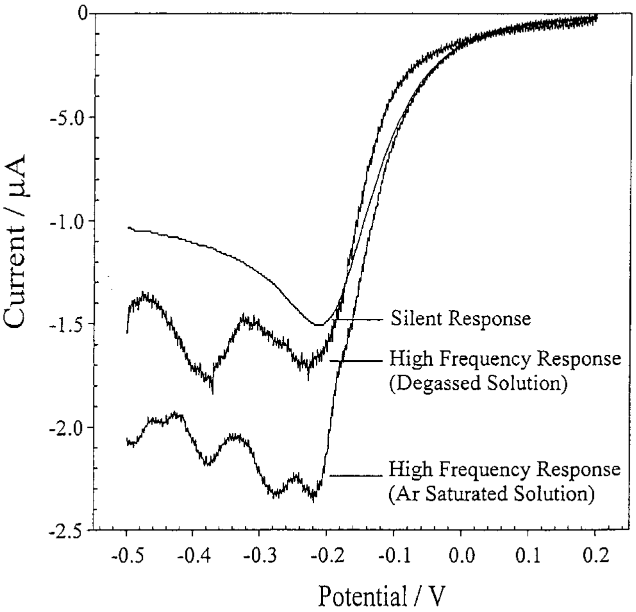

Fig. 5. Linear sweep voltammograms comparing the influence of ultrasound on the response of a platinum electrode to the reduction of 1 mM $Ru(NH_3)_6^{3+}$.

themselves as numerous spikes in the current. The removal of argon from the solution using the degassing protocol results in a substantial reduction in the number and intensity of the current spikes. It is tempting to suggest that by degassing the solution we can significantly improve the lifetime of mercury film electrodes. Removing the dissolved gas reduces the number of cavitational events and hence the erosive capacity of the system but it also reduces mass transport to the electrode. Linear sweep voltammograms detailing the reduction of the ruthenium couple under silent conditions and during the application of ultrasound are shown in Figure 5 with the degassed solution providing little additional benefit over the silent case.

The influence of ultrasound frequency on mass transport was further investigated by comparing the performance of the HF system with a conventional power ultrasound system. The application of ultrasound during the deposition/accumulation stage in stripping analysis is well established and as such the comparative responses of both systems to the analysis of lead and cadmium was selected as a particularly apt test. The performance of each ultrasound system was assessed using a bare glassy carbon electrode rather than a MF electrode to avoid any ambiguities that mercury erosion might incur and so retain the integrity of the comparison. The electrodeposition of the metal ions (0.3 μM to 2.6 μM Pb^{2+} or Cd^{2+} in 0.1 M HNO_3) was conducted using both power ultrasound and the HFU system and the results compared with the more traditional silent method. The analysis was conducted through maintaining a deposition potential of −1.5 V for 10 s and an equilibration time of 5 s at −1 V to allow the solution become quiescent. Square wave stripping voltammetry was then initiated over the potential range −1 V to −0.2 V (frequency 25 Hz, amplitude 0.05 V, step potential 0.002 V) with the stripping peaks measured at −0.55 V and −0.8 V for lead and cadmium, respectively. The results for the lead analysis are shown in Figure 6 with cadmium providing a similar set of responses (not shown). Power ultrasound undoubtedly provides superior performance, although the imposition of HFU still imparts considerable benefits to the deposition process over the silent case.

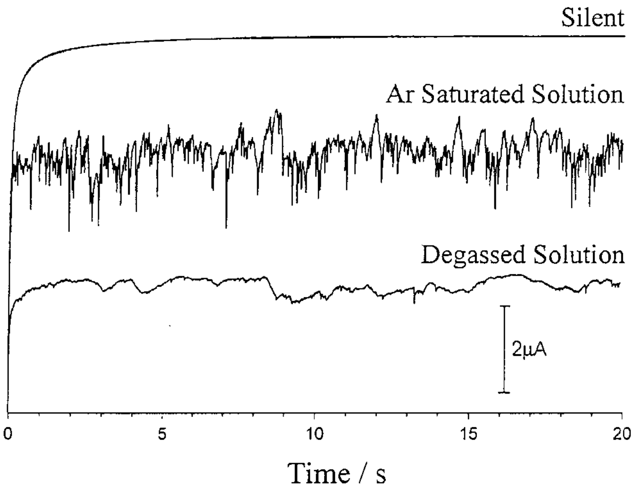

Fig. 4. Current–time profiles detailing the reduction of 1 mM $Ru(NH_3)_6^{3+}$ at a platinum electrode under various regimes.

Ultrasound induced degassing and the effects on the transport of Pb^{2+} and Cd^{2+} to the electrode was initially assessed by examining repetitive stripping measurements (retaining the deposition time of 10 s) over a period of 2 min. No diminution in the height of the stripping peak was observed. A reduction in the magnitude of the stripping peak was however observed if the insonation time was extended beyond two

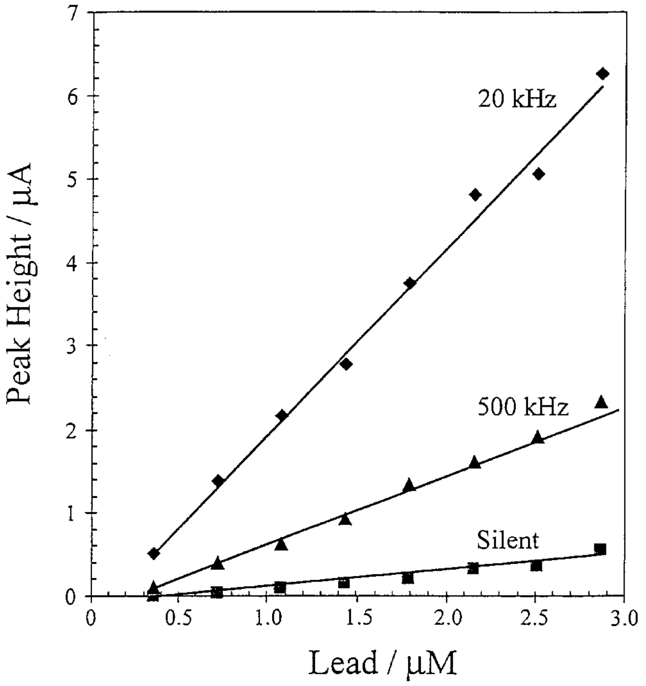

Fig. 6. Influence of power ultrasound, high frequency ultrasound and traditional silent techniques on the deposition (10 s at −1.5 V) and stripping of lead at a bare glassy carbon electrode.

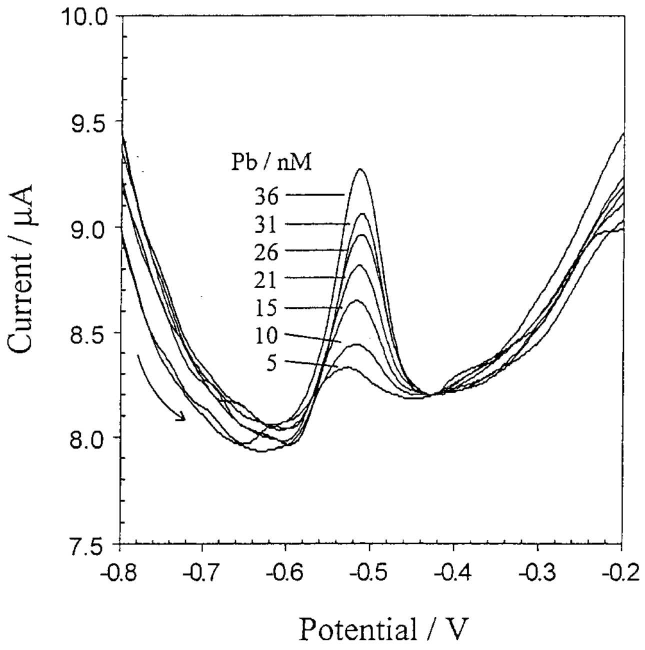

Fig. 7. Square-wave voltammograms detailing the stripping of lead at a bare glassy carbon electrode after a deposition time of 60 s during which high frequency ultrasound had been applied.

minutes. Three consecutive two minute HFU insonation periods were applied (without changing the electrolyte solution) with the deposition procedure engaged within the last 10 s of each period. The height of the stripping peak was found to decrease by 24% and 53% after the 2nd and 3rd deposition/strip cycle (whereby the electrolyte solution has been subjected to a total of 4 and 6 min of insonation, respectively). This has important implications for the low level detection of metal ions where extended deposition times are commonly employed to preconcentrate the target analyte. This is compounded further by the use of standard addition protocols whereby four or five successive experiments may be required with the same analysis solution. In such cases, the vigorous introduction of argon between additions can serve to rejuvenate the solution with the bubbling time required dependent on the insonation history.

The efficacy of this approach was assessed through examining the response of a bare glassy carbon electrode to increasing additions of lead (covering the range 5–40 nM). Consecutive square wave voltammograms recorded after an accumulation period of 60 s are shown in Figure 7. Argon was bubbled through the solution for 10 min prior to commencing each measurement in order to counteract the effect of degassing. A linear relationship between peak height and lead concentration was observed with a limit of detection of 2.5 nM Pb^{2+} (based on $3s_{\mathrm{b}}$). This level is comparable to that attainable using mercury free carbon electrodes under the traditional, silent, conditions [18–20] but can be achieved through utilising a markedly shorter accumulation period. The main advantage in applying ultrasound will however undoubtedly lie in the ability to maintain electrode activation through cavitational cleaning effects. The effectiveness of such processes has been demonstrated previously through the erosion of the mercury thin films and Prussian blue layers [8] from the electrode surface.

4. Conclusion

The erosion of mercury from the surface of conventional electrodes by high frequency ultrasound has been demonstrated. Degassing the solution prior to the onset of insonation has been shown to extend the lifetime of the mercury layer but only at the cost of significantly reduced mass transport. The potential application of high frequency ultrasound within electrochemical systems remains to be fully explored but it would appear to offer no performance gain over conventional power ultrasound systems for the electrodeposition of metals. The effects of slow solution degassing in particular would require considerable vigilance on the part of the operator to ensure reproducibility. Nevertheless, the system provides significant sensitivity enhancements over conventional stripping techniques with *in situ* cavitational activation of the electrode providing a significant bonus to the analytical process. The smaller physical size of the unit combined with the ability to use it on an open bench without the need for soundproofing also has considerable merits.

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References

1. R.G. Compton, J.C. Eklund and F. Marken, *Electroanalysis* **9** (1997) 509.
2. D.J. Walton, U. Geissler, S.S. Phull, T.J. Mason, J.P. Lorimer, C. Campbell and J. Evans, 'Chemical Processes and Reactions under Extreme or Non Classic Conditions', European Communities Publication (1998) COST Action D6, pp. 83–86.
3. J.P. Lorimer, B. Pollet, S.S. Phull, T.J. Mason, D.J. Walton and U. Geissler, *Electrochim. Acta* **41** (1996) 2737.
4. T.J. Mason, 'Sonochemistry', Oxford Chemistry Primers, Oxford University Press, (1999), and references cited therein.
5. A.J. Saterlay, C. Agra-Gutierrez, M.P. Taylor, F. Marken and R.G. Compton, *Electroanalysis* **11** (1999) 1083.
6. R.P. Akkermans, J.C. Ball, T.O. Rebbitt, F. Marken and R.G. Compton, *Electrochim. Acta* **43** (1998) 3443.
7. C. Agra-Gutierrez, J.L. Hardcastle, J.C. Ball and R.G. Compton, *Analyst* **124** (1999) 1053.
8. F.J. Del Campo, B.A. Coles, F. Marken, R.G. Compton and E. Cordemans, *Ultrason. Sonochem.* **6** (1999) 189.
9. N.A. Madigan, C.R.S. Hagan, H. Zhang and L.A. Coury, *Ultrason. Sonochem.* **3** (1996) S239.
10. C. Agra-Gutierrez, M.F. Suarez and R.G. Compton, *Electroanalysis* **11** (1999) 16.
11. F.M. Matysik, S. Matysik, A.M.O. Brett and C.M.A. Brett, *Anal. Chem.* **69** (1997) 1651.
12. M.E.R. Dam, K.N. Thomsen, P.G. Pickup and K.H. Schroder, *Electroanalysis* **7** (1995) 70.
13. Y.C. Tsai, J. Davis, R.G. Compton and N. Ito, *Electroanalysis*, in press.
14. M.A. Margulis and N.A. Mal'tsev, *Russian J. Phys. Chem.* **43** (1969) 592.
15. J. Wang, J.Y. Wang, W.K. Adeniyi and S.P. Kounaves, *Electroanalysis* **12** (2000) 44.
16. M.A. Nolan and S.P. Kounaves, *Anal. Chem.* **71** (1999) 3567.
17. P.R.M. Silva, M.A. Elkhakani, M. Chaker, G.Y. Champagne, J. Chevalet, L. Gastonguay, R. Laccase, and M. Ladouceur, *Anal. Chim. Acta* **385** (1999) 249.
18. K.C. Honeychurch, J.P. Hart and D.C. Cowell, *Electroanalysis* **12** (2000) 171.
19. T.H. Degefa, B.S. Chandravanshi and H. Alemu, *Electroanalysis* **11** (1999) 1305.
20. J.Y. Qu, M. Liu and K.Z. Liu, *Anal. Lett.* **32** (1999) 1991.