MEETING REPORT
COST D32 Working Group D32/004/04 ‘Ultrasound and Electrochemistry’

1st Meeting - Alicante, Spain 2nd –5th December 2004

Prepared by the Working Group Coordinator, Dr. J. González-García, University of Alicante ES

For: Secretariat of COST D32, European Science Foundation, Avenue Louise, Brussels

Attendees:

EU Experts Sponsored by COST (Expense Forms enclosed with this report):
Coventry University, UK: Professor DJ Walton
Oxford University, UK: Professor RG Compton
University of Franche-Comté, France: Professor J.-Y. Hihn
University of Franche-Comté, France: Dr. M. L. Doche
Paris University, France, Dr. E. Maisonhaute
Prague, Academic of Sciences of the Czech Republic: Dr. J. Klima
Prague, Academic of Sciences of the Czech Republic: Dr. J. Ludvik
Bath University, UK: Dr. F. Marken

Sponsored by Other Sources:
Oxford University, UK: C Banks, A. Simm

Alicante Contributors:
Dr. J. González-García (Local Meeting Organiser)
Dr. V. Climent (Co-organiser)
Ms. V Sáez
Mr. A. Frías-Ferrer

Other Attendees – A number of other Alicante personnel attended the Lecture Sessions and an average audience of approx 20 persons was present during the sessions (Professor A. Aldaz, Professor A. Canals, Professor J. M. Feliu, Dr. J. Solla, Dr. Sánchez, Mr. Vidal-Iglesias, Mr. Diaz-Guerra).

SUMMARY

The Meeting presented an opportunity for the 6 laboratories in the Working Group D32/004/04 to present reviews of the aims and themes of each laboratory and to describe recent scientific developments since the Working Group make-up was proposed in early 2004. There were 13 Lecture presentations given by various members from the laboratories, and a substantial body of work was presented to the audience for discussion. A copy of the final meeting schedule is appended. Discussions between the laboratories towards future experimental collaborations were a key aspect of the meeting, and were most productive. These discussions included in particular
the development of strategies for submissions to the European Union. Possibilities were identified under Research Training Networks (RTN), Transfer of Knowledge (ToK) or New and Emerging Science and Technology (NEST) under the Framework 6 European Initiative, and these will variously be assessed by the laboratories in the Working Group over the next time period. In a longer-term strategy the Group looked towards Framework 7. In addition the discussions identified several possibilities for Short-Term Scientific Missions within D32.

MEETING TIMETABLE

THURSDAY 2nd December: Most visiting attendees travelled to Alicante throughout the day (only the Group from Oxford traveled over on Friday 3rd). Preliminary discussions were held on arrival to update the agenda for the Meeting and the timetable of presentations.

FRIDAY 3rd December: This was a full day of Lecture presentations and visits, detailed below

1) The Local Organiser and Working Group Coordinator Dr. González-García welcomed attendees and set the Meeting into context. Then the Chairman of the COST D32 Professor DJ Walton gave brief overviews of the COST D32 Action (not all those present had been able to attend the earlier D32 Workshop in July), and of how the Working Group fitted into this Action. The remaining presentations concerned scientific matters.

2) Ms. Veronica Saéz reviewed the sonoelectrochemical studies carried out in the University of Alicante. Ultrasound is employed in a range of electrochemical process as such as electrodeposition, active metal synthesis, pollutant degradation and electroanalysis. Ultrasonic irradiation can produce important modifications in several processes; particularly in respect to the phenomenon of cavitation. The propagation of sound waves in an aqueous medium generates mechanical effects that agitate the solution increasing the mass transport to/from the electrode and can also cause chemical effects related to the production of radicals from the sonolysis of the solvent. Characterization of these chemical and physical effects generated by the application of an ultrasound field to aqueous solution becomes important in the efficient design and scale-up. The characterization of sonoreactors in order to identify the actives zones has been carried out in this group. Thus the ultrasound field emitted by a sonoreactor (20kHz, 100W) supplied by Undatim has been characterized using different classical chemical methods and electrochemical methods. The effect of the ultrasound field on different processes and parameters such as ultrasonic intensity, electrode-probe distance has been studied. The process studied include the electrocrystallization of lead dioxide and the degradation of chlorinated organic compounds as pollutants.

3) Mr. A Frias-Ferrer from Alicante discussed the characterization and modeling of several filter-press reactors. Great and informative detail was given since the talk formed part of the speaker’s Doctoral presentation, (which also allowed the COST meeting attendees the opportunity to discuss matters later with eminent electrochemists and engineers present on the jury, and showed a useful timeliness for this meeting). This talk echoed a key theme of the meeting, namely the modeling of systems. The speaker was also involved with the afternoon tour of the pilot plant at Alicante (see below), which is an important part of the facility here and which was one of the reasons for holding the Working Group Meeting at this laboratory. In all chemical processes the extrapolation from a successful laboratory-scale system to scale-up as a pilot for possible production provides a different set of challenges.
electrochemistry a filter-press cell is not often used in the small-scale laboratory, but is regularly employed in scale-up, and proper characterization of flow-patterns caused by the inherent design of the cell, due to concentration changes during the particular reaction and due to viscosity and other parameters of the reaction medium are essential. Use of turbulence promoters is routine in these scaled-up systems, while ultrasound itself affects turbulence, and these modeling studies are a very necessary part of any scale-up system.

4) **Visit to Pilot-Scale Plant** During the Meeting the European Experts were taken around the pilot-scale facility at Alicante by Professor Aldaz, Dr. González-García and by A Frias (who also gave the lecture presentation on the modeling of scaled-up systems described above). The existence of this facility is an important aspect of the operation at Alicante, which is not available at other laboratories in the network. The pilot-plant has recently been moved to a new building on the Alicante campus, which is well-equipped and serviced, and it is instructive to observe the chemical engineering aspects necessary for scale-up. The pilot plant can operate on a scale of tens of kilograms, and the filter-press electrochemical cells are only one of the processes that might be necessary in a reaction sequence. For example in the electrochemical production N-acetyl L-cysteine which takes place at Alicante, there is a chemical reactor for a necessary acetylation step, then an electrodialysis step to modify the ionic content of the electrolyte (all electrochemical systems require ions to be present and their concentrations may need modification between stages of the process), before the electrolysis stage. Other processes under study at Alicante include electrocoagulation and electrofloculation, which are electrophysical processes that may be incorporated into scaled-up reaction sequences. The evening allowed fruitful discussions between all the laboratories, and also with Professor F Walsh, from Southampton University UK, who was a member of the PhD examination jury for Mr A Frias-Ferrer.

**SATURDAY 4th December:** This was a full day of Lecture presentations, detailed below.

1) **Professor RG Compton** gave an overview of the physical basis of sonoelectrochemistry with an emphasis on sonoelectroanalysis, and in particular he described systems relevant to real practical applications, which often differ from laboratory test conditions. This talk was a tour-de-force regarding electroanalyses of bioimportant species in real-life media. These are all analyses that are difficult for various reasons in silent electrochemistry, such as being in difficult media such as blood, egg-white, beverages, contaminated fluids etc, or else possess other drawbacks, such as a reliance on use of the toxic metal mercury as electrode material. The Oxford laboratory has contributed to the ‘Measuring up to the Environment’ consortium in the UK, which has addressed new apparatus and methodologies for environmental applications. Ultrasound obviates electrode fouling and other deleterious processes in these analyses as well as enhancing cell hydrodynamics and improving the measured electrochemical response. It should be noted that some competing technologies, such as Atomic Absorption Spectroscopy and Inductively-Coupled Plasma, are quite sensitive, but are cumbersome to perform, use expensive equipment that is kept remote from the site of analysis, and necessarily involve delay before results are obtained. The necessary equipment is also rare in some countries, and the speaker therefore introduced a new portable battery-powered sonoelectrode system for sonoelectroanalysis, which has been produced in collaboration with a commercial company, which addresses a useful niche in the market of great potential benefit in environmental monitoring.
2) **Mr. A. Simm** from Oxford presented the sonoelectroanalysis of Arsenic. This is a problem in Bangladesh, where failure to recognize arsenic levels in river waters is the subject of controversy. Electroanalysis of this element suffers from interference from other elements and sonoelectrochemistry avoids some of these drawbacks. The hand-held sonoelectroanalytical device is ideal for studies in countries such as Bangladesh, and the Oxford work showed that the River Cherwell near Oxford is less contaminated with arsenic than are rivers in Bangladesh.

3) **Mr. C Banks** from Oxford presented the sonoelectrosynthesis of hydrogen peroxide on suitable electrocatalytic materials and studying their reactivity in the electrocatalytic reduction of oxygen. In addition, the immobilization of small molecules such as anthraquinones, known to homogeneously catalyse the formation of hydrogen peroxide, onto the surface of different carbon materials was shown to be beneficial. The use of azobenzenes in the regard had not previously been well-known. The effect of pH on the mechanism of the oxygen reduction mechanism was studied using cyclic and hydrodynamic voltammetry, including the use of rotating disc and ring-disc electrodes. For the coated electrodes, coverages were estimated and electrocatalytic rate constants deduced via the Swayant method (from cyclic voltammetry) or the Koutecky-Levich approach (from rotating discs). Double electrode experiments provided information about reaction intermediates. The reactivity of the immobilised catalytic coatings was contrasted with their homogeneous reactivity. The study identified optimised electrode materials and solution conditions (pH, supporting electrolyte) for the reduction of oxygen to hydrogen peroxide, a well-known process that remains problematic.

4) **Dr. F. Marken** from Bath showed an overview of the interactions between Microwaves and Electrochemistry under the title "Microwave effects and Applications in Electrochemistry". Over the past year substantial progress has been made with the experimental design and the understanding of electrode processes in the presence of microwaves. Exceptionally high rates of mass transport are now observed routinely in a wide variety of solvents and the mechanism responsible for this effect is likely to be a dynamic vapor bubble. In the presentation the evidence for and applications of the microwave effect in electroanalysis have been discussed. A close relationship has been proposed for processes in the presence of ultrasound (a field of cavitation bubbles at ambient temperature affects the electrode process) and in the presence of microwaves (a single dynamic bubble at high temperature affects the electrode process). The possibility of thermally inducing cavitation processes at interfaces has been explained. New methods for kinetic analysis of chemical processes in the presence of focused high intensity microwave fields have been discussed.

5) **Professor DJ Walton** discussed the electrooxidation and photoelectrooxidation of Thiophene-S-oxides (thiophene monoxides) and compared these with substituted tetracyclones, which differ only in the presence of a carbonyl group instead of a sulphoxide group. Thiophene-S-oxides are relatively new compounds, less stable than the better-known thiophene-S-dioxides. They are useful synths in applications such as the production of pharmaceuticals, and have interesting photochemical properties. The work is a collaboration with Professor T Thiemann at Kyushu University in Japan. This connection between Coventry and Professor Thiemann has a Europe sponsorship since it originated in a Human Capital and Mobility Network that came out of COST D6. In the talk preparative electrolyses for a range of differently-substituted derivatives of both
types identified distinct differences in behaviour, with the preference in the carbonyl system for a Bayer-Villiger oxygenation, while the sulphur analogues undergo different and unusual reactions, including novel intramolecular cyclisations leading to products with various sulphur oxidation levels. There are also desulphurised products in which the sulphur atom has been lost, a result of possible environmental significance for desulphurisation systems. The voltammetry of these different classes of compounds was discussed, and the effect of ultrasound was mentioned. Preliminary photochemical experiments were described in which furans and thiophenes were obtained from photolysis of aryl-substituted thiophene oxides, which in the presence of pyrrole (which can relatively easily be oxidized) appeared to cause further reaction of the heterocycle, but the quantum yields are low and the products remain to be identified.

6) Dr. M.-L. Doche gave the first of two talks from Besançon on the overall theme of this meeting, which was the better modelling of sonoelectrochemical systems. This remains an outstanding issue in the area and forms a key part of the scientific thrust of the Working Group. Reactors of various type and shapes were discussed. Transducer frequencies (in the range 20 kHz – 60 kHZ) and diameter were also considered. In these different cases, the distribution of ultrasonic waves and subsequent stirring and energy inside the reactor is an essential parameter to be considered for the process optimization. The quantitative method used here consists in the determination of mass transfer coefficients by cyclic voltammetry using the well known quasi-reversible redox couple Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$. The Sherwood number variation, which derives from the mass transfer coefficient, measured as a function of the distance between the electrode and transducer presents some higher stirring points in agreement with the stationary wave system. Closer examination of the area next to the transducer was performed by similar electrochemical measurements. The mass transfer coefficient is this time converted into an equivalent flow velocity $U$ to allow further comparison with other techniques. Except in one particular cell geometry, the flow velocity does not simply decrease when getting away from the transducer. Some high speed flow bumps (10-15 m.s$^{-1}$) are recorded. The flow speed-Transducer distance plots are greatly affected by the wave frequency and power but also by physical parameters such as the electrolyte viscosity and the relative pressure. A subsequent visualisation of this zone was performed thanks to Laser Tomography and Particle Image Velocimetry, showing an intense cavitation activity especially in the presence of the electrode on which waves are reflected. However the flow speed recorded does not exceed a few decades of cm.s$^{-1}$.

7) Professor J.-Y. Hihn from Besançon gives the second talk from Besançon following Marie-Laure Doche. He tries to demonstrate that for any studies involving a surface and an ultrasonic irradiation, electrochemistry can bring an essential help in the phenomena understanding. So, as for the previous talk, electrochemistry can be taken as a tool for ultrasound inquiries. At the same time, the surface irradiation by power ultrasound can lead to interesting applications in electrochemical processes enhancement. Evident improvements were also noticed in some works carried out in Besançon during the last years like in the case of electroless coatings or gold and nickel electroplating. Some of them were made in collaboration with Coventry University. Many coatings properties show a great sensitivity to ultrasound such as hardness, internal stress, morphology, practical adhesion and plating rates. Thanks to these results, new emerging fields are now opening in the team of Besançon (Electrochemistry in Room Temperature Ionic Liquids under ultrasound Irradiation of polymers in bulk and polymers in films, Cleaning applications, ultrafiltration and membranes synthesis under ultrasound, New HIFU reactor design and characterization).
Prof J-Y Hihn also discussed the 3 relevant points which can fit WG objectives
   a. Definition of reproducibility and characterization of operating conditions
   b. Identifications of problems in applications or phenomenon needing theoretical understanding
   c. Sonoelectrochemical reactor design

The ways to reach these objectives may be in a large discussion into the WG members on the operating parameters characterizations and the elaboration of an open listing of theoretical needs. He finally presents a French Government communication in respect of Framework 7, and the Working Group audience noted that collaborative ventures towards Framework 7 should now be considered so as to be prepared for when the Framework will commence.

8) Dr. J Klima from Prague presented a talk entitled "Problem of Intensity of Ultrasound in Sonochemical and Sonoelectrochemical Measurements". In sonochemistry, sonication is often used just by a trial and error method, and for better application it is necessary to understand the physical background of the process. In particular the effects of a most fundamental parameter, the ultrasonic intensity. This remains a controversial matter in sonochemistry, and source geometry and type, and cell design and shape can affect the consequences of insonation in systems that might otherwise be thought similar. Since virtually all sonochemical processes are connected with cavitation, an applied intensity should be higher than the cavitation threshold. However, it is in the case of low intensity that its determination is well solved, but at higher intensity when cavitation takes place measurement of intensity is difficult and it is necessary to be careful in the interpretation of results. The most frequently used method for determination of ultrasonic intensity is calorimetry which is believed to be an absolute (i.e. not only relative) one. This method determines an amount of ultrasonic energy absorbed (and changed to heat) in the studied solution per unit of time. It is supposed that this energy is equal to the total power entering the cell and that the intensity can be obtained by dividing of this power by an area by which it enters the cell. The speaker showed that this presumption is often not fulfilled and that this approach can give incorrect values - results can be garbled due to only partial absorption of ultrasound and by interferences such as reflections from cell walls. The limits of the method were discussed and an alternative approach based on the knowledge of spreading and absorption of ultrasound was offered.

9) Dr. J. Ludvik from Prague presented a talk entitled "Electrochemical reduction and dimerization of halogenated benzothiophenes and benzothiophene-2-oxazolines. Use of sonication ". In this talk, results from new synthetic routes to 3,3'-bibenzothiophenes via electrochemical reduction of methyl 3-halobenzo[b]thiophene-2-carboxylates at platinum, mercury, and nickel electrode was presented. It was shown that the mechanism of electroreductive dehalogenation in non-aqueous DMF is strongly dependent on the electrode material and on additives present. While potentiostatic electrolysis at platinum or mercury electrode is a two-electron process leading through reductive dehalogenation to the reduced monomer (even if a mediator and/or sonication are used). In contrast galvanostatic electroreduction on a nickel electrode in the presence of a catalyst (2,2'-dipyridylamine) gives the dimer in a good yield (78%). A similar (sono)electrochemical study was done also with three 3-halogenated chiral benzothiophene-2-oxazolines. Irradiation by power ultrasound prevents blocking of the electrode by adsorbed species or polymer film and thus continually reactivates the electrode surface. Simultaneously on a reactivated electrode the process proceeds closer to the standard redox potential. This shows another useful effect of ultrasound.
10) Dr. E. Maisonhaute from Ecole Normale Supérieure, Paris, presented the talk "Ultrafast Sonoelectrochemistry". The current in sonoelectrochemical experiments has two origins. The first one is a macroscopic term originating from the hydrodynamical flux of solvent over the electrode. The second one is microscopic and is due to the local stirring of the solution by the cavitating bubbles. When using standard millimetric electrodes it is hard to discriminate between each contribution, first because several cavitating bubbles may act on the electrode at the same time, and second because access to submicrosecond timescales necessary to follow the fast movements of the cavitating bubbles is prevented with such large size electrodes. Using nanosecond time-base potentiostat (this equipment originating from this French laboratory in Paris) and ultramicroelectrodes, it was shown that single cavitating bubbles could be detected. Their lifetime was estimated to be less than one millisecond, with a shift from stable to transient cavitation when the electrode / horn distance diminishes. Using ultramicroelectrode arrays, it was demonstrated that the bubbles were flat on the surface. A quantitative model for the bubble evolution was proposed. It revealed that the electrode / bubble distance was a few tenths of nanometers and that collapse velocities were more than $100 \text{ ms}^{-1}$. This model allowed a better understanding of the cavitation effects on a surface.

11) The later business of the day was a series of round-table discussions to address existing and future activities of the Working Group. These included discussions in respect of the submitted bid for a Research Training Network to address fundamental and development of a reliable sonoelctrochemical reactor at laboratory scale to be used in synthetic and environmental applications of sonoelectrochemistry. Also discussion of possible Sixth framework opportunities for further collaborations. Other agenda items were the date and venue of the next Working Group Meeting, and of other relevant conferences and meetings, particularly those organized by, or otherwise involving Working Group members.

Sunday 5th December: This was a breakfast meeting, before the attendees left to travel home. There were a number of fruitful final discussions, for example representatives from Alicante, Besançon and Prague discussed plans for joint studies on the fundamental characterization of sonoelectrochemical reactors, in light of the necessity to establish standard methods for the ultrasound intensity measurements in the reaction medium. This should involve an STSM from Prague to Alicante, and a STSMs from Alicante to Besançon. STSMs involving other laboratories were also proposed. A title and theme for a possible Transfer of Knowledge project were proposed. The various working group laboratories will now consider these various options. The remaining paragraphs cover some of the areas of discussion and give the efforts of working group laboratories in the field:

1) Proposals
In accord with the Work programme presented in the Working Group application, the planning of several STSMs for next year (2005) is in hand. These visits are needed in order to establish bilateral collaborations among the laboratories for mutual exchange of expertise and training in this five-year collaboration. From all these discussions it became clear that there is a need for a well-characterized multipurpose device able to provide homogeneous and optimized reaction conditions for a range of sonoelectrochemical applications and so it was decided to produce a draft proposal involving contributions from each laboratory in the Working Group. This is aimed
towards Marie Curie RTN and/or ToK applications to be submitted nearer to the next WG Meeting. In order to consolidate this strengthening among laboratories, the Working Group Coordinator has been awarded funding from the Spanish Government to visit Oxford University for one year in 2005. This will permit stronger collaboration between the British Departments and Alicante and will help production of the documents for the suggested proposals.

2) STSM:
Applications for TWO further STSMs are in hand (more are imminent). These STSM applications have come as direct results of this COST Working Group Meeting. The first, between Alicante and Prague, planned in January 2005, with Professor J. Klima from Prague working in the Alicante Laboratory. The second, between Besançon and Alicante, planned in Spring 2005, with Ms. V. Sáez from Alicante working at Besançon. Both of these one-month grants are direct focused on the collaborations between laboratories set up under the COST initiative, and show clearly the benefit of COST Working Groups.

3) Contributions to Conferences Held
The 9th Meeting of the European Society of Sonochemistry was held at Badajoz, Spain in April 2004. This conference series, which was sponsored by the Ministry of Science and Technology of Spain, and the other Administrations from Extremadura, covered the range of sonochemical endeavour, but in particular at this event the subject matter of the sonoelectrochemistry (fitted exactly the topics of the Working Group) supplied more than 15 contributions (among 50). The conference offered an excellent opportunity for speakers from the Working Group to broadcast expertise to a European and International audience, and there were other aspects of extreme conditions in electrochemistry that were reported by speakers from outside the Working Group, thereby allowing important and useful cross-pollination of ideas. A full account of the Working Group’s contribution was given in the Coordinator’s report for the Working Group Meeting that was held concurrently, but it is worth re-emphasising that our laboratories presented a very creditable total of 11 oral and poster contributions to this major international conference.

4) Contributions to forthcoming conferences:
   a) Electrochemistry 2005, Newcastle UK,
   b) Meeting of the Electrochemical Society in Quebec Canada.
   c) Journées d’Electrochimie 2005, St Malo France
   d) 7th European Symposium On Electrochemical Engineering 2005 -Toulouse France

These are both major international conferences, with parallel sessions. It can be seen that the Working Group is making a major contribution to European and International electrochemical events, and there are several other contributions in hand to conferences in 2005.

Date of Next COST Working Group D32/004 Meeting
This was agreed to be held at the J. Heyrovsky Institute of Physical Chemistry in Prague in a year’s time (1st/2nd/3rd December 2005), organizers J Klima and J Ludvik. Funding for this meeting will shortly be requested in the usual way. Members of the working group will contribute to the second COST D32 Workshop, to be held in Modena Italy in September 2005.
APPENDIX

Expense Claims for European Experts

(to follow with receipts)