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ELECTROCHEMISTRY WITH ULTRASOUND: STATE OF THE RESEARCH IN THE FIELD

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ABSTRACT
Sonoelectrochemistry, in which an electrochemical cell is irradiated with sound waves, has now become a most promising technique in view of recent developments in both sonochemical and electrochemical technologies. Many electrochemical systems are influenced by ultrasound, and the methodology offers considerable practical benefit in a wide range of applications [1]. In the last two years there have been over one hundred papers published on the topic, and a survey of this literature shows that Europe has the leading role in this effort. The contribution to the field from European laboratories amounted to over 200 papers by 2004, including several reviews [2-5], and this number has increased in the last three years.

INTRODUCTION

Electrochemistry involves the transfer of electrons at an electrode with associated chemical reaction(s). Electron-transfer reactions produce altered valencies and intermediates such as radical-ions, ions, free-radicals and similar species [6]. Important electrochemical processes include electrosynthesis, electroanalysis, electrocatalysis, electrodeposition, electrodissolution and corrosion. Intrinsic electrochemical parameters include the inherent reactivities of components, the nature of the electrode material (which involves surface energies and differential absorption phenomena), also the diffusion characteristics of species approaching or leaving the electrode area, the structures of ensuing diffusion layers, the consequences of the choice of solvent, supporting electrolyte and so on. Extrinsic parameters to be controlled by the experimentalist include the applied electrode potential, choice of potentiostatic or potentiodynamic methodologies, concentrations of species, and electrolysis temperature [7]. Scale-up from laboratory to practical industrial capability requires specialist principles of electrochemical engineering [8].

Sonochemistry is the study of insonated reaction systems using frequencies above 20 kHz. Key ultrasonic parameters are power, frequency, source-type, system geometry and configuration, and sonochemical phenomena include cavitation, micro-streaming, mixing, emulsification, enhanced hydrodynamics. In addition the coupling of ultrasonic energy into a system is affected by dissolved gases, immersed surfaces, suspended solids, particles and other nucleation-enhancing species; also the shape, composition and size of the reactor. Ultrasound is particularly effective at heterogeneous interfaces such as an electrode surface [9].

In Sonoelectrochemistry, insonation improves the hydrodynamics of a cell, increasing voltammetric limiting currents by factors of up to ten-fold and over [10]. This is of straightforward benefit for example in electroanalysis [11] and in most electrochemical sensor systems. Also ultrasound improves the hydrodynamics of a solid electrode material, allowing replacement of the toxic liquid metal mercury in stripping voltammetry and also benefits unusual electrode materials, such as boron-doped diamond. Many electrosynthetic mechanisms are multipathway, and the range of products depends upon the reaction conditions [12]. Ultrasound alters kinetic regimes close to the electrode and can switch mechanisms between different products [13]. Ultrasound also influences phase phenomena, and usefully allows the replacement of organic solvents by aqueous media in which an immiscible reagent is emulsified so as to allow the necessary mobility in the reaction medium, thereby obviating direct use of organic solvents [14]. This is of particular benefit since high-dielectric organic solvents are environmentally hazardous. Ultrasound also affects systems involving the evolution of gases and has a known degassing effect. Otherwise in environmental applications, ultrasound is useful for analyses in real-life media, which are often contaminated, and is also useful preparatively for the removal of pollutants (waste remediation and degradation) [15], the obviation of environmentally-damaging species ('green chemistry', 'clean synthesis') and the study of natural processes in the environment (e.g. corrosion) [16]. Furthermore many electrosyntheses and electroanalyses are often hampered by formation of inhibitory electrode coatings, and ultrasound can mitigate against this effect. However, the formation of coatings on the electrode is not necessarily undesirable, and electrogenerated conducting polymers such as polypyrrole are influenced by insonation. On occasion insonation may actually make an electrode fouling problem worse, and this shows nicely how alteration in the balance of rates of steps in a mechanism can influence the products. Mechanistic elucidation of these competing kinetic regimes is important, and here the use of rapid-scan voltammetry and other high-speed techniques is important [17]. Electrochemical mechanisms are consequent upon the heterogeneous nature of the electrode/electrolyte interface, and the manner in which ultrasound is imposed influences behaviour. Therefore comparisons of different frequencies (from 20 kHz up to 1 MHz) are necessary. It is clear that many electrochemical systems, such as corrosion, electroanalysis, electrosynthesis, electrochemical degradation reactions, metal electrodeposition and dissolution, the formation of reactive nanopowders [18], and the formation and usage of modified electrodes may all be manipulated by the innovative combination with ultrasound. The desirable results to be obtained can benefit a range of different electrochemical applications, including those of considerable socio-economic importance, in analysis, synthesis, environmental science, biotechnology, catalysis, sensor science, polymers and other major industries and technologies.

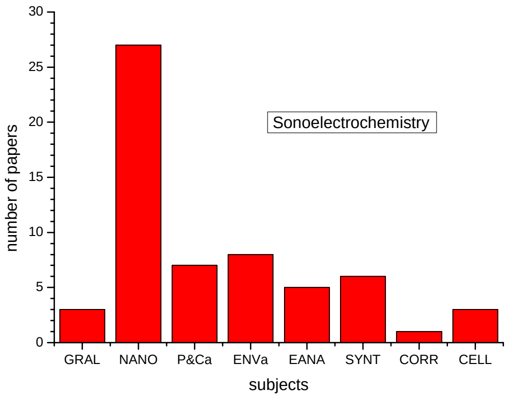
SONOELECTROCHEMISTRY: STATE OF RESEARCH IN THE FIELD

Sonoelectrochemistry can be considered as an example of chemistry in high-energy microenvironments in which the microenvironment is located near the electrode surface. The key scientific principle is the placing of electrochemical systems into non-equilibrium conditions, largely by the use of ultrasound, and contrasted with the effects of rapid heating, the use of very rapid change of potential or otherwise by alteration of the electrode surface and cell parameters so as to influence consequent phenomena. The key aim of the work is to obtain an underpinning fundamental elucidation of sonoelectrochemical effects, to benefit the widest range of practical applications. The global objectives and expected achievements may be summarized as follows, with mention of one recent paper on each topic:

- The development of enhanced electroanalytical procedures that are effective in real media (contaminated water, landfill leachates, foodstuffs, biofluids, emulsions), leading to improved sensors and biosensors [19].
- Sensitive electroanalyses for metal ions and other deleterious electroactive species in the environment [20].
- Novel electrosynthetic reactions and their applications in organic chemistry and biochemistry [21].
- Novel functional materials and their practical applications, including nanoparticles made from a range of materials and for a range of purposes, also conducting polymers [22].
- Improved strategies for waste minimisation, better energy efficiency and obviation of environmentally-unfriendly systems in synthesis, such as by use of aqueous emulsion media to replace organic solvents, use of ionic liquid solvents, and sonoelectrochemical reactor design [23].
- The degradation of pollutants and enhanced environmental clean-up using sonoelectrochemistry [24].
- The development of new electrode materials and the understanding of surface processes in these and other components of electrochemical systems [19, 25].
- Improved methods for electrodeposition, electrodissolution, including effects on morphology, hardness, microstructure and other properties, also applications including batteries and power sources as well as for improved real-time measurement of corrosion. Comparison of electroless and electrolytic systems[26, 27].
- Scale-up from micro-scale to pilot-plant scale for appropriate systems [28].

- Other combinations of methodologies for enhanced electrochemistry, for example thermal excursions (higher and/or lower) in the presence of ultrasound [29].
- Understanding of fundamental principles, where new techniques have provided results for discussion [30,31].

It is informative to compare the progress of sonoelectrochemistry as a topic by analysis of publications in the refereed literature since 2002, as shown in figures 1 and 2. Figure 1 refers top the keyword ‘sonoelectrochemistry’ while figure 2 refers to combination of the separate keywords ‘sonochemistry’ and ‘electrochemistry’



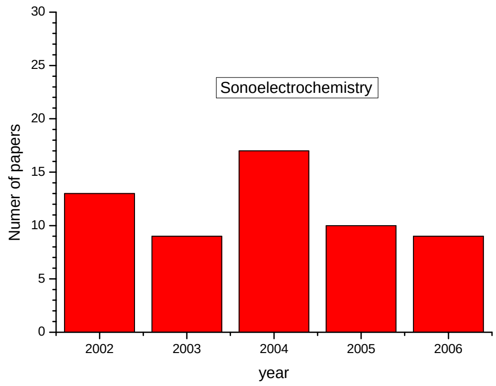
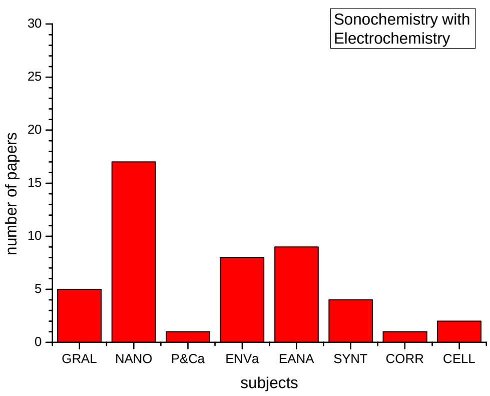


Figure 1a figure 1b

Figure 1.- (a) Number of paper found as ‘Sonoelectrochemistry’ since 2002. Gral: reviews and general aspects; Nano: synthesis of nanostructures; P&Cs: physical and chemical aspects; ENVa: environmental applications; EANA: application in electroanalysis; SYNT: application in organic and inorganic synthesis; CORR: application in corrosion and CELL: characterization & design of sonoelectrochemical reactors. (b) Number of papers in Sonoelectrochemistry by year.

Figure 1 shows the number of papers published in pure sonoelectrochemical aspects in the 2002-2006 period. Sonoelectrochemistry is studied in a relatively small but active group of laboratories and the activity within the last five years has kept constant (cf the successful 9th Meeting of the European Society of Sonochemistry held in Badajoz, Spain, 2004). Regarding breakdown of topics studied we can see in figure 1 that the most active subject is the application of ultrasound in the preparation of nanoparticles, nanotubes or nanowires by electrochemical methods. After that, applications in environmental protection treatment, electroanalysis and synthesis present a lower and similar activity compared to studies on fundamental physical and chemical aspects.



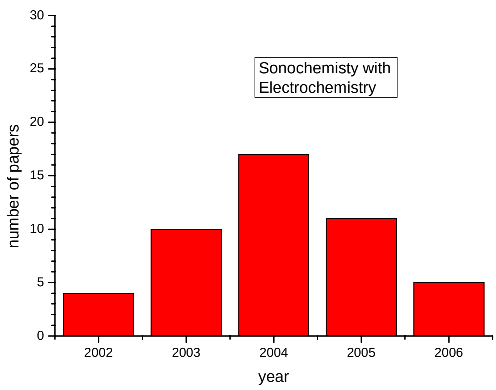


Figure 2a Figure 2b

Fig 2. (a) Number of paper in Sonochemistry with Electrochemistry since 2002. Gral: reviews and general aspects; Nano: synthesis of nanostructures; P&Cs: physical and chemical aspects;

ENVa: environmental applications; EANA: application in electroanalysis; SYNT: application in organic and inorganic synthesis; CORR: application in corrosion and CELL: characterization and design of sonoelectrochemical reactors. (b) Number of paper in Sonochemistry with Electrochemistry by year.

The situation is similar if we analyze combinations of the terms Sonochemistry together with Electrochemistry. The results are shown in Figure 2. The most popular activity remains the synthesis of nanostructures, following by the applications in the enviromental protection and electroanalyisis.

Finally, we analyze trends in different topics within this period of time. Subjects such as electroanalysis, environmental applications and fundamental physical and chemical aspects present a low but constant activity. However, synthesis of nanostructures presented the greatest activity since 2004 with an averaged activity of 4 papers/year.

Regarding recent activity by country, Taiwan (Liu Yu Chan et al) has produced 8 papers, Israel 7 papers (Gedanken et al), UK with 11 (Compton et al and Birkin et al) and USA (Burda et al) with 4 papers. China has produced 7 papers (Jun-Jie Zhu et al). Laboratories in other countries such as France, Spain, Czech Republic also show sonoelectrochemical activity.

The substantial european contribution to Sonoelectrochemistry is shown by the choice of the topic as theme in 2 COST Actions: COST D10 'Innovative Transformations in Chemistry' and COST D32 'Chemistry in High-Energy Microenvironments', providing a useful network for collaboration and interaction of the Sonoelectrochemistry with other related subjects such as acoustic cavitation, environmental applications, analytical procedures...

CONCLUSIONS

Sonoelectrochemistry is a subject that is now maturing. Papers on the fundamental physicochemical principles are now being succeeded by applications-oriented efforts, as shown for example in nanoscience.

References:

[1] M. Atobe: Review lecture to 9th European Sonochemical Society Meeting, Badajoz, Spain, April 2004
[2] D. J. Walton: Sonoelectrochemistry-The application of ultrasound to electrochemical systems. Arkivoc (2002) 198-218
[3] D. J. Walton, SSPhull: Sonoelectrochemistry. Advances in Sonochemistry Vol. 4 Ed. TJ Mason (JAI 1996)
[4] C E Banks, R. G. Compton, Ultrasonically-Enhanced Voltammetric Analysis and Applications –an Overview' Electroanalysis **15** (2003) 329-346
[5] J. C. Ball, R. G. Compton: 'Application of Ultrasound to Electrochemical Measurement'. Electrochemistry **67** (1999) 912
[6] M. M. Baizer, H. Lund (eds): Organic electrochemistry. ·3rd Edition, Marcel Dekker, 1991
[7] C. M. A. Brett, A. M. Oliveira Brett : Electrochemistry, principles, methods and applications, Oxford University Press, 1993.
[8] D. Pletcher, F. Walsh: Industrial Electrochemistry, Kluwer Academic 1990
[9] See for example various issues in the Series 'Advances in Sonochemistry' Ed TJ Mason (JAI Press)
[10] JP Lorimer, TJ Mason 'Applications of Ultrasound in Electroplating' Electrochemistry **67** (1999) 924-930
[11] A. Saterlay, R. G. Compton: Sonoelectroanalysis-An overview "Fresenius". Journal of Analytical Chemistry, **367** (2000) 308
[12] D. J. Walton, T. J. Mason: Organic electrochemistry in Organic Sonochemistry. Ed. J.-L. Luche. Plenum 1998
[13] D. J. Walton, J. Iniesta, T. J. Mason, J. P. LorimerA. Chyla, T. Thiemann, S. Mataka: Sonoelectrochemical effects in electroorganic systems. Ultrason. Sonochem. **10** (2003) 209-216.
[14] JD Wadhawan, F Marken, RG Compton, Biphasic Sonoelectrosynthesis- A Review' Pure & Applied Chem. **73** (2001) 1947-1955
[15] CE Banks, R. G. Compton, The Analyst **129** (2004) 678-683 'Ultrasound: Promoting Electroanalysis in Difficult Real-World Media'
[16] M. L. Doche, J. H. Hihn, A. Mandroyan, R. Viennet, F. Touyeras: Influence of ultrasound power and frequency upon corrosion kinectics of zinc in saline media. Ultrason. Sonochem. **10** (2003) 357-362
[17] E. Maisonhaute, P. C. White, R. G. Compton: Surface acoustic cavitation understood via nanosecond electroctrochemistry. J. Phys. Chem. B. **105** (2001) 12087-12091.

[18] I. Haas, S. Shanmugam, A. Gedanken: Pulsed sonoelectrochemical synthesis of size-controlled copper nanoparticles stabilized by Poly(N-vinylpyrrolidone). J. Phys. Chem. **110** (2006) 16947-16952. (and other papers from this group).
[19] A Goodwin, AL Lawrence, CE Banks, F Wantz, D Omanovic, E Komorsky-Lovric, RG Compton: On-site Monitoring of Trace Levels of Free Manganese in Sea-Water Via Sonoelectroanalysis Using a Boron-Doped Diamond Electrode. Analytica Chimica Acta **533** (2005) 141-145
[20] AO Simm, CE Banks, RG Compton The Electrochemical Detection of Arsenic (lll) at a Silver Electrode' Electroanalysis **17** (2005) 1727-1733
[21] see the series: M Atobe, T Aoyagi, T Fuchigami 'Ultrasonic Effects on Electroorganic Processes Part 26. Current Efficiency and Product Selectivity in the Anodic Cyanation of N-Methylpyrrole' Electrochemistry **72** (2004) 821-823
[22] SK Mohapatra, M Misra, VK Mahajan, KS Raja 'A Novel Method for the Synthesis of Titania Nanotubes Using a Sonoelectrochemical Method and its Application for Photoelectrochemical Splitting of Water' J Catalysis **246** (2007) 362-369
[23] C Villagran, Banks CE, WR Pitner, C Hardacre, RG Compton: Electroreduction of N-Methylphthalimide in Room Temperature Ionic Liquids Under Insonated and Silent Conditions. Ultrasonics Sonochemistry **12** (2005) 423-428
[24] VO Abramov, OV Abramov, AE Gekhman, VM Kuznetsov, G Price: Ultrasonic Intensification of Ozone and Electrochemical Destruction of 1,3-Dinitrobenzene and 2,4-Dintrotoluene. Ultrasonic Sonochemistry **13** (2006) 303-307
[25] Z Galbacs, H Van Langenhove, G Galbacs: The Effect of Sonication on Glass Electrodes. Talanta **66** (2005) 809-812
[26] A Galal: Characterisation of Conducting Poly (3-Methylthiophene) Films Prepared Under Sonoelectrochemical Conditions. J Appl Poly Sci **102** (2006) 2416-2425
[27] JW Kang, YH Shin, YS Tak: Growth of Etch Pits Formed During Sonoelectrochemical Etching of Aluminium. Electrochimica Acta **51** (2005) 1012-1016
[28] J. González-García, C. E. Banks, B. Sljukic, R. G. Compton: Electrosynthesis of hydrogen peroxide via the reduction of oxygen assisted by power ultrasound. Ultrasonics Sonochemistry 14 (2007) 405-412.
[29] CA Paddon, CE Banks, IG Davies, R.G. Compton: Oxidation of Anthracene on Platinum Macro and Micro Electrodes: Sonoelectrochemical, Cryoelectrochemical and Sonocryoelectrochemical Studies' Ultrasonics Sonochemistry **13** (2006) 126-132
[30] P Birkin, HM Hirsimaki, JG Frey, TG Leighton: Mass Transfer Enhancement Produced by Laser Induced Cavitation. Electrochemistry Communications **8** (2006) 1603-1609
[31] AD Clegg, AV Rees, CE Banks, RG Compton: Ultrafast Chronoamperometry of Single Impact Events in Acoustically Agitated Solid Particulate Suspensions. Chem Phys Phys Chem **7** (2006) 807-811